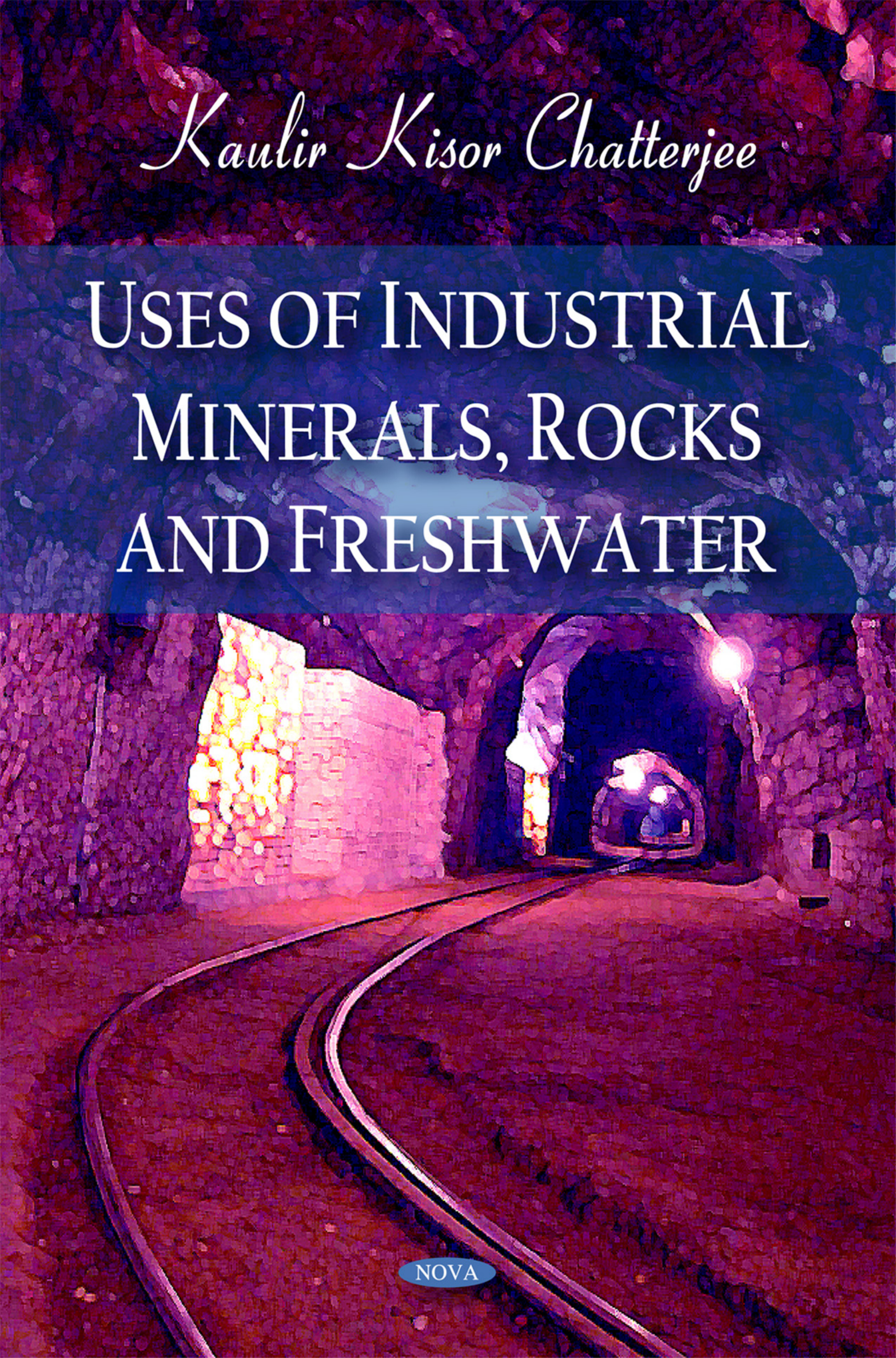

Kaulir Kisor Chatterjee

USES OF INDUSTRIAL MINERALS, ROCKS AND FRESHWATER

NOVA

USES OF INDUSTRIAL MINERALS, ROCKS AND FRESHWATER

USES OF INDUSTRIAL MINERALS, ROCKS AND FRESHWATER

KAULIR KISOR CHATTERJEE

Nova Science Publishers, Inc.
New York

Copyright © 2009 by Nova Science Publishers, Inc.

All rights reserved. No part of this book may be reproduced, stored in a retrieval system or transmitted in any form or by any means: electronic, electrostatic, magnetic, tape, mechanical photocopying, recording or otherwise without the written permission of the Publisher.

For permission to use material from this book please contact us:
Telephone 631-231-7269; Fax 631-231-8175
Web Site: http://www.novapublishers.com

NOTICE TO THE READER

The Publisher has taken reasonable care in the preparation of this book, but makes no expressed or implied warranty of any kind and assumes no responsibility for any errors or omissions. No liability is assumed for incidental or consequential damages in connection with or arising out of information contained in this book. The Publisher shall not be liable for any special, consequential, or exemplary damages resulting, in whole or in part, from the readers' use of, or reliance upon, this material. Any parts of this book based on government reports are so indicated and copyright is claimed for those parts to the extent applicable to compilations of such works.

Independent verification should be sought for any data, advice or recommendations contained in this book. In addition, no responsibility is assumed by the publisher for any injury and/or damage to persons or property arising from any methods, products, instructions, ideas or otherwise contained in this publication.

This publication is designed to provide accurate and authoritative information with regard to the subject matter covered herein. It is sold with the clear understanding that the Publisher is not engaged in rendering legal or any other professional services. If legal or any other expert assistance is required, the services of a competent person should be sought. FROM A DECLARATION OF PARTICIPANTS JOINTLY ADOPTED BY A COMMITTEE OF THE AMERICAN BAR ASSOCIATION AND A COMMITTEE OF PUBLISHERS.

LIBRARY OF CONGRESS CATALOGING-IN-PUBLICATION DATA

Chatterjee, Kaulir Kisor.
Uses of industrial minerals, rocks, and freshwater / Kaulir Kisor Chatterjee (author).
p. cm.
Includes index.
ISBN 978-1-60741-400-1 (E-Book)
1. Industrial minerals. I. Title.
TN799.5.C4885 2008
620.1'98--dc22
2008010236

Published by Nova Science Publishers, Inc. ✧ New York

> “Science does not sit and pray for things to happen,
> But seeks to find out why things happen.”
>
> — Jawaharlal Nehru

Dedicated to my inner God.

CONTENTS

PREFACE

First the necessity and then arises the will to find the means! I first felt dejected during my student days some four and half decades ago, when without any ready resource to fall back upon for satisfying my scientific quest for reasons, I was forced to cram the lists of grade-specifications of various minerals for use in different industries. Ever since that time my curiosity to find out why a product should require one particular grade of a particular mineral, and not some other grade or some other mineral, kept growing. A decade later, when I was a junior officer in the Mineral Economics Division of Indian Bureau of Mines, I became more aware about the lack of comprehensive literature that linked the grade-specifications of minerals with the technology of their uses. It was some time around 1977 that I first got the idea of going into the depth of this issue of scientific and technological reasons for every use of not only all the minerals but also the metals and the industrially usable rocks, and I obtained plenty of opportunities for studying the workings of and interacting with all kinds of industries in the course of my over three-decades-long tenure in the Indian Bureau of Mines.

I never considered the use of a mineral or a metal as an independent entity. To understand it fully, it should be linked backward with the history of evolution of the use and with the physical and chemical characteristics of the metal or the mineral; and it should be linked forward with the utilization of the wastes generated during and due to its processing or use, and with the prospects of its being substituted by some other material. After I had collected sufficient materials and acquired a good grasp, I decided one day in April, 1991 to write about what had been so close to my heart.

My two books, “Uses of Energy Minerals and Changing Techniques” and “Uses of Metals and Metallic Minerals” were published in 2006 and 2007, respectively. And now this book dealing with all the industrial minerals, the industrial rocks and freshwater!

Besides my personal field studies and interactions, this writing has required me to rummage through whatever relevant literature including physics, chemistry and metallurgy that I came across and to surf through the internet and old United Nations and other study reports. For keeping myself up-to-date with news of new developments, the newsletters published by the Federation of Indian Mineral Industry, the Mining Metallurgical Geological Institute of India, and the Mining Engineers’ Association of India, various other journals and the newspapers were also helpful.

While writing this book during the last several years, I have received physical and chemical support from many. I gratefully and most humbly remember them.

Nagpur , India
January, 2008

Kaulir Kisor Chatterjee

INTRODUCTION

Kautilya said, “Minerals are the wealth of a nation.” He said this twenty three hundred years ago. But long before him, about a million years ago, commenced the gainful usage of stones and the Stone Age. And perhaps in the course of the first few hundred thousand years, a mineral — now called by the name flint — became the backbone of the economy of man. This hard mineral with sharp edges became sine qua non for all his economic activities which, of course, were limited to defending himself, hunting for food and (much later, when the Ice Age was threatening to freeze him to death) tearing animal hides for protection against cold. Still later, man invented fire by rubbing two stones — pieces of the same mineral flint. Now he could cook the raw food. But he was destined to be different from his animal mates; he was not born just to hunt, eat, breathe, mate and die. He had to make use of not just one mineral, but also his main asset — his intelligence. After all he was to be christened by his descendants as “Homo Sapiens,” the “intelligent man.”

Not stopping at inventing fire, he went on using his flint-made tools (and animal bones of which there was plenty) to dig, take out different kinds of material from the nature’s treasure house and experiment with them. By the time of Kautilya, many such experiments had already been successfully accomplished through innumerable trials and errors, and a number of metals and alloys had been invented—copper, lead, zinc, tin, brass, bronze, iron — to make more useful tools, more lethal weapons and more experiments with more materials. Power of animals, power of intelligence, power of fire were all at his command to fire up his ever-increasing quest. But before all these happened, a distant ancestor of Kautilya who lived around 10,000 years ago, was thoughtful enough to guide his herd to settle down in colonies, to start and institutionalize families and to begin a social order on a give-and-take basis. What took thousands of years for single men to achieve, now could be done in no time by herds of socialized men. Descendants of those men, us, have honoured them as the first civilized men and regard that time as the beginning of civilization.

And it was then that houses needed to be built — initially with rocks and logs of wood, later with clay-bricks. Those civilized men developed tastes for food other than animal meat and wild fruits. They learned to grow grains, store them in earthenware pots for cooking and eating in a regulated manner over a long period. Clays were probably the second earliest mineral processed and used by men. Ancient men living as early as 10,000 years ago knew how to make not only fired potteries, but even painted ones, and also to make building bricks. All through this time gemstone mining kept getting support from the royalty and aristocracy.

The oldest mineral flint which has survived the ages and has lived until recently in some cigarette lighters, is no longer talked or heard about much now. But clay the second oldest mineral to be used, is an omnipresent mineral today with its indispensability in construction and ceramics. And not only is the use of each mineral multiplying, but also the number of minerals entering into the realm of usage is multiplying in leaps and bounds. From the oldest mineral used — flints to the newest ones — staurolite which has graduated from a stone-collector's delight to an industrial mineral only about a decade ago, and Shirasu, as the Japanese call their pumice-like volcanic ejects, it is a long saga of evolution — not just evolution of man's knowledge about usage of minerals, but evolution of his civilization.

Today, more than 3,000 minerals have been reported and named, of which 1,800-2,000 have been fully studied and described. But even after a million years of experimentation, we are able to gainfully use only around 100 or so minerals. Of course, none of these "usable" minerals can be consumed as such by people. They can neither be eaten nor worn nor fought with. They have to be converted to various products that can be used in living their material lives. Through interactions amongst different minerals, innumerable materials are turned out for fulfilling our material needs. And though there are some uni-product minerals, a majority of the minerals are the ones which eventually yield a multiplicity of final consumable products. Thus, there are a few minerals from which we get only metals — (lead from galena, zinc from sphalerite, copper from chalcocite, caesium from pollucite, molybdenum from molybdenite etc.) which need to be subjected to further processing to yield consumable products. There are also some which mainly give us metals for further processing and, at the same time, which are also processed directly for obtaining some final products — [hematite (iron), psilomelane (manganese), chromite (chromium), bauxite (aluminium), uraninite (uranium), monazite (thorium), etc.]. There are still a few which serve mainly as raw materials for yielding some products directly and at the same time have some minor metal values — borax (boron), barytes (barium), zircon (zirconium); and there are others from which no metal is extracted and which are used directly [asbestos, clays, coal, diamond, mica, natural gas, petroleum, phosphorite, quartz, etc.].

Thus, the economically usable minerals automatically classify themselves into four broad groups based on the stages of processing required for conversion to finally usable products: (i) those that are mainly used directly in consumer product industries, (ii) those that are not used without first extracting metals from them, (iii) those that are used both ways, but mainly valued for their metal contents, and (iv) those that are also used both ways, but their direct uses are of importance and their metal values are of minor significance. It has become a convention to refer to the first and fourth groups as "industrial minerals" (earlier term non-metallic minerals) and the second and third groups as "metallic minerals". Some minerals from both groups are the main sources of energy now and, because of the intensive worldwide attention they are receiving today and for convenience of statistical reporting and governmental planning, these minerals are now segregated as a separate group and termed "energy minerals" which include coal, petroleum, natural gas, uraninite, and monazite as the principal minerals. So, in the final reckoning, there are today three groups — energy minerals, metallic minerals and industrial minerals. This book is about the uses of industrial minerals.

Geologically, minerals are different from rocks inasmuch as the latter form more or less definite units in the earth's crust and may be made of one or more minerals. Thus granite, marble, limestone, phosphorite, dunite, coal are all rocks. But all over the world, the same laws apply to the rocks and minerals, and the manner and economics of their uses are also the same as the industrial minerals. Amongst the industrial minerals, limestone, phosphorite and clay are exceptions. Strictly speaking, limestone and phosphorite are rocks and clay, being composed of a number of clay minerals, is neither a rock nor a mineral. But mineral economists, mining engineers and law-enforcing agencies have been traditionally looking at them as minerals. Barring these, the other rocks —especially the hard ones — have been included in this book under a separate section named Industrial Rocks.

Water falls in an altogether different category. It may be salty seawater or freshwater. Seawater is not used directly for human consumption and is used for recovering some useful minerals which have been covered in this book under the respective minerals. But freshwater is consumed directly by humans and animals and also in agriculture and industries for producing various consumable goods. Hydrologists consider it as one system extending from the visible domain (surface freshwater) downward to the invisible one (groundwater). To a mineral economist also, both surface freshwater and groundwater are the same use-wise and they can be used interchangeably. But the lawmakers lay more emphasis on the visibility/invisibility dimension of the two subsystems. Since the invisible subsystem groundwater behaves no differently from any hidden mineral deposit, they have categorized it as a mineral. Because this book is mainly about economic uses, both groundwater (which is a mineral in the eye of law) and surface freshwater have been discussed under a third section titled "Freshwater".

Importance of the energy minerals and the metallic minerals in today's economy cannot be overemphasized and uses of these minerals have already been covered in two earlier books of the author. Value-wise, the industrial minerals come third after them in India, having accounted for only 3.6% (Rs 27.28 billion) of the total value of production of all minerals which was Rs 756.99 billion during the year ending March, 2006 (c.f., energy minerals 81.2%, metallic minerals 15.2%). Yet the study of uses of minerals will remain incomplete without an appreciation of the roles played by the industrial minerals and rocks in the countless objects that we are so accustomed to using in our everyday life. Amongst the minerals and metals produced in India, the highest foreign exchange earner is an industrial mineral — diamond (cut and polished), and the third is an industrial rock — granite (dimensional rock). Without industrial minerals and rocks, there would not have been houses to live in, roads to drive our vehicles along, clothes to cover our bodies and papers to write on. These are the minerals which have taken us through the green revolution and into the electronic and communication revolution. These are the minerals which have brought the space within our reach.

It is also recognized that without an idea of the history of evolution of the various uses of a mineral or a rock, its present day uses will not be fully appreciated by the readers. So, this aspect has been given due importance while laying emphasis on the uses of the minerals.

Why is a particular mineral or a rock used to perform a particular function or to make a particular product? That is because every mineral or rock possesses a unique combination of physical and chemical properties, and in this respect no two minerals or rocks are exactly the same. So a particular use of a mineral or a rock can be best understood if the use is linked to the particular set of physical and chemical criteria. And that has been done all through this book. Further, while dealing with physical and chemical criteria, invariably some technical terms pertaining to physics and chemistry are bound to come up. As far as possible, these terms have been explained in a simple easily understandable manner in the glossary as well as in the text wherever they are encountered.

Now, gone are the days when all the high grade deposits of minerals and rocks were there asking to be dug out and processed for some end-products. Those deposits are all finished by our forefathers. Today, we are left with only the relatively poorer grade minerals for our needs. Can we use any grade of a mineral or a rock for any product? The answer is yes and no.

The answer is yes, because first, man is not the producer of the mineral or the rock. It was produced by nature hundreds of millions of years ago and stored in safe custody within rocks and formations of the earth. What man does is only draw some quantity from nature's store house, and so, he has to accept whatever grade nature has created and whatever, out of the nature's treasure house, his forefathers have left for him. Second, in case of a mineral, its processing often depends not on its grade alone, but on an interplay of four factors, namely grade of the mineral, grades of other input materials for its processing, technology and prices of the final products based on the mineral. Out of these, the price is determined by the market forces of demand-supply on which the producer has no control. But the other three factors are in the domain of the producer. He may mine a high grade mineral at a high cost, and use low grades of other input materials and employ low level technology to manufacture a product of a specified quality, or he may choose to mine an easily available low grade mineral at low cost, and use high grades of other input materials and employ high level technology to achieve the same quality of his end-product.

The answer is no, because at a given point in time there is a particular technology developed, and only one particular set of input materials with fixed qualities are available for processing a mineral. So, only one particular grade of the mineral can be processed with that technology and with those input materials, and only that particular grade has to be used at that point in time.

However, in today's fast developing situation, there is always a multiple choice available for technologies and grades of input materials. So, technology and input materials can be chosen to suit any grade of a mineral that is available in nature. The only constraints are the market price and the cost of mining the mineral. The cost has to always be less than the market price, the vagaries of which limit the range of flexibility regarding the specifications of grade. But, even if these specifications are not flexible enough at some point in time, the principles underlying the specifications remain valid all the time. And those principles, rather than the specifications, have been emphasized in this book.

The story does not, however, end with processing a mineral or a rock for obtaining various consumer products. Minerals and rocks do not come one hundred percent in usable grade or form. During beneficiation of a low grade mineral, tailings are generated. Waste materials are also generated during the interactions amongst the mineral and non-mineral raw materials. In fact, wastes generate at every stage of economic activity, but it has been the experience that yesterday's waste is today's asset and today's waste will be tomorrow's asset. This happens because the developments in technology are not only about using minerals and rocks, they are also about utilization of the so-called wastes. After all, technology is for minimizing the costs at every level starting from mining of the mineral down to the final consumption, so that at every stage the cost is less than the market price.

The second consideration in favour of maximization of the utilization of the wastes is related to the environmental problems. Some of the wastes remain on the ground, some go to the rivers and the ground water, some go into the air. The pace at which mining is going on at present, is far faster than it was a few decades ago. Wastes are also being generated at a very fast pace. If nothing is utilized properly, then the amount of damage these wastes will cause to the land, water and air in a few decades hence, is unimaginable.

The third consideration is about concerns for conservation of mineral resources. Conservation as such is not a new concept. Emperor Ashoka thought about it about 2,300 years ago. But he thought about conserving the forests, birds and animals. In the 3rd century BC, the edicts that he got inscribed on the rocks and iron pillars can be translated is as thus: "Twenty-six years after my coronation, I declare that parrots, mynas, the aruna, ruddy geese, the nandimukha, cranes, bats, queen ants, terrapins, boneless fish, rhinoceros and all quadrupeds which are not edible are not to be killed; forests must not be burned". Conservation of mineral resources have become a concern only after World War II in 1945, when it was realized with alarm by the US Government, followed gradually by other governments, that higher grade parts of many minerals had all been mined out to meet the needs of the war and the economy, and there is urgent need to conserve what still remained. Conservation does not mean keeping the mineral deposits idle without mining. It means judicious mining, it means avoidance of wasteful practices of use, it means total utilization of the material mined without wastage. In other words, conservation means using not only the minerals and rocks, but also the wastes generated during their mining and processing to the maximum possible extent. Conservation and ignoring the waste materials generated during mining, processing or the use of minerals and rocks do not go together.

There is another dimension of the usage of minerals and rocks – substitution. Though there are some minerals which are indispensable in certain uses, there are also some which can be replaced by some other material in a use. This happens if the cost advantages of using a mineral or a rock vis-à-vis its performance are lost and a cheaper and/or better material becomes available. Even freshwater can be and is being substituted. In this book, issues related to both of these dimensions, waste utilization and substitution, have been addressed with regard to their present and emerging trends, wherever relevant and important.

This book covers all these aspects for all the industrial minerals and rocks that are economically important today. Industrial minerals have been grouped in much literature under refractory minerals, fertilizer minerals, gem stones, ceramic minerals, etc. But many of these minerals transcend their group boundaries, and in this book this sub-classification has not been adopted.

Freshwater is steadily assuming importance not just for drinking, but as an industrial raw material. Nowadays, investors are regarding freshwater as the third most critical component of feasibility of an industry after land and mineral raw materials. Many people are already voicing apprehension that the next world war will be fought not over oil or minerals but over water. Groundwater reservoir, a subsystem of the freshwater system, behaves like a mineral deposit in many ways. Therefore, it has not been thought proper to leave it out and a chapter has been devoted to freshwater with special reference to groundwater.

At the end, the repertory of uses is a new concept introduced. It should serve as a kind of ready-reckoner containing the names of the mineral-based products arranged in alphabetical order and indicating against each, the names of the industrial minerals and rocks that go into making that product. After knowing the names of the minerals/rocks, a reader can straightaway look up those particular chapters for details.

It is hoped that this book should be of everyday use to not only the students and teachers of economic geology, mineral economics and mining engineering, but also to all those who are directly or indirectly concerned with industrial minerals and rocks or are otherwise interested in knowing and understanding the whats, whys and hows of their uses.

PART I:
INDUSTRIAL MINERALS

Chapter 1

ASBESTOS

Asbestos is a Greek word meaning “inextinguishable”. The central characteristics are fibrous structure and resistance to fire. According to the definition of the American Standard for Testing Materials (ASTM), asbestos is a term applied to six naturally occurring minerals exploited commercially for their desirable physical properties, which are in part derived from their asbestiform habit, with the individual mineral particles having length-to-width ratio not less than 20:1. The six minerals belong to two groups:

a) Serpentine group
(1) Chrysotile [Hydrous magnesium silicate, $3MgO.2SiO_2.2H_2O$], also called *white asbestos* or *rock cotton*.

b) Amphibole group
(2) Amosite [Iron-bearing hydrous magnesium silicate]
(3) Crocidolite [iron- and sodium-bearing hydrous magnesium silicate]
(4) Anthophyllite [$7(Mg,Fe)O.8SiO_2.H_2O$]
(5) Tremolite [$2CaO.5MgO.8SiO_2.H_2O$]
(6) Actinolite [$2CaO.5(Mg,Fe)O.8SiO_2.H_2O$]

Some authors have considered amosite as only a special variety of anthophyllite. The name chrysotile has originated from the Greek words “chrysos” meaning “gold” and “tillein” meaning “to pluck”, and the name amosite is derived from Amosa mine of South Africa.

The largest and the best known deposits of asbestos (chrysotile variety) are located in Quebec, Canada and in the Urals, Russia. But since the early 1980s, due to vigorous campaign by the environmentalists and a series of law suits by asbestos mine workers caused virtual death of the mining industry of the different varieties of asbestos in many countries and gradual dwindling in others including India (discussed in more details later in this chapter).

Until early 1980s, asbestos was a much sought after industrial raw material finding its way into more than 3000 products from roof tiles and window boxes to children’s toys, from brake lining and drain pipes to tooth brushes and black boards. Erstwhile USSR and Canada were the leading producers, the other important producing countries being Brazil, Italy, China, South Africa, Zimbabwe, Swaziland, Cyprus, India and Australia. So far as the varieties amosite and crocidolite are concerned, South Africa was the leading producer. In India, chrysotile, tremolite and actinolite are of significance.

Geologically, the chrysotile variety occurs in deposits consisting of irregular cross-fiber veins (often in the form nets of fine mesh) of slip-fiber zones in massive serpentine which is a secondary mineral formed due to an alteration of a non-aluminous silicate containing magnesium (e.g., chrysotile, amphibole, pyroxene). In a few deposits (e.g., those of Arizona), the serpentine zones are associated within massive limestone. Amosite and crocidolite occur as irregular veins in schist, quartzite, banded ironstone, etc.

HISTORY

Asbestos was known and its fibers were used by the Romans 2,000 years ago as torch wicks in temples, although there is no record regarding how they used to get it. The first mine of chrysotile asbestos was started in Quebec, Canada in 1789, and in the following year the first processing facility was set up. The estimated world annual production in 1911 was 91,000 tons rising to 181,000 tons in 1923, and to about 500,000 tons during the 1930s, before World War-II. After the War, the demand started increasing rapidly. In 1949 its production was 975,000 tons which rose to 1,375,000 tons in 1953 and reached a peak of 5.18 million tons in 1976. Thereafter, the production showed a declining trend due to the closing down of many mines and a ban on any opening of new mines in many countries on environmental ground. In 1986, it dropped to 3.63 million tons and by the beginning of the 21st century, 2001, the production came down to 2 million tons. Until the early 1980s, chrysotile variety constituted 90% of world asbestos production, and crocidolite and amosite contributed 2-3% each. Currently, chrysotile accounts for almost 99% of the world asbestos production.

In India, small occurrences of tremolite was known in parts of East Singhbhum (Jharkhand) and Mayurbhanj (Orissa) districts, in Karnataka, in Central India in Rajasthan. The first recorded mining operation dates back to 1904 in Central India. A mine started for the first time in 1921 in Saraikela (Jharkhand). This was followed by sporadic mining from 1940 onwards in the Mayurbhanj district. So as far as chrysotile is concerned, high grade economic deposits are known only in the Pulivendla area of the Cuddapah district in Andhra Pradesh where mining started in 1924. But the quantities of production from these mines were very small — the total production of all varieties of asbestos from 1904 till 1950 from all these areas taken together was less than 9500 tons, with the annual average varying from 80 to about 610 tons. From 1950 onward, the production has increased several-fold with two significant jumps in 1955 and 1974. In 1955 it jumped to 1,418 tons from 395 tons the previous year, and in 1974 it increased to 23,685 tons from 12,359 tons in 1973. After reaching a peak of 38,000 tons in 1989, the production in India, in keeping with the worldwide trend, declined to 11,148 tons during the year ending March 2002 and to only 2,366 tons in the year ending March 2006. In India, amphibole variety accounts for most of the asbestos produced.

PROCESSING

1. Chrysotile: Chrysotile asbestos is the most valued, and its value depends on the lengths of the flexible fibers. But since the fibers are intimately interwoven in the form of nets within the serpentine rock, they have to be separated first, and the separation process should cause minimal damage to them and minimum reduction in their lengths. Long distinct fibers are first separated by hand sorting of the asbestos-bearing pieces of the rock by "combing", and then the remaining portions of the rock are subjected to dry milling.

Dry milling consists of chipping off 2.5 mm size pieces from the rock, feeding the chips into a hammer mill and then screening by a series of screens of different meshes. Due to hammering, the serpentine is ground into powders while the fibers, being flexible, by and large remain intact. The latter can, therefore, be separated by screening, and according to the mesh size of the screens, can be classified into different length fractions.

In 1983, a wet process was developed in Australia for processing low-grade rocks and tailings from dry process. It consisted of two stages. In the first stage, the rock is crushed, made into a slurry with water, ground to release and open up the bundles of fiber, and then the rock powder containing fibers are concentrated in a spiral concentrator. In the second stage, the concentrate obtained from the first stage operations is cleaned by low-pressure hydro-cyclone, and then separated into two fractions — well-opened and poorly opened fibers — by high-pressure hydro-cyclone. The well-opened fibers are dewatered by high-pressure filtration and the poorly opened ones are hammer-milled and recycled.

2. Amphibole: The fibers of these varieties of asbestos are hard and brittle, and hence, can neither be separated nor used as such. Their processing involves only crushing and grinding into ordinary powders and ultra-fine powders (called *fluff* in the industrial circle).

GRADES OF ASBESTOS

Different systems of classification for chrysotile are followed by different sets of producers and user industries. But all the systems are based primarily on length and flexibility/brittleness of the fibers, both together being an indicator of their spinnability.

The international benchmark is the *Quebec standard*, according to which crude chrysotile is classified into two grades: (i) that consisting of fibers of a minimum length of 3/4 inches (19.05 mm) and (ii) that consisting of fibers of lengths 3/8 to less than 3/4 inches (9.525 to less than 19.05 mm). The Quebec standard classification for milled chrysotile is based on spinning tests and broadly the grades are: (i) spinning fibers, (ii) shingle fibers (i.e., the fibers of different lengths jumbled up irregularly), (iii) paper fiber (i.e., the fibers sticking together in the form of papers), and (iv) waste, shorts and refuse.

In India, four sets of grades are in vogue — two for crude, one for hand-sorted and one for milled chrysotile. There are no specific names attributed to them. These are as follows:

1. Crude

(a) Grade 'A' Special or 'AS' - 25.4 mm fibers or longer.
'AS_1'- 25.4 mm fibers and longer but brittle compared to AS.

‘A’ - 19.05 to 25.4 mm fibers.
‘A_1’ - 19.05 to 25.4 mm fibers but brittle compared to A.
‘A_2’ -19.05 to 25.4 mm fibers but brittle compared to A_1.
‘B’ - 6.35 to 19.05 mm fibers.
‘B_1’ - 6.35 to 19.05 mm fibers.
‘B_2’ - 6.35 to 19.05 mm fibers but brittle compared to B_1.
‘C’ - Below 6.35 mm fibers.
(b) Special Grade ‘A’ : Above 31.5 mm
Grade ‘A’ : Between 19 and 31.5 mm
Grade ‘B’ : Between 6.3 and 19 mm.
Grade ‘C’ : Below 6.3 mm including powder.
Grade ‘D’ : Dust.

2. Hand-sorted

‘A’ special or ‘AS’: 45 mm and above
‘A’: Between 25 and 45 mm
‘B’: Between 12 and 25 mm

3. Milled

‘C’: Above 16 mesh
‘D_3’ 24 mesh
‘D_4’ 40 mesh
‘D_6’ 60 mesh

Insofar as amphibole varieties are concerned, the grades are crude, powder and fluff.

CRITERIA OF USE

Pure chrysotile is usually white, but if iron and other impurities are present, then the colour may become yellowish to greenish and even to blackish. The colours of crocidolite and amosite are blue and brown respectively. But colour is not an important criterion for their industrial uses. For most of the uses of chrysotile, its unique fibrous structure is the key while for the other varieties of asbestos, certain other properties assume importance. The fibers of chrysotile are hollow and tubular (like hair), made up of sheet-like crystals and formed by a combination of metamorphism, folding, faulting and shearing. The key properties which determine the nature of usage are as follows:

1. *Nature of fibers:* Scope of application depends to a great extent on whether the fibers can be spun and woven. As per the definition of asbestos, the individual fibers must have length-to-width ratio not less than 20:1. In case of chrysotile, this ratio may go up to 10,000:1. This does not mean that the fibers have to be very long, but, in fact, this means that they are exceptionally thin. This thinness makes the fibers of chrysotile soft and flexible like silk and yet strong making them amenable to spinning and weaving. On the other hand, the fibers of amphibole varieties of

asbestos, although may be long (as in crocidolite), are also thick and brittle making them impossible to weave.

2. *Chemical properties:* All types of asbestos are characterized by a strong resistance to acids, alkalis and atmospheric decay and corrosion. But the chemical composition has no role in their use except in some applications where the specification demands limitation or absence of iron.
3. *Specific gravity:* Asbestos is fairly light, chrysotile being the lightest. Depending on the variety, specific gravity varies from 2.55 (chrysotile) to 3.5 (amosite).
4. *Thermal properties:* Asbestos is incombustible and a poor conductor of heat. It is difficult to fuse, fusion temperatures of its different varieties being 1,500^{0}C (chrysotile), 1,200^{0}C (crocidolite), 1,400^{0}C (amosite), 1,450^{0}C (anthophyllite), 1,315^{0}C (tremolite), 1,400^{0}C (actinolite). Their decomposition temperatures are 450-700^{0}C (chrysotile), 400-600^{0}C (crocidolite), 600-800^{0}C (amosite), 600-850^{0}C (anthophyllite), 950-1040^{0}C (tremolite), 620-960^{0}C (actinolite).
5. *Electrical and acoustic properties:* Asbestos has a high resistance to electricity, high dielectric strength (indicates the voltage that an insulating material can withstand before breakdown) and low dielectric constant of 4-12 indicating weak electrical conductivity (c.f., value for air, one of the poor conductors of electricity, is 1) and it is a good soundproof material.
6. *Bonding characteristic:* Asbestos bonds excellently with cement. The colloidal particles of cement in water can enter into the hollow fibers and this strengthens the bond.
7. *Surface properties:* The surface of amphibole varieties of asbestos is hard and they can resist wear and tear.

USES AND SPECIFICATIONS

Spinnability and fire resistance are the primary criteria for all the applications of chrysotile, and the other properties come into play after this. The important applications of different varieties of asbestos are as follows:

(1) Asbestos textile products
(2) Asbestos cement (A-C) products
(3) Asbestos paper and millboard
(4) Asbestos filters
(5) Jointing sheets
(6) Heat insulators
(7) Sound insulators
(8) Electrical insulators
(9) Filler in plastics
(10) Russian vodka
(11) Friction materials
(12) Sealants

These uses are explained below.

(1) Asbestos textile: Fibers are spun into yarns and then woven into fabrics of varying weight, thickness and shape, that require fire-resistance properties. The common products are ropes, tapes, felts, safety curtains in theatres, fireproof clothes and gloves, conveyor belts etc. in this application, the longer and softer the fibers are, the more suitable the asbestos. Generally, chrysotile is the preferred variety. The minimum length of fibers is specified by the industry to be 3/4 inch (19.05 mm). Sometimes, up to 20% cotton is mixed to facilitate spinning. A little of amosite and crocidolite is also tolerated.

(2) Asbestos cement (A-C): The products include flat and corrugated roofing tiles, boiler sidings, pipes, etc. In the manufacture of asbestos cement, silica powder, R_2O_3 and CaO are reinforced with asbestos fibers which become interlocked around a sand-cement paste. Here, the ability of asbestos to absorb and bond with cement, and also its heat-insulating property and light weight are the main criteria. Since the fibers are directly reinforced into the cement and pressed and no spinning is involved, the short-fiber asbestos can be and are utilized. Usually, chrysotile with a fiber length shorter than 3/4 inch (19.05 mm) meets with the requirements, but short-fiber crocidolite is also used. In India, even tremolite and actinolite are used in low-quality A-C pipes and fittings.

(3) Asbestos paper and millboard- Such papers and boards are used as insulator covering around air cell pipes, steam pipes and ovens, as gaskets, as washers etc. A mix containing 80% of asbestos in pulp form and 20% of china clay and some binder like starch or sodium silicate is processed in standard paper-making machines. Since asbestos is used in pulp form, it is obvious that very short-fiber (less than 1/2 inch) chrysotile variety can be used. The main criterion is the poor thermal conductivity.

(4) Asbestos filters: The purpose is to filter liquid chemicals. So, the asbestos must be strongly resistant to acids, alkalis, etc. Generally, amphibole varieties (specially anthophyllite) are the best suited. Iron tends to react with acids and hence the asbestos must be free from it. Short fibers do not affect the filtration efficiency and chrysotile asbestos with ¼- ½ inch long fibers are utilized.

(5) Jointing sheets: In such sheets, the poor thermal conductivity of asbestos is combined with the elasticity and resilience of rubber. They can be cut into washers, gaskets, etc. For manufacturing them, a mixture containing 20-60% chrysotile asbestos and the rest rubber, some filler and naphtha is pressed into sheet form. Very short fibers of ½ - ¾ inch length can be utilized.

(6) All-asbestos heat insulators: Such insulators in blanket form find applications in boiler, turbines and engine rooms of ships and in jet engines where temperature may go up to 480^0C. Poor thermal conductivity and light weight are the principal criteria. Practically 100% asbestos with only a little binder is used. And for efficient binding a rougher and harder surface is preferable. Amosite is generally used for this purpose.

(7) Sound insulation: The poor sound conductivity and lightness are the main criteria. Poor thermal conductivity is an additional advantage. Asbestos is pressure-sprayed on a wall before coating the latter with stucco. Not only light weight, but also short fibers facilitate spraying. Chrysotile with less than ½ inch long fibers can be utilized. This technique has been used for acoustic insulation of the walls and surfaces of the tubes of the London Underground Railways and also in mattresses for use in railway coaches.

(8) Electrical insulators: In this application both electrical and thermal insulation properties of chrysotile are taken advantage of. Chrysotile fibers are used to cover electric

wire in traction motors and coils which have a tendency to become overheated. The longer and softer the fibers, the more convenient it will be to wrap them around the wire. Also, the chrysotile must be pure — especially free from iron, because iron is an electrical conductor. So the highest grade of long-fiber and pure (i.e., white) chrysotile is specified for this application.

(9) Filler in plastics: The main purpose here is to impart thermal resistance to plastics. Asbestos is suitable because of its poor thermal conductivity and light weight. Chrysotile is best suited for this purpose. It is used in fine form., less than 1/16 inch sized dust, which can spread evenly throughout the matrix.

(10) Russian vodka: Real Russian vodka, developed in the 14th century as a medicine, is made from grape, rye, potato or potato peel. However, according to the connoisseurs, it is not important what it is made from, but the method of distillation and filtration. It is here that asbestos has a role to play. After distillation, the classical vodka is filtered through charcoal and chrysotile asbestos in order to get a mellow clear drink with a neutral flavour.

(11) Friction materials: Chrysotile is used for making woven brake linings and clutch facings. In India tremolite and actinolite are also used for these purposes. Low wear and high thermal resistance are the principal criteria.

(12) Sealants: Sealant is an organic substance soft enough to pour or extrude and capable of subsequent hardening to form a permanent bond with the substance. Chrysotile asbestos in fine form, which can spread evenly throughout the matrix, is used as a filler in certain formulations of sealants to impart strength and non-sagging property and to act as a thickening agent.

(13) Other uses:

a) Chrysotile is used for making different types of packing, vinyl sheet backings, filler in floor tile and in asphalt compounds, caulking compounds and roof coatings.
b) Amosite is used for making lightweight fire-resistant marine particle board.
c) Long-fiber crocidolite is woven into fabrics for locomotive boiler lagging and for acid-resistant packing and gaskets.
d) Anthophyllite and actinolite, often in conjunction with magnesia, are used for lagging boilers and steam pipes, and also for acid filtration.
e) Tremolite and actinolite have been used in Germany, the UK and the USA for manufacturing chemical resistant plastics while in India, they are used in insulation material and in asbestos-bituminous products.
f) Different varieties of amphibole asbestos are used in hard-setting magnesia composition and as a filler in asbestos paints and various asbestos moulded articles.

WASTE UTILIZATION

Asbestos is non-recyclable, because any attempt to remove the fibers from a host matrix destroys them. However, towards the end of the 20th century, a technology was developed in Quebec, Canada to recover magnesium metal from chrysotile asbestos tailings. In this process, magnesium and silica were separated by industrial electrolysis, and a pilot plant has been set up in 1998.

ENVIRONMENTAL PROBLEM

Asbestos is the toughest of all known fibers. When these fibers enter into a human body, they get permanently entrenched in different organs causing cancer of the lungs, bronchus, alimentary tract and kidneys. The carcinogenic diseases namely *asbestosis, pulmonary fibrosis, mesothelioma, silicosis* and *pneumoconiosis* acquired by intake of asbestos fibers was known since 1935. But the first corrective measure was taken in 1963, when the practice of spraying asbestos in British naval ships which had started in 1944, was abandoned. In 1975, the US Government issued rules curtailing the use of sprayed asbestos and banning its use in moulded pipes and insulation. But the health hazards associated with asbestos came into real focus worldwide due to the famous *Manville case*. On 26th August, 1982, Manville Corporation, the then largest producer of asbestos and asbestos-containing products among the market economy countries and having mines in Canada and plants in USA, filed a bankruptcy petition. The action was triggered by as many as 16,500 outstanding lawsuits against it by affected workers and consumers. Eventually, after 1984, it had to wind up its operations and sell all its mines and plants in order to pay huge amounts of compensation. In July 1982, the government of Sweden prohibited the use of asbestos. Since 1983, various environmental groups have been campaigning to build public pressure on governments to either totally ban or severely restrict mining and usage of asbestos. By 1986, within a number of countries like India, South Africa, USA, Denmark, Norway, Sweden and Finland debate was going on regarding various measures including stricter environmental regulations to mitigate its hazardous effect. On 9th July, 1986 the Government of India issued an order prohibiting the grant of a new asbestos mining leases as well as further expansion of the existing ones. Since around the same year, the use of crocidolite and amosite has been prohibited in the UK and uses of chrysotile have been prohibited in phases during the period 1992-1999. Poland and Saudi Arabia also followed suit. In February, 1990, in California State, USA, the Air Resources Board (ARB) set a maximum limit of 5% for asbestos-content in serpentine rock to be used for surfacing. A technical amendment to the European Commission's Marketing and Use Directive which became European Law in September, 1999 required all European Union members to cease the marketing and use of chrysotile after January 1, 2005. But, certain exemptions like use of chrysotile in compressed gaskets in situations involving hazardous substances, in fire-protective clothing and in research work was allowed beyond this deadline.

However, much of the actions against use of asbestos was based on the linear model of risk analysis and the concept of maximum tolerated dose (MTD). In the linear model the toxic effect of a substance at extremely high doses is extrapolated to conclude that it will also have a health impact at lower levels even if there is no observable effect at this level. The MTD method involves injecting laboratory animals with the highest tolerable dose and based on their response and the level of cancerous effect produced, predictions are made regarding the carcinogenicity of lower exposures in humans.

But in 1992, the Asbestos Institute, Montreal, Canada, backed up by scientific studies in different universities and scientific bodies like McGill University, the School of Medicine of the University of Southern California and the Advisory Review Board of the US National Toxicology Program began questioning the very basis of the adverse conclusions drawn from linear modeling technique and MTD method. According to their conclusions, the pattern and the order of magnitude of response to a toxic substance depends on the level of the dose and it cannot be extrapolated by a linear model, and further, there is no simple correlation between the effects on animals and on humans. Fingers were also raised against some of the alternative materials (e.g., fiber glass, PVC, ductile iron) for their potential health risks. All these issues were intensively debated in the 9th International Symposium on Epidemiology and Occupational Health held in September, 1992 in Cincinnati, Ohio, USA. In that forum, acceptance of the notion of a threshold level of cancer induction was strongly advocated by the asbestos industries supported by a section of the scientific community. It was concluded that any excess cancer mortality was found only among workers exposed to more than 50 fibers/cubic centimetre (f/cc) for a period of 20 years or more. As a sequel to these findings, a ban on asbestos products imposed by the US Environmental Protection Agency was reversed by the Fifth Circuit Court of Appeals, and the once thriving A-C pipe industry of USA was revived. In 1999, there was a 3.1% increase in world chrysotile production compared to the previous year.

All these debates notwithstanding, the environmentalists argue that in the course of normal wear and tear of asbestos products during their usage, the fibers tend to break into very tiny fibers some 700 times smaller than human hair which are virtually indestructible by high temperature up to 600^0C or by chemicals and which remain air-borne indefinitely. Hence pose a risk for not just the workers of the asbestos mines and industries but also for a much larger population. This was supported by the finding that in California State, USA, the total emission of asbestos from serpentine rocks used in pavements and other exposed structures was estimated in 1997 at 2,132 Kg per year. By the end of 2000, more than 20 countries have imposed a ban on asbestos usage. Japan has done so in October, 2004. China has effected a partial ban on its commercial use. With regard to India where 95% of the mined asbestos is used for manufacturing A-C products, short of a blanket ban, it still follows a regulatory approach based on the provisions and rules of the Environment (Protection) Act, 1986.

SUBSTITUTION

The worldwide campaign against mining and using asbestos triggered intensive research and development to find a suitable substitute. A substitute must approach the strength, chemical inertness, durability and cost of asbestos. The following efforts and products are worth considering.

1. The earliest substitute product in the world was introduced in 1970 by Du Pont. The product was trade-named *Kevlar* the chemical composition of which is poly-para-phenylene-terephthalamide or para-aramide in short. It belongs to the nylon family and it was the first organic fiber produced. It was made by extrusion through spinnerets. It is light in weight (specific gravity 1.44-1.47) and has high tensile strength, high resistance to both abrasion and impact and also thermal stability at temperatures up to about 600^0C. But it suffers from the disadvantages of proneness to absorb water, environment-sensitivity, poor compressive strength and difficulty in cutting and shaping. It has been used as a substitute of asbestos in its application as a filler in sealing materials and also for making fire-resistant gloves.

2. In 1978, a highly texturized form silica trade-named *Zetex* was developed by Sudhakar Dixit, an employee of an asbestos company in USA. He started manufacturing it in commercial scale through a company called Newtex in Victor, New York State and it is marketed in USA and many other countries for use in different applications as a substitute of asbestos. It has been reported that it is 5-6 times stronger than chrysotile fiber while retaining 50% of its strength at 100^0C and that it can be used in the applications where asbestos is used (e.g., in thermal insulators, in fireproof curtains, clothing, gloves, etc., in pipe castings, in heat conservation tapes).
3. The earliest serious work in UK was undertaken by the oldest British company Turner and Newall of Manchester which was formed in 1920 and associated with the manufacture of asbestos-based products—mainly drum brake linings, disc brake pads and clutch facings for the automotive industry. During 1978-1982, the company tested many thousands of potentially suitable materials including mineral, ceramic, glass and organic fibers in their laboratory and pilot plant. Some of them satisfied many of the criteria but failed on health and safety grounds, others performed well but were too costly. Finally the company zeroed in on a non-asbestos fiber (nature and composition not revealed), two or more of which in a resin-bonded composite yielded good results. Although it was expensive, but its life was twice as long as asbestos. During late 1980s, the company was manufacturing this product on a large scale.
4. During the 1980s, a project to identify a material to substitute asbestos was taken up by the Quebec Government’s Societe Nationale de l’Amiante (SNA). But, ironically, the material that came closest to meeting the criteria, used asbestos as the major raw material. The new product called *chrysophosphate* was developed by altering the surface characteristics of chrysotile asbestos through a phosphating process. It was claimed that although it was more expensive, its biological effect was significantly less than that of chrysotile without compromising with virtually any of the physical and engineering characteristics of the latter.
5. Around mid-1980s, the Central Building Research Institute, Roorkee, India reported that substitution of chrysotile by wollastonite to the extent of 25% was possible. But the experiments were on a laboratory scale only.
6. Around mid-1980s, the Regional Research Laboratory, Jorhat, India experimented with water hyacinth.
7. Around mid-1980s, the Central Glass and Ceramic Research Institute, India developed an asbestos-free product which was named as *marinite*. It was claimed to possess strength, machinability and thermal insulating properties and could be used as a substitute of amosite.
8. During the 1980s, research was underway in USA to develop slate-limestone glass fiber to partially substitute chrysotile to the extent of 40%, in A-C products. Towards the late 1980s, products based on it were marketed under the name *microlith glass fiber products*. These products were claimed to be incombustible, nontoxic, decay-proof and strongly resistant to both high temperature and chemicals.
9. Since the late 1990s, the anti-asbestos environmentalists have been suggesting *polyvinyl alcohol* as a cheap substitute.

10. Expanded (or exfoliated or flexible) graphite has emerged as an effective substitute of asbestos in one of its most popular uses as a sealing material in high-performance engines and as gaskets in petrochemical and thermal power plants where high temperatures are encountered. Flexible graphite is a binderless all carbon material having practically infinite life and which can be easily cut, punched, glued and pressed into dies. The process of converting natural graphite to expandable graphite was first developed in the late 1970s. (For details see the chapter on graphite.)

However, not a single material has been developed so far which possesses all the properties of asbestos and which can match asbestos in cost, in order to substitute it in all its applications.

Chapter 2

BARYTES

The name barytes (also known as *barite*, *heavy spar*, *bar*, *tiff* and *baryta*) is derived from the Greek word “baros” meaning “heavy”, referring to its most striking feature. Barytes is a naturally occurring barium sulphate with a chemical formula $BaSO_4$ (BaO 65.7% and SO_3 34.3%). It is the most widespread anhydrous sulphate after anhydrite. In nature, barytes is generally of hydrothermal origin and sometimes it also formed by leaching of barium compounds from rocks. As an accessory mineral it is found in the sulphides of manganese, iron and other metals. Barytes is also widespread in sedimentary rocks as concretions.

Barytes occurs both as veins and as bedded deposits, and mining is by both underground and opencast methods. The world’s largest bedded barytes deposit occurs in Mangampet, Cuddapah district, Andhra Pradesh, India. Of the total world production of 7.4 million tons in 2001, about 54% was accounted for by China alone. The other leading producers were India, Morocco, USA, Iran and Mexico.

HISTORY

A 17th century alchemist Vincentinus Casciarolo of Bolognia, Italy found a heavy crystalline stone with glass at the foot of a volcano and fired it in a charcoal oven intending to convert it to a noble metal. He obtained no noble metal, but found the sintered stone emitted red light in the dark after exposure to sunlight. He named this phenomenon *phosphorescence* and this stone *Bolognian stone*. Now we know that it was barytes which, when fired, yields BaS a phosphor.

Its first mining in USA where numerous deposits occur was reported in around 1850 and its use was confined to the manufacturing of paint and some chemicals. Its main use today —volume-wise—is as a weighting agent in drilling mud started for the first time in 1926.

In India, barytes mining started in 1918 and since then, till 1946, a total of 276,000 tons was produced, mostly from Andhra Pradesh. Since 1947, the production history of barytes is as shown below.

Year	*Production*
1947	25,000 tons
1950	12,000 tons
1960	17,000 tons
1970	79,000 tons
1980	442,000 tons
1990	633,000 tons
Year ending March, 2001	845,000 tons
Year ending March, 2006	1.19 million tons

The phenomenal increase in production in the 1970s was largely due to the discovery of large reserves in Mangampet deposit of Andhra Pradesh, opening of a large opencast mine there and worldwide increase in oil exploration activities triggered by the *oil shock* of 1973 (sudden fourfold increase in oil price by the OPEC). Almost 99.5% of the production nowadays comes from Andhra Pradesh with the rest coming from Himachal Pradesh and Rajasthan.

CRITERIA OF USE

Barytes is a crystalline (orthorhombic) mineral occurring in globular, massive, rosette, fibrous, and crystal forms. It has perfect cleavage. But the most important properties from the point of view of industrial application are as follows.

1. *Specific gravity:* The most striking characteristic of barytes is its high specific gravity. The specific gravity of pure barytes is 4.5 (c.f., magnetite 5.18) and this can vary downward, depending on the impurities present. The mineral even feels heavy in hand.
2. *Sound-deadening ability:* The high density enables barytes to slow down propagation of sound waves and it is thus an efficient sound-deadener.
3. *Radiation adsorption*- Barytes can adsorb different kinds of radiation—X-rays, neutrons, gamma-rays.
4. *Colour and other optical properties:* Pure barytes is bright snow-white opaque to transparent but impurities cause a wide variation in colour. Brightness of pure barytes as measured in terms of the reflectance of blue wave of light (wave length 457 micron) is 98.5 (c.f., for TiO_2—a standard reference, the value is 97-98). Whiteness of such barytes as measured in terms of ‘L’ value is 99 (c.f., for TiO_2—a standard reference, the value is 98-100). Its lustre is vitreous to resinous. Refractive index of barytes is about 1.64.
5. *Hardness and fracture:* Its hardness varies from 3 to 3.5 on Mohs scale and it is brittle, easily breaking with an uneven fracture. These properties make it non-abrasive in character.
6. *Chemical characteristics:* Chemically, barytes is $BaSO_4$, but, in nature, it usually contains impurities like SiO_2, Al_2O_3, Fe_2O_3, clay, fluorite and carbonates. Barytes

contains little or no soluble salts and it is insoluble in water and acid. It is chemically inert with pH value 6-8 (pH value of 7 means neutrality).

7. *Oil absorption:* Its oil absorption is low.
8. *Thermal property:* Barytes dissociates into barium sulphide (BaS) and oxygen at 1300^0C.

USES

The important uses of barytes are:

1. Oil-well drilling
2. Paint
3. Chemicals
4. Barium metal recovery
5. Glass
6. Paper
7. Rubber
8. Coal washing
9. Explosive
10. Concrete aggregate
11. Nuclear reactors and other radiation equipments
12. Radiology
13. Children's toys
14. Adhesives

These uses are elaborated as follows.

1. Oil-well drilling: In the oil industry, barytes is chiefly added to the drilling mud to increase the specific gravity of the latter. Rotary drilling is generally adapted for the development of oil fields in which circulation of drilling fluid or mud is a main feature. As the drill bit of the oil rig grinds its way through the rocks in search of oil, mud is pumped down the hollow drill rod. It passes into the drill hole through openings in the bit and rises to the surface through the space between the wall of the hole and the drill rod. The main functions of the drilling mud are:

(a) to cool the drilling bit and drilling string;
(b) to remove cuttings from the bits and to transport them to the surface;
(c) to have thixotropic or gelling properties so that in the event of a pump failure, the mud will gel and hold all the cuttings in suspension;
(d) to seal the open wall of the well to counteract any tendency for a loose formation to cave into the well;
(e) to counter and confine the pressure of oil and gas in the well and to prevent them from blowing out of the hole and from causing hazards; and
(f) to lubricate the space between the rod and the wall.

So, the main criteria for using barytes are its high specific gravity — 4.5 for pure barytes, low oil absorption (thus causing minimal loss of oil flowing into the well) and also its chemical inertness. The specific gravity will, however, tend to be slightly less because of impurities. A high $BaSO_4$-content will automatically ensure less impurities. There has to be a balance between grade and cost.

Amongst the deleterious constituents are SiO_2, Al_2O_3, Fe_2O_3 and clay because all of them tend to reduce the specific gravity of the barytes. In addition, silica in the form of grits will have an abrasive effect on the drilling rod, although quartz of certain specifications is added in some special cases (see chapter on silicon). Water solubility has to be low because the barytes particles along with the mud are to remain in suspension in the drilling fluid and not in solution. To help the barytes particles to remain in suspension, they must be in very fine size so as to expose as large a surface area as possible.

The industries generally prefer barytes with specific gravity 4.15 (min) and containing 94% (min) $BaSO_4$, 1.5% (max) SiO_2, 0.15% (max) Al_2O_3 and Fe_2O_3 each, 0.02% (max) water-soluble matter and as low as possible clayey matter. In 1984, the Bureau of Indian Standards (BIS) has prescribed specifications as: *90% (min) $BaSO_4$, 4.15 (min) specific gravity, 4.2% (max) $SiO_2+Al_2O_3$, 0.02% (max) water soluble matter, less than 53 micron particle size.*

2. Paint: Barytes is used in two ways—as a pigment and for making colouring matter.

(a) *Pigment*: Pigments serve mainly to impart or reinforce or extend certain properties of a paint for suiting specific purposes. Barytes mainly serves to increase the weight of oil paints so that they can settle on the painted surface better. In addition, white-coloured barytes serves to augment the hiding power of white paints. There are two types of barytes-based white pigments: (i) very high grade natural barytes with high specific gravity as near to that of pure barytes (4.5) as possible, and (ii) chemically precipitated pure $BaSO_4$ called *blanc fixe* (although its specific gravity is less i.e., 3.36, it is still heavier than many other substances).

Natural barytes pigment is used in both white and coloured paints depending on its purity—the bright snow-white barytes (high reflectance of blue wave light and high 'l' value) for white paints and off-coloured barytes for coloured ones. Chemically precipitated $BaSO_4$, on the other hand, is generally very pure and is used in high-quality white paints. The higher refractive index of barytes (1.64) than that of linseed oil (1.48) serves well to enable the paint to hide spots. Chemical inertness of both natural barytes and precipitated $BaSO_4$ is an advantage.

Oil absorption should be optimum. Since oil is the medium, very high oil absorption will mean that much of the oil will be absorbed by the pigment leaving less for the main colouring matter, but slight absorption is desirable as otherwise the paint will not act well. Size of particles is important as only very fine-sized ones with large surface areas can keep the paint particles in suspension. Volatile matters is undesirable because, when the paint dries, they may go off leaving holes on the painted surface. Carbonates (e.g., $BaCO_3$, $CaCO_3$) are generally hard with a tendency to have an abrasive effect on the painted surface besides contributing to volatile CO_2 and hence are considered deleterious.

In 1972, the Bureau of Indian Standards (BIS) has recommended the specifications of both natural barytes and precipitated $BaSO_4$ as follows.

1. Natural barytes: 95% (min) $BaSO_4$, 2.24% (max) $BaCO_3$, 0.5% (max) volatile matter, 6-12% oil absorption, 0.5% (max) water-soluble matter and particle size varying from less than 40 micron (400 mesh) to 53 micron (300 mesh).
2. Precipitated $BaSO_4$: 97% (min) $BaSO_4$, 0.45% (max) $BaCO_3$, 0.5% (max) volatile matter, 15-30% oil absorption, 0.5% (max) water-soluble matter and particle size less than 40 micron (400 mesh).

The higher oil absorption specified for precipitated $BaSO_4$ is because it is of bright snow-white colour and is mainly used as a white colouring substance which should be saturated with oil for durability of the paint coating.

Earlier, barytes used to be a popular material for adding weight to paints because they used to be sold by weight. Nowadays, they are generally sold by volume, and so adding barytes to paints for the sole purpose of increasing weight is no longer a common practice unless, of course, other purposes are required to be served as explained above. It however continues to be used as a weighting agent in some primers.

(b) Lithopone: Lithopone is a chemically prepared white-coloured mixture of $BaSO_4$ and ZnS used as an indicator in X-ray photographs. For preparing it, snow-white coloured barytes is first roasted with carbon (coal or coke) at 1300^0C to produce BaS, which is then reacted with $ZnSO_4$ solution to precipitate the mixture of $BaSO_4$ and ZnS or lithopone.

The particle size of barytes is important because too fine a size will result in dust loss and too coarse a size will not mix well with the powdered coal/coke at the time of roasting. Iron oxide is objectionable because it melts at about $1,100^0$ C, i.e., below the roasting temperature and inhibits the roasting operation. alumina and silica in the form of aluminium silicate (e.g., clay) melts below $1,300^0$C, the roasting temperature of barytes and inhibits the roasting operation. Besides, iron oxide, alumina and silica react with barytes to yield water-insoluble compounds and remain mixed with the BaS reducing its reactivity with $ZnSO_4$, and getting precipitated along with the lithopone. Further, compounds of iron as well as of manganese, if present, reduces the efficiency of reduction of $BaSO_4$ because some carbon is used up by them reducing its availability for actual roasting operation. Iron oxide is also a colouring substance. Fluorite melts at almost the same temperature i.e., 1360^0C and becomes a free-flowing low-viscosity liquid getting mingled with the BaS, and hence is considered deleterious. Strontium sulphate or $SrSO_4$ (celestite) which is often associated with barytes because of their isomorphous relationship has similar thermal properties as barytes and also reacts with carbon at the same temperature i.e., 1300^0C to form strontium sulphide, thus eating up a part of the carbon. Hence it is not desirable. So far as CaO and MgO are concerned, these are highly reactive at the roasting temperature and readily forms low-melting aluminosilicates which remain in molten state mixed up with BaS, hindering operation.

The industries generally prefer barytes with snow-white colour and containing 95% (min) $BaSO_4$; 1.0% (max) Fe_2O_3 and $SrSO_4$ each; as low as possible Al_2O_3, SiO_2, CaO, MgO and clayey matter; the other criteria are absence of fluorspar and particle size 0.85-4.0 mm.

3. Chemicals: Barium sulphide (BaS) prepared from barytes by roasting as described above is the starting point for making various barium chemicals. In this case, instead of reacting with $ZnSO_4$, the BaS which is soluble in water, is leached and separated from the insoluble coal ash. The specifications may be slightly different depending on the quality of the chemicals to be produced. In 1984, the Bureau of Indian Standards (BIS) has prescribed specifications for barytes for manufacturing ordinary and high quality chemicals as:

i. Ordinary quality chemicals: 90% (min) $BaSO_4$, 6.0 % (max) SiO_2+Al_2O_3, 1.5% (max) Fe_2O_3, 2.0% (max) CaO+MgO.
ii. High-quality chemicals: 97% (min) $BaSO_4$, 2.0% (max) SiO_2, 0.1% (max) Al_2O_3, 0.1% Fe_2O_3, o.1% (max) CaO+MgO.

The chemical industries, in addition, specify 1.0% (max) strontium sulphate, low manganese, trace fluorine and particle size 0.85-4.0 mm.

Strontium sulphate gets roasted at the same temperature, i.e., 1,300^{0}C producing strontium sulphide which is soluble in water like its barium counterpart. So, both get leached away and are difficult to separate, and hence the presence of strontium sulphate in the barytes is not desirable. The reasons for the specifications with respect to the other deleterious constituents like alumina, silica , iron oxide, CaO, MgO , fluorine and the particle size are the same as explained for lithopone above.

Major barium chemicals obtained from barytes (other than barium sulphate which is a pigment and has been described under paint) are as follows.

(1) Barium carbonate ($BaCO_3$): It is used as a component of glass, ceramic glazes and enamel to prevent formation of scum on their surface. It melts the scum as soon as it forms. It is also used for removing impurities from phosphoric acid and for case-hardening of steel.
(2) Barium chloride ($BaCl_2$): It is used for hardening the surface of leather and cloth, for preventing scum on brick , in water treatment and for recovering barium metal.
(3) Barium oxide (BaO): It is used in glass-making and for making barium peroxide. BaO is added to ceramic glaze along with copper oxide. While CuO imparts a turquoise colour the BaO serves to enhance its blue shade.
(4) Barium peroxide (BaO_2): It is used in electric arc furnaces to increase the life of the linings and to stabilize the arc. In metallurgy, it is used to reduce sulphur and slag viscosity. It is also used for making hydrogen peroxide (H_2O_2).
(5) Barium hydroxide [$Ba(OH)_2$]: It is used in the preparation of barium salts of organic acids and are employed as additive for lubricating oils and as stabilizer for PVC. In recovering sugar, it can be added to molasses to form barium saccharate and eventually to separate sugar. It also prevents scum formation on ceramic products by melting the scum.
(6) Barium nitrate ($BaNO_3$): It is an ingredient in green signal flares, in primers and detonators of explosives.

4. Barium metal recovery: Barium metal is recovered by electrolyzing fused barium chloride. Barium is a soft silver-coloured metal having melting point 850^{0}C. It has a strong affinity for oxygen and is used as a deoxidizer of copper and for degassing vacuum tubes of electronic equipments. Besides it has a high electron emission when subjected to electric charging and, by virtue of this property, it has been used as a component in alloys for making spark plugs and elements of electronic tubes. Its alloy with yttrium, copper and oxygen (Y-Ba-Cu-O) is used as superconducting shields in some rockets at 77 K.

5. Glass:

(1) *Ordinary glass*: Common standard glass is an amorphous, hard, brittle and transparent substance and chemically, it is a mixture of the silicates of sodium, calcium and magnesium — $18Na_2O.2MgO.8CaO.72SiO_2$ (for details see the chapter on silicon). Barytes serves four purposes in glass manufacturing as follows.

(a) For making glass in continuous tanks, barytes is used because it dissolves in fused soda ash (Na_2CO_3) to form a heavy solution which sinks to the bottom of the tank and when the temperature is raised, it reacts with silica to yield gaseous SO_2 and oxygen. The escaping gas bubbles stir the melt and remove occluded gases and thus homogenize the glass.

(b) It imparts brilliance to the finished glass by virtue of its brightness and higher refractive index (1.64) than glass (1.54).

(c) It fluxes (i.e., melts and imparts free mobility) to the melt thus preventing froth formation on the surface (it melts the scum as soon as it forms).

(d) Barytes makes the glass more workable by increasing its density.

BaO or $BaCO_3$ are also added, to serve the purposes partially, but it is barytes that is added most commonly because of its high specific gravity, brightness and higher-than-glass refractive index.

Barytes crushed to granular size is added. This particle size is very important. Too coarse a size may not dissolve completely in the soda ash and too fine particles will tend to ball up or coagulate in the mixture and become coarse.

Chemically, the main constituent, i.e., $BaSO_4$, should obviously be as high as possible within the cost constraints. With regards to impurities, iron oxide and alumina are particularly objectionable. The former has a colouring effect while the latter increases the melting temperature of the raw materials mixture. Silica is the main constituent in the glass, but it has to be in the right proportion. It is added in the form of the essential raw materials quartz and feldspar. Any additional input of it through the barytes may disturb its proportion in the glass and will create operational difficulties.

The Indian industries specify about 96% $BaSO_4$ (minimum 90% for low-quality product), 1.5% (max) SiO_2, 0.15% (max) Al_2O_3, 0.1% Fe_2O_3 (maximum 0.5% for low-quality product) and usually 200-500 micron grain size (but sometimes up to 2.0 mm).

(2) *Photochromatic glass*: Barium is a component in one of the special types of glass namely, *photochromatic* or *photochromic glass*, which is a borosilicate glass that has the unique property of temporarily darkening when exposed to sunlight especially ultraviolet light) and is used in spectacles and other optical lenses. It is made by adding silver chloride (or Al_2O_3 and Nb_2O_5), an alkali metal (lithium or sodium or potassium) and barium to the raw material mix for borosilicate glass.

6. Paper: It is used as a filler in the manufacture of products requiring heaviness, stiffness and brilliant white finish all attributes of barytes. In addition, inertness of barytes is also a criterion. Very often, natural barytes with the required brilliance is not available and blanc fixe or chemically precipitated barium sulphate is used. The most common ones amongst such products are *bristol board* (thin cardboard in a variety of colours with a smooth surface ideal for presentations, drawings, and pictures), heavy printing papers and playing cards.

7. Synthetic rubber: Natural rubber is a processed natural vegetable gum which is present as tiny droplets in the juice called *latex*. It consists of long chains of interconnected isoprene molecules containing C, CH, CH_2 and CH_3. The normally entangled chains can straighten up when stretched, giving rubber its most important characteristic — elasticity. Synthetic rubber (or *Buna*), on the other hand consists of a mixture of butadiene and styrene approximately in the ratio 75:25. The principle involved in the manufacture of synthetic rubber involves a process of polymerization, i.e., small molecules are added successively to a molecule (monomer) to give rise to a big molecule. In industrial practice, polymerization is allowed to proceed in an emulsion of butadiene and styrene in an aqueous medium containing a combination of activators (an emulsion is a dispersion of liquid in another immiscible liquid). After completion of polymerization, the resultant product obtained resembles natural latex, which is coagulated with help of hydrochloric acid and other chemicals.

Barytes is added before polymerization, for increasing the weight of the finished rubber goods and also imparting white colour when white-coloured product is to be made. Inertness, brilliant white colour and high specific gravity are the chief criteria. But very pure grade is required with extremely low to nil contents of moisture, matters soluble in water and acid, Fe, Mn and Cu. Besides fine particle size is also important.

Since the medium of the emulsion is aqueous, water-soluble matter is not desirable, and since the latex is treated with HCl-acid, presence of matter soluble in that acid is also not desirable. Manganese, Fe_2O_3 and copper interfere with the polymerization process and are objectionable. The particles are to be uniformly dispersed throughout the medium and hence their size should be very fine.

Generally, barytes of 99.5% or even higher purity is preferred (which practically does not occur in nature) and as such, precipitated $BaSO_4$ (blanc fixe) is used. The Bureau of Indian Standards (BIS) has standardised the specifications in 1973. According to this standard, barytes for this use should contain 0.5% (max) each of water and acid-soluble matter, 0.005% (max) Mn, as low as possible Fe and Cu, and the particle size should be less than 75 micron.

8. Coal washing: In heavy medium separation of coal from shale matter, the principle involved is to feed the ground mixture of the two into a medium which is heavier than coal (specific gravity 1.14-1.40) but lighter than shale and other mineral matter (specific gravity 2.5-3.5), so that the coal particles can float while the shale particles sink. As for heavy medium, nowadays, water containing the right proportion of fine-sized grains of magnetite (specific gravity 5.18) in suspension (so as to achieve the right specific gravity) is used. But, ground barytes has also been used due to its low cost and high specific gravity. Moreover, after the shale is separated, coal and barytes grains can be separated easily because the latter settles down at the bottom.

9. Explosive: In certain applications like mining, seismic prospecting etc., the impact of the intensity of an explosive is required to be controlled. In such explosives, finely ground barytes is used as a high-density filler. It weakens the shattering effect or *brisance* because of the slowing down of the sound energy passing through it. Its chemical neutrality is also a useful criterion.

The most objectionable constituent is grit which contributes to the damage when thrown out due to explosion and moreover, it increases the grinding cost of the barytes. $BaCO_3$ are considered deleterious because it will tend to dissociate into CO and CO_2 which will get added to the gases generated which is the main cause of explosion. Common explosives are made of liquid glycerol trinitrate which is an acid, and hence acid-soluble matter is not desirable in the barytes. Further barytes must remain dry and should not absorb moisture and any water-soluble matter is also not desirable.

The Bureau of Indian Standards (BIS) has specified the grade of barytes as 90% (min) $BaSO_4$, 1% (max) $BaCO_3$, 3% (max) acid-soluble matter, 0.5% (max) water-soluble matter, 0.001% (max) grit) and particle size below 63 micron.

10. Concrete aggregate: *S*tandard concrete has a bulk density 2.72 tons/m^3. However, in certain applications like parking areas, airport runways and pipeline coverings in marshy land, heavier concrete which can weigh down as a compact mass, is preferred as the paving mixture. For making such concrete, barytes is added because of its high specific gravity and chemical inertness. The density of typical barytes concrete is more than 3.52 tons/m^3.

11. Nuclear reactors and other radiation equipments: The heavy concrete as described above is also used in nuclear reactors, particle accelerators, laboratory hot cells, etc. in order to shield the fast neutron and gamma-ray radiations by slowing down their transmission. Besides imparting heaviness, barytes also enables the concrete to adsorb the radiations.

12. **Radiology:-** The high X-ray adsorption capability and inertness are the main criteria. It is used in the following ways.

(a) It serves as a contrast medium for the examination of gastrointestinal tract for diagnostic purpose.
(b) It is added to bone and dental cements so that progress of bone/tooth implantations can be monitored with the help of periodic X-ray photography.
(c) It is used as a filler in plastic medical instruments so that in case they are accidentally left by the surgeon inside the body, they can be easily detected with the help of X-ray photography. Plastic as such cannot be detected by X-ray.

Natural barytes, precipitated $BaSO_4$ (blanc fixe) or a mixture of the two can be used.

13. Children's toys: In some plastic toys, barytes is used as a filler. Here, the relative low cost, in addition to high X-ray adsorption capability and inertness, is the main criterion. The purpose is to easily detect such toys by X-ray photography in case they are accidentally swallowed by children, as otherwise, it will be difficult to detect them.

14. Adhesive: Adhesive is an organic or inorganic substance capable of bonding together other substances by surface attachment. Fine-grained barytes is used as an additive to certain adhesives because of its low oil-absorption, whitening effect, chemical inertness and ability to disperse uniformly within the matrix.

Chapter 3

BORAX AND RELATED MINERALS

Borax (so named after Persian “burah” or”burak”) is a sodium borate with 10 water molecules of crystallization. But, commercially, the term borax is often used to denote a group of closely related sodium borates differing in the contents of *crystal water* and of a natural derivative of borax, namely, boric acid. The compounds are:

1. Anhydrous borax ($Na_2B_4O_7$, 69.2% B_2O_3)
2. Tincalconite or borax pentahydrate ($Na_2B_4O_7 \cdot 5H_2O$, 47.8% B_2O_3)
3. Tincal or borax decahydrate ($Na_2B_4O_7 \cdot 10H_2O$, 36.5% B_2O_3)
4. Kernite ($Na_2B_4O_7.4H_2O$, 50.9% B_2O_3)
5. Natural boric acid (H_3BO_3, 56.3% B_2O_3)

Of these, the decahydrate or tincal is the most common form and (unless otherwise specified) borax is understood by this form (“suhaga’ in Indian language). But, on exposure, it tends to dehydrate to the pentahydrate (tincalconite). Besides, there are some other boron compounds, some of which can substitute borax in some of its uses. These are:

1. Ulexite ($Na_2O.2CaO.5B_2O_3.16H_2O$, 42.9% B_2O_3)
2. Colemanite ($2CaO.3B_2O_3.5H_2O$, 50.8% B_2O_3)
3. Szaibelite ($2MgO.B_2O_3.H_2O$, 41.4% B_2O_3)
4. Hydroboracite ($CaO.MgO.3B_2O_3.6H_2O$, 50.2% B_2O_3)

Of these, ulexite and colemanite are important from the point of view of industrial usage.

Commercially sold borax is usually partially dehydrated. In nature, borax occurs naturally in *evaporite* deposits (resembling cotton balls) produced by the repeated evaporation of seasonal lakes. Borax can also be produced synthetically from other boron compounds and from some lake brines. It is believed to be known over 4,000 years ago.

In India, borax deposits occur in Puga Valley in eastern Ladakh, Jammu and Kashmir which is an extension of the borax-rich belt of south-western Tibet. The earliest record of these occurrences dates back to 1563. Historically, crude borax used to be imported to India across the Indo-Tibetan border which reached a peak at 1,625 tons in 1885 and refining used to take place in India. Of the total import, the major part used to be exported from India to UK. After this year, exports dwindled due to discovery of deposits in the USA. Subsequently, in 1925, the transborder trade was stopped. Some insignificant amounts continued to be produced from Ladakh, but since the 1940s, there is no production of borax in India and the entire requirement is met by imports.

In USA, borax has been mined near the surface in Death Valley, California since the late 1800s. Besides, other commercially important deposits are found in *Turkey* and near *Boron, California* and other locations in the South western United States, Russia, Argentina, Tibet and the Atacama desert in Chile. Of the total world production of 4.64 million tons during 2000, Turkey, USA, Russia and Argentina accounted for over 95 percent.

CRITERIA OF USE

Borax is usually a white powder consisting of soft colourless *crystals*. If left exposed to dry air, borax slowly loses part of its *water of hydration* and becomes a white and chalky *mineral tincalconite* ($Na_2B_4O_7{\cdot}5H_2O$). The important criteria determining the practical use of borax including those of the related minerals and its derivatives are as follows.

1. Low cost: Borax is plentiful in the world, easy to mine due to softness and near-surface occurrence and hence relatively inexpensive.
2. Specific gravity: It is light having specific gravity 1.73.
3. Water solubility:- It dissolves easily in water, its water-solubility being 5.1 gm/100 ml at 20°C. Boiling water can dissolve two times its weight of borax.
4. Chemical nature: The solution of borax in water is mildly alkaline having pH of about 9.5. Borax can be easily converted to *boric acid* (H_3BO_3) by reacting a solution of borax with sulphuric acid. The reaction is:

   $$Na_2B_4O_7{\cdot}10H_2O + H_2SO_4 \rightarrow 4H_3BO_3 + Na_2SO_4 + 5H_2O$$

   Boric acid in its turn can be converted to boric oxide (B_2O_3) and other *borates,* which form the basis for many of its applications. When melted, borax has the ability to melt many chemical elements like iron, copper, nickel, etc.

4. Thermal properties: Its melting and boiling temperatures are low, being 75°C and 320°C, respectively. When borax is burned, it produces a bright orange-colored flame, but it is not inflammable.
5. Electrical conductivity The low electrical conductivity of sodium has been carried into its compound borax.
6. Colour: Borax is a white powder. When fused, it becomes a colourless glass-like substance — an attribute of elemental boron carried into it.
7. Refractive index: Refractive index of borax is low, being only in the range of 1.447 to 1.472 (c.f., ordinary glass 1.54).
8. Elemental boron: Boron is a metalloid belonging to the borderline between metal and nonmetal. Its characteristic properties are as follows.
   (a) It is hard and it retains its strength at high temperatures.
   (b) It is extremely reactive at high temperature with oxygen and nitrogen.
   (c) Amorphous boron burns with a distinct green flare.

(d) It behaves like a nonmetal inasmuch as it is a very weak electrical conductor (semiconductor), but it conducts heat (like a metal).
(e) The heat conductivity gives it a low coefficient of thermal expansion.
(f) One of its isotopes B^{10} is capable of absorbing neutrons without emitting gamma rays, while another, B^{11} has low neutron absorption ability.
(g) It is light compared to many metals, having specific gravity varying from 2.34 to 2.37.
(h) Its melting point is high, 2079^0C, and it boils and sublimates at 2550^0C. But its melting rate is slow.
(i) Of all the elements of the Periodic Table, boron is unique inasmuch as it has the ability to form glass.

9. *Ulexite and colemanite:* Ulexite crystals possess natural strength and flexibility while colemanite has a high B_2O_3-content combines with calcium instead of sodium. These attributes are advantageous in some uses. Besides, these minerals can be processed to yield boric acid by reacting them with sulphuric acid and the boric acid is converted to borax by treating it with soda ash (Na_2CO_3). Borax can also be prepared directly from colemanite by boiling its powder with soda ash solution, filtering and then allowing borax to crystallize from the filtrate.

USES

Borax is generally processed by dissolving in hot water under pressure whereby the impurities are made to remain in suspension and are be filtered out. Then the filtrate is cooled and crystals of commercially usable borax are obtained. Borax has a wide variety of uses. Its important uses are:

1. Flux
2. Insecticide and fungicide
3. Medicinal applications
4. Cleaning material, soaps and detergents
5. Glass
6. Ceramics
7. Enamel
8. Silly-Putty
9. Buffer solution in biochemistry
10. Ultra-hard materials
11. Recovery of elemental boron
12. Ferro-boron
13. Metallic glass

These uses are elaborated as follows.

1. Flux: The low melting point (75°C) and low boiling point (320°C) of borax enable it to not only lower melting temperatures while heating other substances, but also make the melts fluid and mobile. The following are the common applications of borax as flux:

(a) *Welding*: A mixture of borax and ammonium chloride is used as a flux when welding iron and steel. It lowers the melting point of the unwanted iron oxide scales, allowing them to run off.
(b) *Soldering of precious metals*: Borax is used mixed with water as a flux in jewelry-making for soldering metals like gold or silver (solder is an alloy of tin and lead, which is used for joining two pieces of a metal by a process of welding called soldering). It allows the molten solder to flow evenly over the joint in question.
(c) *Artificial gem*: Borax is used as a flux in manufacture of artificial gems.
(d) *Soldering of tungsten and zinc*: Borax is used as a flux in soldering tungsten and zinc. In all these applications, the low melting point of borax is the main criterion.
(e) *Electroplating bath*: Electroplating is the process of precipitating a metal in an anodizing bath through electrolysis (e.g., chrome-plating). Borax serves to facilitate melting of the metal and to make it fluid.

2. Insecticide and fungicide: Boric acid, sodium borate, and sodium perborate ($NaBO_3.4H_2O$) — all derivatives of borax — have a fatal dose from 0.1 to 0.5 gm/kg. These substances are toxic to all cells. These compounds find applications in the manufacture of biological growth control chemicals for use in water treatment, algaecide fertilizers, herbicides and insecticides. The boron salts inhibit the metabolic processes of many organisms. This characteristic allows borax to disinfect and kill unwanted pests, fleas, etc. It prevents mould formation in citrus fruits caused by a fungus. It is also in *anti-fungal* compound for *fiberglass* and *cellulose* insulation.

3. Medicinal applications: Boric acid powder is a common medicine used as an antiseptic application for disinfecting external wounds. However, it has been estimated that boric acid is fatal at concentrations 0.1- 0.5gm/kg. At this concentration, it is toxic to all cells. Boric acid solutions used as an eye wash or on abraded skin are known to be especially toxic to infants. It can also be used for treating a kind of fungal infection of the hoofs of horses and also for treating arthritis.

4. Cleaning material, soaps and detergents: Sodium perborate ($NaBO_3.4H_2O$)—a derivative of borax, has strong oxidizing property and has the ability to clean and bleach by converting some water molecules to hydrogen peroxide (H_2O_2). This reaction is more efficient in hotter water. The pH of borax is about 9.5, so it produces an alkaline solution in water and its derivative sodium perborate is also alkaline in nature. This alkalinity increases the effectiveness of bleach and other cleaners.

Its easy solubility and properties to soften hard water find applications in soaps, cleaners and detergents. Borates bonds with other particles to keep ingredients dispersed evenly in a mixture, which maximizes the surface area of active particles to enhance cleaning power.

Borax crystals are odourless to whitish and alkaline and is not inflammable. It can be mixed with most other cleaning agents, including chlorine bleach.

5. Glass: Physically, common standard glass (also called lime-soda glass) is an amorphous, hard, brittle and transparent substance and chemically, it is a mixture of the silicates of sodium, calcium and magnesium. The composition of typical ordinary glass is [$18Na_2O.2MgO.8CaO.72SiO_2$]. Essentially, the process of manufacture of this glass consists in melting a mixture of 47% silica sand, 14% soda (Na_2CO_3), 12% dolomite-($CaCO_3.MgCO_3$), 3.5% limestone ($CaCO_3$), 2.5% carbon (coke) and the balance broken waste glass (called cullet) at 1400-1500^{0}C and then quenching (for more details see the chapter on silicon).

Sometimes, this lime-soda glass may contain a little boron in the form of up to 0.7% B_2O_3 to:(i) impart strength, (ii) make the dishes, etc., resistant to washing detergents, and (iii) slow down the rate of melting so as to suit the production cycles to the convenience of the manufacturer. However, some special glasses with some special properties are made by replacing much of the soda by boric oxide (B_2O_3) which comes from borax (i.e., tinkal). In all kinds of glass with added borax, its property to become a colourless glass-like substance upon fusion is a common criterion. The special glasses containing significant amounts of boric oxide are as follows.

(a) *borosilicate glass*: Borosilicate glass typically comprises 81% silica and 12.5% B_2O_3 with small amounts of Na_2O (4-5%) and Al_2O_3 (0.2%). Borosilicate glass incorporates within it some of the attributes of elemental boron inasmuch as it is strong and highly resistant to heat and is characterized by very low coefficient of thermal expansion (one-third of common soda-lime glass). Consequently, unlike other types of glass, borosilicate glass does not crack under thermal shock. For making this glass, tincal (typical borax, $Na_2B_4O_7$. $10H_2O$) is desirable because it contains sodium and is devoid of CaO. While sodium is an essential ingredient of the glass, CaO will tend to reduce its heat-resistance.

(b) This glass is used for making special heat-resisting cookware, laboratory wares, chemical process plant and glass fibers for textiles and plastic reinforcement. It is nowadays engineered into hollow lighter-than-water and highly flexible micro-balloons for use as fillers (in refractories, concrete, oil well cement, brake linings etc), sealants and coatings primarily on account of its heat resistance, inertness and high strength. In the glow discharge lasers using a gas as the medium for transforming ordinary light to laser, the operating current is a few milli-amperes and the heating is not severe. Hence, a tube made of borosilicate glass can be used (see also chapter on ruby).

(c) *Art glass*: Art glasses are meant to be cut into artistic shapes unlike the glass wares, pipes tubes etc. which are melted and then blown or moulded. But, glass containing a high amount of boric oxide is very hard and is difficult to cut. In order to achieve a balance between hardness and workability, the B_2O_3-content in such glasses is limited to 3.5 per cent.

(d) *Optical fiber*: Optical fiber is a comparatively recent development in communication. In optical fibers, light, instead of electromagnetic energy (as in copper wires) or radio

waves or microwaves (as in case of wireless communication systems), is used for carrying information in the form of video, voice or data. Optical fibers use the principle of successive total internal reflection of laser beam within a hair-thin glass fiber (one kilogramme of glass is drawn into a 6 km long fiber of 150-200 micron) comprising an inner denser core surrounded by a lighter cladding – both highly transparent. The layers are deposited by a highly complex process called *modified chemical vapour deposition* (MCVD) technique. Light is carried along the core due to total internal reflection at the contact surface between the core and the cladding, even if the fiber is bent. The glass for this purpose has to be of extraordinarily high purity and such glass is made from pure silica prepared synthetically by reacting silicon chloride with oxygen. Then the question arises of increasing the refractive index of the core glass and/or reducing that of the cladding glass. To increase the refractive index, germanium is added and to reduce, one of the materials added is boron. The lower-than-glass refractive index of borax (1.447-1.472) is the main criterion besides the properties of strength, heat-resistance, low thermal expansion coefficient and ability to bear thermal shocks which become necessary as such fibers are laid across all kinds of terrain and even sea and they must not break during handling. However, in such fibers, in addition to strength some degree of flexibility is desirable. Hence, the boron compound ulexite ($Na_2O.2CaO.5B_2O_3.16H_2O$) which has this property naturally, is generally preferred to borax.

(e) *Reinforcement glass fiber*: These fibers are used for impregnating in some matrix of ceramic material to strengthen the latter. Typical composition of this glass is 7.3% B_2O_3, 0.3-0.8% Na_2O, 0.2% K_2O, 18.6% CaO, 15% Al_2O_3, 3.3% MgO, 0.3% Fe_2O_3 and 55% SiO_2. In this glass, CaO, and not sodium, is an essential ingredient. Hence either a processed and refined borax or the calcium-containing boron compound colemanite ($2CaO.3B_2O_3.6H_2O$) is used. Out of the two alternatives, the latter is much less expensive and naturally contains higher B_2O_3 (50.8%) than the former (36.5%), and hence is preferred.

(f) *Photochromatic (or photochromic) glass*: Photochromatic glass is a barium-containing borosilicate glass that has the unique property of temporarily darkening when exposed to sunlight – specially ultraviolet light and is used in spectacles and other optical lenses. It is made by adding silver chloride, an alkali metal (lithium or sodium or potassium) and barium to the raw material mix for borosilicate glass. The $AgCl_2$ and alkali metal can also be replaced by some other substance like Al_2O_3 (introduced through feldspar) and Nb_2O_5. Such glass can also be made by applying some special organic coating to the finished optical glass.

(g) *Lead crystal (or flint or cut) glass*: Lead crystal glass is a lead-potash glass. PbO is used as the flux. It is lustrous with high refractive index. Due to its lustre, brilliance and sparkle this glass is used for ornamental purpose and for making superior tableware. In old times, due to its high refractive index, it was used for making some kind of lenses also. Typical composition of this glass is 2.5% B_2O_3, 2.5% Na_2O, 7.0% K_2O, 1.0% Al_2O_3, and 55% SiO_2.

(h) *Mineral/glass wool*: *Mineral wool* is a general term meaning fibers made from inorganic substances that may include minerals, rocks and metal oxides — synthetic or natural. When the substance is a natural mineral or rock it is called *rock wool* or *stone wool*. Glass wool is a type of mineral wool because it contains minerals. It consists in a very thin string of glass arranged into a spongy texture. For manufacturing glass wool, molten glass is first drawn into fibers which are then cemented into a *fiber mat* with the help of some resin binder (e.g., phenol formaldehyde). The fiber mat is heated to 200^0C to polymerize the resin and make the product a strong and cohesive material called glass wool. It is a light weight, corrosion free, water proof absorbent material capable of absorbing sound and heat. It finds use in thermal and sound insulation, and in fire resistant applications. Typical composition of this glass is 5% B_2O_3, 16% Na_2O, 8% CaO, 3.5% Al_2O_3, 3% MgO and 64.5% SiO_2.

For all these glass products, the borax should be free from any colouring matter like Fe, Co, Ni, Cu, Ti which are considered deleterious.

6. *Ceramics:-*

(a) *Glaze*:- The purpose of glazing is to provide a uniform and firmly adhering coating on the surface of the ceramic body concealing defects such as pinholes, bubbles, etc. Glaze may be *raw glaze* or *fritted glaze*. Raw glaze consists of insoluble material applied as such (soluble components crystallize in the mixture and cause blemishes on the treated surface), while fritted glaze is heated beforehand to cause chemical change in the components. Glaze should not only melt but also spread uniformly. The glaze is made of the same ingredients as the ceramic product being glazed, but with a predominance of quartz and feldspar. The ingredients are mixed, finely ground and mixed with water, and this mixture is the glaze. The moulded raw body of the product is dipped into the glaze and then fired to a higher temperature of about 1400^0 C. Colours and decorative designing, if required, are painted after glazing and before firing.Borax is added either as such or in the form of boric acid, to the glaze mixture for its excellent fluxing property resulting in improved flow, lower thermal expansion coefficient and strong white colour. Borax is soluble in water and hence can only be used in fritted glaze. Further, it has a low refractive index (1.447-1.472) and is particularly suitable when low gloss rather than brilliance of the glazed surface is desired.

(b) *Ceramics*: Borax is used as flux for lowering firing temperature.

(c) *Advanced structural ceramics*: Boron nitride (see number 9 below) is used in some advanced structural ceramics (e.g., aerospace structures) by virtue of a combination of high strength and strong resistance to wear, heat and corrosion.

7. Enamel: Chemically, enamel is a complex mixture of silicates, borates and fluorides of some metals like sodium, potassium etc. It is a glaze coating on metallic surfaces so as to give protection to the latter against high temperature and corrosion. It is prepared by mixing borax, quartz, fluorspar, soda (Na_2CO_3), sodium nitrate, oxides of cobalt, manganese and nickel and an opacifier substance (e.g., tin oxide, titanium silicate, antimony trioxide). In this mixture, borax (34%), quartz (20%) and feldspar (28%) are the dominant components. This mixture is ground, melted and quenched in water to yield a glassy mass. To this glass are added clay and more quartz powder and the mixture is finely ground to powder and made into a slurry with water. This is called *enamel slip*. Metallic objects are dipped in it and fired to about 900^0C. Two to three of such enamel coats are usually applied. Colour effects can be produced by addition of colouring oxides of metals (e.g., iron, chromium, cobalt, uranium, etc.) to the melt before it is quenched. The low melting point and excellent fluxing property of borax are the main criteria. Besides, as in the case of glass, the enamel incorporates within it some of the attributes of elemental boron inasmuch as it is strong and highly resistant to heat and is characterized by a very low coefficient of thermal expansion, with high resistance to thermal shock.

8. Silly Putty:- By mixing silicone (synthetic inorganic polymers in which atoms of silicon and oxygen form the central chain; see the chapter on silicon) with boric acid a product called *silly putty* can be made. It has some unique properties. It can stretch without breaking, but can be snapped off cleanly; it bounces higher than a rubber ball, with rebound of 80%; if it is hit with a hammer, it keeps its shape, but under light even pressure, it flattens easily. First made in 1943, it finds application in the toy industry, as a grip strengthener and as an art medium.

9. Analytical chemistry:

(a) *Buffer solution in biochemistry*: In chemical reactions not involving borax, the latter acts as a buffer, maintaining a stable pH needed to maintain clean chemical reactions. Sodium borate is used in biochemical and chemical laboratories to make buffer solutions in gel electrophoresis of DNA — a technique used for the separation of DNA through an electric charge. It has a low electrical conductivity, it produces sharper bands, and it can be run at high speeds. At a given voltage, the heat generation and hence the gel temperature is lower than many other buffers and, therefore, the voltage can be increased to speed up electrophoresis. *Lithium borate* is similar to sodium borate and has all of its advantages, but permits use of even higher voltages due to the lower conductivity of lithium ions as compared to sodium ions. However, lithium borate is much more expensive.

(b) *Borax-bead test*: It is a common technique for identification of elements like copper, chromium, cobalt, iron, nickel, uranium. The low melting temperature and ability of molten borax to dissolve these elements are the criteria.

10. Ultra-hard materials: In this group falls some compounds made from B_2O_3. These are:

- (a) *Boron nitride*: Boron nitride (BN) is made from B_2O_3 and is as hard as diamond (hardness 10 on Mohs scale) while at the same time it can withstand very high temperature up to 1800^0C. It behaves like an electrical insulator, but conducts heat like a metal; it also has lubricating properties similar to graphite; it is a light-weight material. It is also sold under the trade name *borazon*.
- (b) *Boron carbide*: Boron carbide (B_4C) is made by reacting B_2O_3 with carbon in electric arc furnace; it is extremely hard and abrasive and is able to absorb neutrons. It finds application in diamond dressing, in pellets and shields in nuclear rectors, in ballistic armour, in precision tool parts and ceramic tooling dyes.

11. Elemental boron: Boron is difficult to recover because of its strong reactivity with both oxygen and nitrogen, and its extraction has to be done in inert atmosphere or in vacuum. Boric acid [H_3BO_3] is converted to boric oxide [B_2O_3] by calcination. Boric oxide is reduced to boron by pyrolysis or reaction with magnesium metal at high temperature of the order of 2000^0C (the melting point of boron is 2079^0C). To obtain high purity boron, the impure element is degassed in vacuum. The two isotopes of boron namely B^{10} and B^{11} are separated by fractional distillation or by diffusion at above 2550^0C, which is the sublimation temperature of boron. The direct uses of boron are as a moderator and a shielding material in nuclear reactors, as rocket igniter, in semiconductor devices, in optical fibers, as a soil micronutrient, etc.

12. **Ferro-boron:** This alloy contains 15-20% B and the balance Fe. It is made by reducing together iron oxide and boric acid (H_3BO_3) or boric oxide (B_2O_3) by either carbo-thermic or alumino-thermic process. It is in the form of this ferro-boron that boron is added to steel as a hardening agent for imparting high strength at elevated temperature. Also, by virtue of its strong affinity for oxygen and nitrogen, it is used in ferrous metallurgy for degassing.

13. **Metallic glass:** Metallic glass is a special kind of ferro-boron containing 92% Fe, 5% Si and 3% B prepared by very rapidly cooling the molten alloy. The rate of cooling is incredibly fast (@ one million degrees per second) i.e., practically instantaneous, and thus cooled alloy becomes a glassy mass. Besides, the unique ability of elemental boron to form glass is also taken advantage of. This is used in electrical transmission and distribution transformers. The ferro-boron for this purpose is made by reducing together iron oxide and boric acid (H_3BO_3) or boric oxide (B_2O_3) as in the case of normal ferro-boron, but in this case the reduction has to be necessarily by carbo-thermic process and not by alumino-thermic process. In the latter case, traces of aluminium remains in the alloy and it is highly deleterious.

14. **Other uses:**

(a) *Cosmetics*: In cosmetics, borax is used as an antiseptic and emulsifying agent.
(b) *Pyrotechnics* : Borax is sometimes used for homemade pyrotechnics on account of its ability to produce a bright orange-colored flame when burnt.
(c) *Food additive*: A small quantity of borax is added to act as a stabilizer in the preparation of iodized salt by adding trace amounts of *iodine* in the form of sodium iodide, *potassium iodide* or *potassium* to edible salt to increase iodine intake by common people prone to incidence of simple *goiter*. In France and Iran, it is added like salt to caviar preparations. But use of borax in food items is banned in the United States.
(d) *Textile*: In the textile industry, borax is used as a decolourising agent as well as for maintaining the alkalinity of solutions which are used for producing rayon.
(e) *Vanaspati (vegetable-based edible fat)*: In Vanaspati, borax is used as a decolourising agent.
(f) *Toothpaste*: Because of its mild alkalinity and germicidal nature, borax is used in manufacturing tooth pastes and mouth washes.
(g) *Agriculture*: In agriculture, borax provides essential plant nutrient, essentially by virtue of its boron-content.

(h) *Ink* : Some types of indelible ink used in *dip pens* is made by dissolving *shellac* in heated borax.
(i) *Superconductr* : Magnesium diboride (MgB_2) is an unconventional superconductor.
(j) *Rocket fuel* : Boron hydride has been used.
(k) *Fire retardant* : By virtue of its high crystal water content, borax is sometimes used for fireproofing wood, textiles, etc.
(l) *Nonferrous metallurgy* : Borax is used for shielding slag.
(m) *Paper* : Borax finds use as a surface glaze.
(n) *Hydraulic brake fluid* : Sodium organo-borate (also known as *liquibor*) is used as an ingredient to increase volatility and corrosion resistance.

Chapter 4

CALCITE

Calcite, also known by the name c*alcspar*, is calcium carbonate ($CaCO_3$) containaing 56% CaO and 44% CO_2. It gets its name from "chalix", the Greek word for lime. Calcite which crystallizes in a trigonal form, has two polymorphs, namely, *aragonite* (orthorhombic) and vaterite (hexagonal). Amongst these, calcite is the most stable mineral at most temperatures and pressures and in most environments. Aragonite, although a common mineral, changes to calcite at 470^0 C and vaterite is extremely scarce and rarely seen.

Though chemically same, calcite is different from limestone inasmuch as the former is a crystalline mineral and the latter is a rock. Calcite is a chemical or biochemical *calcium carbonate* and is one of the most widely distributed minerals constituting about 4% of the earth's crust. It is a common constituent of sedimentary rocks, limestone in particular. It is also the primary mineral in metamorphic marble. It also occurs as a vein mineral in deposits from hot springs, and also occurs in caverns as stalactites and stalagmites. Calcite is often the primary constituent of the shells and hard parts of marine organisms like foraminifera, red algae, some sponges and oysters.

In India, the production of calcite has increased from 1,728 tons in 1947 to 73,332 tons in the year ending March, 2005, the mining being limited to only the two states Madhya Pradesh and Rajasthan.

VARETIES OF CALCITE

Calcite is truly a collector's delight. There are many interesting forms as well as colourful and beautiful varieties found in nature. The following are the varieties based on crystal form, mode of formation and physical properties that are of significance for the museum collectors, tourists and industries.

(a) *Travertine*: It is a sedimentary rock. Travertine is a natural chemical precipitate of carbonate minerals (see also the chapter on limestone), typically aragonite, but often recrystallized to calcite, which is deposited from the water of mineral springs (especially hot springs) or streams saturated with calcium carbonate. When pure, travertine is white, but often is brown to yellow due to impurities. When carbon dioxide-rich water percolates through rocks in limestone areas, the water dissolves the limestone and becomes saturated with it. When the water resurfaces later, the sudden drop in pressure and the change in temperature cause the water to release the carbon dioxide gas. The calcium carbonate then recrystallizes, often over minute underwater plants. The resulting rock is typically quite porous with numerous cavities.

(b) *Calcareous tufa*: When travertine is exceptionally porous, it is known as calcareous *tufa* (see also chapter on limestone).

(c) *Iceland spar*: It is the pure crystallized (rhombohedral) transparent variety of calcite. It is basically clear cleaved fragments of completely colourless (ice-like) calcite. It was originally discovered and named after Eskifjord, Iceland where it is found in basalt cavities. Most of today's Iceland spar comes from Mexico**.**

(d) *Scalenohedron or dogtooth spar*: This variety appears as a double pyramid or dipyramid, but is actually a distinctly different form. The point of the scalenohedron is sharp and resembles the canine tooth of a dog, and hence the name. Beautiful clear colourless or amber-orange examples of this variety are considered classics and outstanding specimens come from Pugh Quarry, Ohio; Cornwall**,** England and Elmwood, Tennessee. However, it is found worldwide.

(e) *Cave calcite*: Calcite is the primary mineral component in attractive cave structures like stalactites and stalagmites, cave veils, cave pearls, soda straws and the many other different cave formations that millions of visitors to underground caverns enjoy. It is due to the ability of calcite to readily dissolve that these formations occur. Overlying limestone or marble is dissolved away by years and years of slightly acidic ground water to percolate into the caverns below. In fact the caverns themselves may have been the result of water dissolving away the calcite-rich rock. As the calcite enriched water enters a relatively dry cavern, the water starts to evaporate and thus precipitate the calcite in a variety of forms that are attractions for tourists.

(f) *Mexican onyx*: Mexican onyx is soft and is different from *onyx* which is a variety of quartz and is hard.

CRITERIA OF USE

1. Colour: Calcite is generally white or colourless but sometimes, due to inclusion of impurities, it shows variable colours like light yellow, orange, blue, pink, red, brown, green, black and grey. Occasionally, it is iridescent (i.e., varying in colour when seen in different lights or from different angles).

2. Lustre and transparency: Lustre is vitreous in crystals, and resinous to dull when in massive form. Crystals are transparent to translucent. Iceland spar is highly transparent (like ice).

3. Crystal system and cleavage: Calcite crystallizes in trigonal form, but its habits are highly variable with almost any trigonal form possible. Common among calcite crystals are the scalenohedron, rhombohedron, hexagonal prism, and pinacoid. Combinations of these and over three hundred other forms can make a multitude of crystal shapes, but always trigonal. Twinning is often seen and results in crystals occurring in some unique shapes, making them attractive to people. Cleavage is perfect in three directions, forming rhombohedrons.

4. Refractive index: Calcite shows strong birefringence with refractive index varying from 1.49 to 1.66 in normal light causing a significant double refraction effect. At a wavelength of about 590 nanometre, calcite has ordinary and extraordinary refractive indices of 1.658 and 1.486, respectively (high degree of birefringence). Iceland spar is particularly remarkable for its double refraction. Double refraction occurs when a ray of light enters the crystal and due to calcite's unique optical properties, the ray is split into fast and slow beams. As these two beams exit the crystal they are bent into two different angles because the angle is affected by the speed of the beams. There is only one direction that the beams are both of the same speed and that is parallel to the C-axis or primary trigonal axis. By contrast, the direction perpendicular to the C-axis will have the widest difference.

5. Polarization: As white light waves propagate through space, the vibrations take place in all possible directions on all possible planes. But due to certain factors, these vibrations are modified so as to take place on a single plane only. This light vibrating on a single plane is called *polarized light*, and the phenomenon of such modification is called *polarization*. The polarizing factors are: (i) partial reflection, (ii) double refraction or birefringence, and (iii) absorption. When light is incident on an object, some of its rays are reflected back and some are refracted, and both the reflected and the refracted rays are polarized. When the object is doubly refractive, each of the two refracted rays is polarized. In case of absorption (as in case of a dark coloured object), light rays vibrating in all but one plane are absorbed within the object and the rays emerging out from it are thus polarized. Polarized light is used for seeing the colour of an object in thin section under microscope, otherwise in unpolarized light it will appear as almost colourless unless the object is very dark coloured. Calcite in general and Iceland spar in particular is a strong polarizer of light by double refraction. In fact, Iceland spar is used in demonstrating the *polarization of light.*

6. Luminescence: Many substances easily gain energy and emit light without being heated very much. They do this through a process called *luminescence*. Atoms of some luminescent materials emit light only during their exposure to exciting energy and they are called fluorescent. If the exciting energy is heat, then the phenomenon is called *thermoluminescence*. Atoms of some luminescent materials stay excited for some time before they de-excite and consequently, they glow in the dark long after they have received extra energy. They are called phosphorescent. *Triboluminescence* is a property that occurs in some objects when it is struck or put under pressure and in a dark room such objects glow. Fluorescence, thermoluminescence, phosphorescence and triboluminescence are shown by some specimens of calcite (e.g., specimens of massive calcite containing a small amount of manganese that is found in Franklin, New Jersey, USA fluoresce a bright red colour under ultraviolet light; some specimens of Mexican Iceland spar phosphoresce purple or blue colour after ultraviolet light source is removed).

7. Water solubility: Calcite is practically insoluble in water having solubility of only 0.0013 gm/100 gm of water.

8. Hardness: Hardness is variable on different faces from less than 2.5 to 3 on Mohs scale.

9. Specific gravity: Approximately 2.7.

10. Mechanical properties: Calcite grains possesses low modulus, high tensile strength (ability to elongate without breaking) and good slump-resistance (resistance to heavy fall while at the same time transferring pressure).

USES

The important uses of calcite are:

1. Optical instruments
2. Glass
3. Ceramic glaze
4. Decoration and ornamentation
5. Synthetic marble
6. Water treatment
7. Adhesive

These uses are elaborated as follows.

1. Optical instruments: Iceland spar is used in the optical instruments for its transparency, strong birefringence with consequent ability to polarize light and to split images.

(a) *Microscope*: The transparent crystals of Iceland spar free from flaw is greatly valued in the optical industry for the manufacture of *nicol prism* in polarizing microscopes. Iceland spar for this purpose should have a high degree of purity (totally free from both cloudy inclusions and cavities of foreign substances), perfect crystalline structure and transparency, and the mineral pieces must be of at least 2.54 cm. long by 1.27 cm. thick (2 inch cube is preferred) and colourless. It should be free from internal iridescence due to incipient cracks along cleavage planes and from twinning other than parallel to the base.

(b) *Distance-measuring instrument*: The double image of a distant object viewed through a crystal of Iceland spar produces *parallax* effect, i.e., the apparent displacement of an object as seen from two different points that are not on a line with the object. By rotating the crystal, this parallax can be brought to zero and at that position of the crystal the two images coincide with the actual object. By calibrating the distances with the angle of rotation of the crystal, the distance of an object can be measured. Instruments based on this principle were used by bomber pilots and gunners during World War II (1940-1945) for estimating distances of targets. During that time, Iceland spar used to be classified as a strategic mineral.

(c) *Quarter-wave plate for optical instruments*: A wave plate or retarder is an optical device that alters the polarization state of a light wave passing through it by shifting the phase of light wave between two perpendicular polarization components. A typical wave plate is simply a birefringent crystal with a carefully chosen thickness. A quarter wave plate can change polarized light to circular light and vice versa. When plane polarized light passes through this plate, it is split into two components with relative shift of one quarter wave length. This shift causes light wave to propagate in helical fashion. Thus circular polarized light is produced. Birefringence of calcite makes it suitable for this application in polarizing microscope, in photo-elastic stress/strain benches for modelling stress distribution in bridges and buildings, in helium-neon laser systems, as beam-splitters etc. For this purpose, plates 10-25 mm diameter and thickness around 0.025 mm are used. The exact thickness, however depends on the wave length of light selected. Blue light requires thinner plate than red light.

2. Glass: The composition of typical common colourless soda-lime glass is sodium calcium silicate [$18Na_2O.2MgO.8CaO.72SiO_2$]. Essentially, the process of manufacture of glass consists in melting a mixture of 47% silica sand, 14% soda (Na_2CO_3), 12% dolomite ($CaCO_3.MgCO_3$), 3.5% $CaCO_3$, 2.5% carbon (coke) and the balance broken waste glass (called cullet) at 1400-1500^{0}C. The $CaCO_3$ is generally in the form of limestone, but often, it is partly replaced by calcite to adjust the purity. The lime introduced into the charge in the form of calcite, limestone and dolomite acts as a flux (along with soda and broken glass) for lowering the melting point of silica from 1580^{0}C to 1400^{0}C. The low-melting soda and broken glass become liquid first and silica (quartz) being soluble in boiling soda, dissolves in this liquid to form low-melting sodium silicate which then reacts with the CaO and MgO to form glass. The calcium silicate component imparts great chemical stability to the glass and also reduces the latter's thermal expansion (for more details. See the chapter on silicon).

Fe_2O_3 and TiO_2 form low-melting iron-titanate glass causing blisters in the products and consequent increase in porosity. Besides, Fe_2O_3 makes the product coloured (even in coloured glass in which iron oxide is added later, its presence in the initial charge hampers control of the colour). TiO_2 also has a high melting point and it will unnecessarily increase the firing temperature. Both these constituents are therefore objectionable.

A little MgO may not objectionable, because it also forms a component of the charge. Lime has a tendency to form crystals and addition of magnesia helps prevention of this devitrification. The CO_2 of the carbonates of calcium and magnesium are expelled reducing them to CaO and MgO. But calcite is primarily added to introduce a high proportion of lime for balancing its ratio with MgO and hence it should contain as high CaO as possible. So MgO-content in the calcite should be minimal.

The industries specify calcite containing 95% (min) $CaCO_3$, 0.15% (max) Fe_2O_3 and TiO_2 each and 2% (max) $MgCO_3$ with powder size ranging from 180-850 micron.

3. Ceramic glaze: The purpose of glazing is to provide a uniform firmly adhering coating on the surface of the ceramic body concealing defects such as pinholes, bubbles etc. Glaze may be *raw glaze* or *fritted glaze*. Raw glaze consists of insoluble material applied as such (soluble components crystallize in the mixture and cause blemishes on the treated surface), while fritted glaze is heated beforehand to cause chemical change in the components. The glaze is made predominantly of quartz and feldspar. The ingredients are mixed, finely ground, and mixed with water, and this mixture is the glaze. The fine grinding ensures that the materials do not settle quickly and remain in suspension in the water long enough for them to deposit as a uniform coating on the body. The moulded raw body of the product is dipped into the glaze and then fired to a temperature of about 1400^0 C. After firing, it becomes lime and combines with the silica of quartz and the alumina of feldspar to form calcium alumino-silicate which is a hard glassy substance (cf. blast furnace slag) making the glazed surface hard and impervious.

For lowering the fusion temperature of the mix limestone is often added, and to improve the lime content of the mix, calcite is invariably added.

As regards specifications, since calcite is added to improve the CaO input in the mix, a high content of $CaCO_3$ is desirable and impurities should be minimal. Industries usually specify 97% (min.) $CaCO_3$ content in calcite. The super white calcite of 500 micron or 30 mesh is generally used.

4. Decoration and ornamentation: Although beautiful crystals with attractive colours often showing iridescence are available, calcite is not regarded as a gemstone because of its softness (Mohs hardness 2.5-3). However, it is sometimes used in jewelery where it is not subject to rough handling, and great care has to be taken while cutting and polishing it. But for the same reason of softness, some of the varieties of calcite are used for sculpting decorative artefacts. Mexican onyx is one such variety preferred by the sculptors. It is used extensively for ornamental purposes. It is carved into inexpensive decorative objects like figurines, vases, bookends, plates, statuettes etc. Mexican onyx is banded with multiple orange, yellow, red, tan, brown and white colours that have marble-like texture.

5. Synthetic marble: Synthetic marble is a strong, homogeneous, dense, translucent product which can be cast into different shapes and sizes. It finds use in bathrooms and as structural components. It is made by casting and heat-curing (in presence of a catalyst) a finely ground mixture of alumina and resin matrix with some filler material. The filler constitutes 50-85% of the weight of the mixture and includes calcite, silica, oxides of antimony and titanium and talc. The refractive index of the mixture vis-à-vis the resin matrix is so manipulated as to give an illusion of depth. Calcite used is in the form of powder of size less than 250 microns (60 mesh).

6. Water treatment: In the conventional process, calcite is added to water to form $Ca(OH)_2$ which increases the pH to around 6-7, and the conversion is very slow. Hence, this process can be suitable for treating small volumes of still water. However, for treating large volumes of flowing water, now-a-days, caustic magnesia is preferred (see also chapter on magnesite).

7. Adhesive: Adhesive is an organic or inorganic substance capable of bonding together other substances by surface attachment. Generally, high-purity white dolomite is added to certain adhesives with a view to: (i) adjusting the colour, (ii) reducing shrinkage due to internal stress by virtue of its moderate hardness, and (iii) maintaining flexibility by virtue of its porosity. But, for high-performance adhesive where even a minute shrinkage associated with cracks is not permissible, dolomite is mixed with pure and white powdered calcite because of the latter's low modulus, ability to elongate without breaking and resistance to heavy fall while at the same time transferring pressure. Thus made adhesives are used for grouting ceramic tiles. Due to low water-solubility of calcite, such adhesives can be used in wet conditions.

8. Other uses:

(a) *Rubber*: It is used in powdered form as a filler as substitute of precipitated calcium carbonate or PCC to increase whiteness and hardness (see chapter on limestone).

(b) *Textiles*: In pulverized form it is used as a filler mainly on account of white colour of the pure calcite.

(c) *Paint*: In the same way as above, it is used as an extender in white paint.

(d) *Chemicals*: For making lime-containing chemicals like bleaching powder etc., calcite is sometimes used as a substitute of limestone-based lime. Calcite for this purpose, should contain at least 99% $CaCO_3$ and no more than 0.5% of Fe_2O_3, 2 ppm of As and 10 ppm of Pb.

(e) *Cosmetics*: It is used as filler in ultra-fine form and the calcite should have 97% $CaCO_3$, 200 ppm Fe, 10 ppm (max.) Cu, 100 ppm (max.) Mn and 0.2% (max) moisture.

(f) *Electrode*: Sometimes, calcite is added as a flux and the industries specify 95% (min) $CaCO_3$, 0.01% (max) P, 0.035% (max) S and 2% (max) SiO_2.

CALCITE AND ENVIRONMENT

Some environmentalists believe that calcite and other carbonate minerals are very important minerals in the ocean ecosystems of the world and for checking the *global warming*. In a way, calcite is intricately tied to carbon dioxide. Since many sea organisms such as corals, algae and diatoms make their shells out of calcite, they absorb carbon dioxide from the sea water to accomplish this according the reaction

$$Ca + H_2O + CO_2 \rightarrow CaCO_3 + 2H$$

Now, carbon dioxide is a *green house gas* and it contributes to the global warming. This biological activity allows more of the carbon dioxide in the air to dissolve in the sea water and thus acts as a carbon dioxide storehouse for the earth. Environmentalists are now actively engaged in determining if this activity can be increased by human intervention.

Chapter 5

CELESTITE AND STRONTIANITE

Strontium is an alkaline earth metal closely related to calcium and barium. Although it is widespread in rocks and waters, there are only two commercially important minerals. Celestite or *celestine* ($SrSO_4$) and strontianite ($SrCO_3$) are both natural sources of strontium . Celestite, which is a faint blue crystalline mineral having obtained its name from the word "celestial," is relatively more abundant. Celestine mostly occurs in sedimentary rocks as crystals, and also in compact massive and fibrous forms. It is often associated with the minerals gypsum, anhydrite, and halite. The largest known deposit is in Ohio, USA, and some minor occurrences are in Madagascar, Slovakia, Switzerland, Italy, UK, Mexico and Egypt. In India, there is an occurrence of celestite in Thiruchirapalle district of Tamil Nadu, first discovered in 1893 by H. Warth and later investigated by many others. Here celestite was found associated with gypsum veins.

Strontianite, which have varying colours of apple green, yellow, grey, brown etc., generally occurs in veins of limestone, and rarely in igneous intrusives or in metal veins. The most commercial deposit of strontianite is located in Germany and relatively minor occurrences are in Austria, Scotland and USA.

USES

Celestite is a soft (Mohs hardness 3.0-3.5), white to pale blue coloured mineral having specific gravity 3.96. In their industrial usage, physical properties are irrelevant and their strontium-content and cost of availability are important. Celestite contains 56.4% strontia (SrO) and strontianite, 70.1% SrO. Both are used mainly in crude mineral form for manufacture of strontium-based chemicals and also as a source of strontium metal. But, celestite being more abundant, is used widely. The uses are as follows.

1. Strontium carbonate: Strontianite being rare, the more easily available celestite is converted to strontium carbonate. For converting celestite to strontium carbonate, generally two methods are employed.

(1) Celestite is digested in hot soda ash (Na_2CO_3) solution which yields strontium carbonate.

(2) Celestite is burnt at 1300^0C with powdered coal or coke to yield a mixture of ash and strontium sulphide. The latter, being soluble in water, is leached away and filtered. The filtrate is then treated with CO_2 to produce strontium carbonate.

Strontium carbonate is marketed in the form of granules and powders and is used in glass manufacturing. A typical grade for this use marketed by a Mexican producer contained 98.5% $SrCO_3$, 1% $BaCO_3$, 0.005% CaO+MgO, 0.2% Na_2CO_3, 0.0018% Fe_2O_3, 0.18% SO_3, 0.2% SiO_2, and 0.15% moisture.

2. Strontium nitrate: Strontium nitrate [$Sr(NO_3)_2$] is produced by first converting celestite to less soluble strontium carbonate as above and then reacting the latter with nitric acid. In case of strontianite (or strontium carbonate), the first step is not necessary.

The most characteristic property of strontium nitrate is the typical brilliant red colour of its flames. This property has been made use of in:

(1) Pyrotechnics
(2) Distress signal devices (ships, submarines, trains trucks and aircrafts send signals by firing strontium-containing bullets or parachute flares or rockets)
(3) Tracer bullets (these are strontium-containing bullets that, when fired, emit red fire throughout their flights enabling a shooter to judge the accuracy of his aim)
(4) Tactical signaling by army
(5) Night illumination by army

3. Strontium peroxide and oxalate:-These are used in the same way as the nitrate.

4. Strontium hydroxide: Strontium hydroxide [$Sr(OH)_2$] has been used in Germany and France for separating *beet sugar* from beet-molasses. Here, it reacts with sugar to form strontium saccharate which is insoluble and is precipitated, filtered and treated with CO_2 to form $SrCO_3$. The latter is precipitated and can be recovered while the clear sugar in solution is crystallized by evaporation.

5. Strontium titanate: This is used as one of the different kinds of artificial diamond. Artificial diamonds consist of elements that are naturally occurring, but combined in forms that are not found in nature.

6. Strontium metal and alloys: Strontium metal is produced either (i) by electrolyzing strontium chloride with ammonium chloride or (ii) by thermally reducing strontium oxide with aluminium metal (*alumino-thermic process*). Small amounts of both the metal and its alloys are used for extracting traces of gas from electronic tubes.

7. Celestite powder: Powdered celestite as such finds use in some minor applications as follows.

(1) *Oil well drilling*: It has been used in the drilling mud as an inferior substitute of barytes by virtue of its specific gravity (3.96).
(2) *Paints and pigments*: It has been used because of its colour (white to pale blue).

(3) *Steel metallurgy*: Its role can be desulphurization of molten steel and also as a flux to increase fluidity of the slag.
(4) *Purification of caustic soda*: Small amounts have been consumed.

Chapter 6

CLAY - GENERAL

Clay is the most widely known material, but, at the same time, it has remained a complicated subject all along. First of all, there is the unresolved question of whether it should be included in the list of rocks or in that of minerals, while in popular perception, strengthened by traditions and conventions through centuries and millennia, it is neither a rock nor a mineral. In the regimes of legislation and commerce, however, clay is a group of mineral commodities. But the fact remains that each of these mineral commodities is again an assemblage of more than one clay mineral. So needless to say, different authors treat them differently depending on the objective and on the limitations of testing facilities. The problem lies, essentially, in the tendency to use non-standard terms to describe different types of clay encountered in the field.

DEFINITION

Clay is a subset of the omnipresent material called "*soil*". Soil is essentially the waste material originating from rocks due to weathering and decayed plant and animal matter. Modifications in the nature and composition of soil may be caused by a combination of physical, chemical and biological processes. It constitutes the top layer of the ground.

Clay is the finest grained fraction of the soil, and it comprises very fine minerals composed of hydrous silicates called "*clay minerals*". But, defining clay has been a subject of research and controversy for a long time, and even now there seems to be no universal agreement on a standardized definition. According to Wentworth's scale (1922), clay comprises particles of size below 1/256 mm (cf., silt: 1/256- 1/16 mm, sand: +1/16 – 2 mm, granular gravel: +2 – 4 mm, gravel: +4 mm). Twenhofel (1937) considered that in clay, the clay minerals must constitute at least one-fourth of the total matter. Bateman (1942) laid emphasis on chemical composition, colloidal nature, plasticity and fired properties. According to him, clay is an earthy substance consisting chiefly of hydrous aluminium silicates with colloidal material and specks of rock fragments, which generally become plastic when wet and stone-like when fired. However, as we see today, not all types of clay are plastic, and all of them are not necessarily fired before use. According to Pettijohn (1949), undue reliance on grain size may often be misleading. The US Bureau of Mines (USBM) and the US Geological Survey (USGS) have accepted a simplistic and general definition that clays are hydrous aluminium silicates of a great many mineral species, containing varying proportions of impurities.

All these controversies stem from the fact that no two clays are similar, and industries have never cared for definition of the clays that they use. Instead, they have all along relied on the trial tests and on the past records of performance of the clays drawn from historically well-known sources. Nevertheless, clay minerals form an important component of any clay. These are the nanometre-sized products of decomposition by weathering of primary silicate minerals. All clay minerals (some of which are similar enough to form broad groups) are essentially hydrous aluminium silicates, but they show variations in mineralogy, in chemical composition and in crystal form. The known clay minerals are:

A. Kaolinite group [$(OH)_8Al_4Si_4O_{10}$] or [$Al_2O_3.2SiO_2.2H_2O$]

1. Kaolinite
2. Nacrite
3. Dickite
4. Anauxite

B Smectite Group (earlier name Montmorillonite Group) : Composition uncertain, one of the suggestions is [$(Al, Mg)_8(Si_4O_{10})_3(OH)_{20}.nH_2O$]. In addition, calcium, lithium or sodium may also be present.

1. Montmorillonite
2. Beidellite
3. Nontronite
4. Hectorite

C. Illite group: Contains iron, magnesium and potassium.
D. Halloisite :- Contains more water than kaolinite.

1. Halloisite
2. Metahalloisite
3. Allophane
4. Endellite

E. Palygorskite : Contains magnesium instead of aluminium.

1. Sepiolite
2. Attapulgite

F. Chlorites : Magnesium-rich clay minerals.

This list should never be taken as exhaustive. With invention of more and more sophisticated microscopes, the chance of identifying newer and newer clay minerals remains always open. Clay contains one or more of the clay minerals. In addition, there are some so-called “impurities” found in clays. they include sericite, paragonite, quartz, chlorite, serpentine, limonite, hematite, pyrite, calcite, dolomite, feldspars, zeolites, rutile and carbonaceous matter.

In industry, shale is often included within the broad meaning of clay. Petrologically, however, shale is indurated clay (*claystone*) which is generally found buried under the surface and which has developed lamination or fissility caused by the pressure of overburden.

There are 16 terms currently used in industrial circle — china clay or kaolin, ball clay, fire clay, sodium bentonite, calcium bentonite or pascalite, attapulgite or fuller's earth, brick clay, stoneware clay, pipe clay, roofing tile clay, pottery clay, terracotta clay, terracotta clay shale, brick-making clay shale, flint clay and pozzolanic clay.

HISTORY

Clays were probably the earliest mineral used by civilized men. The first archeological evidence of clay dated back almost to the beginning of the Copper Age. But by that time the techniques of using clay had already reached an advanced stage. Ancient men living as early as 10,000 years ago knew how to make not only fired potteries, but even painted ones, and also to make building bricks. Artifacts comprising potteries with attractive designs painted on them, have been dug out from the ruins of Mohenjo Daro and Harappa (Indus valley), Nile Valley, Hoang-Ho (China), Turkestan (Central Asia), Chaldea (Mesopotamia), Parsepolis (Iran) — the civilizations flourishing during the period 5000-3000 BC. So much evidence of such painted potteries belonging to the period 8000-4000 BC have been found, that some historians have described the civilization during that whole period as "*Painted Pottery Civilization*". Apart from potteries, other ancient objects made of clay have also been found. For example, toys made of clay during the period of 'Rig Vedas' (scripture believed to be 6,000 years old) have been unearthed in Mohenjo Daro and Harappa; and clay tablets with hieroglyphics engraved in them, have been found in Sumeria (3000 BC). Extremely thin-walled terracotta vases have been unearthed in Beluchistan, Pakistan. Fuller's earth , as we know, is used for dry-cleaning purpose. But its first recorded use for this purpose was in Cyprus Island in 5,000 BC, and this clay was then called "*cymolean earth*". Technique of making clay tiles – often glazed and decorated, were known to the Muslims who later introduced them in India.

China clay is another clay with a long history of use in China. During the reign of Sui dynasty (581-617 AD), some glass made its way to China. Chinese craftsmen, while trying to imitate it with local clay, ended up in a kind of impure but first real "china". When the reign of Tang dynasty (618-906 AD) was coming to an end and that of Sung dynasty was beginning (906 AD) i.e., around the first half of 10th century, porcelain (a product based on china clay) made its appearance. Throughout the rules of Sung dynasty and subsequent Ming dynasty the art of porcelain received royal patronage and encouragement, and highly artistic porcelain vases and other objects were made during this period. In 1191, tea-drinking was introduced for the first time in Japan by a Buddhist Monk, and this boosted demand for porcelain cups made in China. Later on, Japanese learnt the art from China. This porcelain grade clay became intimately associated with China and the outside world started calling this type of clay, wherever it was found, china clay. The original name 'kaolin' also owes its name to a Chinese word "kauling" meaning high ridge – the name of a hill where it was first mined.

Compared to pottery clay, terracotta clay, tile clay, fuller's earth and china clay, the history of bentonite is very recent. It started in 1830 with the discovery and naming of a new type of clay by Emille Pascal on a mountain in Wyoming, USA. In 1847 a similar clay was later found in a place called Montmorillon in France and christened montmorillonite. The name bentonite was popularized by an American geologist after he found the clay in Benton Formation in Rock Creek area of Wyoming in 1888.

GENERAL PROPERTIES OF CLAY

Although non-ceramic applications of some clays are not uncommon, clays are essentially ceramic materials. In fact, the word "ceramic" derived from Greek originally meant fired and fused common clays. But in modern usage it includes some other inorganic materials mixed with clays in different forms (common clay, china clay, ball clay, etc.) which are fired together and fused, but clay still remains the core component. One may come across in literature several physical properties that are required to be tested for determining the suitability of a clay for ceramic or other industrial uses. Some of these are tested in raw state and others in fired state. These are as follows.

1. Raw clay:

(1) *Raw clay colour*: The industrial colours is expressed in terms of what are called "*LAB parameters*". 'L', 'A' and 'B' indicating different colours as:

   (i) "L" means white
   (ii) 'A+' means red
   (iii) 'A-' means green
   (iv) 'B+' means yellow
   (v) 'B-' means blue

This is important only when the clay is to be used without burning (as in paper, paint etc.). Otherwise, this is no indication as to the purity of a clay. Some of the darkest ball clays become perfectly white on burning.

(2) *Raw clay brightness***:** Like raw clay colour, brightness is also important only when the clay is to be used without burning (as in paper, paint etc.). Brightness is measured as a percentage value of the reflectance of clay from blue light having wave length 457 microns (the range of wave length of visible light is 400-700 microns).

(3) *Particle size*: Coarse granular materials are usually analyzed for particle size distribution using sieving techniques. Dry sieving is normally used for materials in the size range down to 150 microns, and wet sieving is the standard procedure in the next finer range down to about 50 microns. The finer size ranges (clay particles may be as small as less than 2 microns) which have important effects on the physical properties of clays (e.g., plasticity, shrinkage) are normally measured by methods based on sedimentation techniques (Stokes' decantation and Andreasen Pipette methods).

(4) *Deflocculation behaviour*: This property is particularly relevant to china clay and ball clay which are to be used in casting applications. The test involves dispersion of clay

in de-ionized water, partial deflocculation by addition of sodium silicate in increments, and measurement of viscosity at each stage of increment.

(5) *Plasticity and liquid limit*: It is the ability of a clay to undergo non-reversible change of shape in response to applied shear stress. Although the exact mechanism of plasticity is not fully understood, it is believed that a combination of certain factors like grain size, binding power, tensile strength, extensibility, adsorption, texture and molecular constitution is responsible for it. Depending on the amount of water held, a clay can be liquid, plastic, or solid. *Attenberg plasticity limit* marks the passage of the plastic condition to the solid condition and is defined by the water holding of a small roller of soil which, on rolling, breaks in morsels when its diameter reduces to 3 mm. Plasticity of a clay is expressed either by the percentage of water at the plasticity limit or by what is called *Attenberg number* (also called *plasticity index*) which has been expressed in terms of a chart by taking the difference between the water content of a material at the point when it becomes liquid (*liquid limit*) and that at the point when it becomes plastic. But generally, at the preliminary level of testing at least, plasticity is judged by hand feel as low, medium and high or as fair, good and very good.

(6) *Impermeability*: It is proportional to plasticity.

(7) *Base exchanging power*: Base exchange is the exchange of ions in solution for those of a solid. Upon contact with a solid, the solution will undergo a change reciprocal to that of the solid. This is also known as *cation exchange* capacity, which means the quantity of positively charged ions (cations) that a clay mineral can accommodate on its negatively charged surface, and it is expressed as milli-equivalents per 100 gm (*equivalent weight* is the molecular weight of an element divided by its valency). The mechanism is not fully understood. Certain clays are believed to possess a power of selective adsorption by virtue of which they are able to exchange bases with other substances. Montmorillonite shows a large capacity, kaolinite has slight, illite has intermediate.

(8) *Absorptive power*: Absorption is related to porosity so far as pure water is concerned. Absorption limit of a clay corresponds to the percentage of water held at the point when no more water penetrates into the clay. It is measured by making water drops fall one by one on a homogeneous paste till they are absorbed in less than 30 seconds. When a drop is not absorbed in less than 30 seconds, then that is the absorption limit, and the water content at that limit denotes the "*water of absorption*". It is expressed either in terms of percentage by weight of water absorbed or in terms of millilitres/100 gm.

(9) *Swelling index*: It denotes the degree of increase in volume of a clay on absorption of water. Swelling index is the ratio of the weight of water to the minimum weight of clay to produce a gel. It is only partially related to absorption, but the actual mechanism of swelling is still not fully understood. Various theories have been put forth. According to one theory, swelling is driven by capillary forces and/or by chemical gradients – particularly the latter in case of clay. Chemical gradient occurs due to positive difference between the concentration of certain species (sodium, potassium, etc.) in clay and that of the water in contact with clay. According to another theory, swelling is related to microstructure and organization of the pore spaces and water in clays. In clay, the clay minerals are in the form of platelets

arranged in parallel and separated by micro-pores (it is these micro-pores in which the absorbed water resides). The inter-lamellar pores are filled up with single-molecule layers of water. This inter-lamellar water is higher in viscosity and density than free water. It does not flow even if subjected to high hydraulic gradient and, instead, deforms along with the solid part. Due to higher viscosity and density, it exerts outward osmotic pressure.

(10)*Bonding power*: The extent to which a clay can remain plastic when mixed with materials such as sand, etc., is its bonding power. It depends on the plasticity of the clay itself and on the size and nature of particles of the added material and it is also related to swelling due to which a clay is enabled to enter into the pores of a surrounding material and makes the latter a strong, solid and well-bonded mass.

(11)*Strength*:- The higher the plasticity, the greater the strength of a clay. It is evaluated in terms of *modulus of rupture*, which is the load required to break a specimen bar of standard length and cross section area.

(12)*Hardness*: Some types of clay are harder compared to others. For example, clay shales and flint clays are harder than bentonite, china clay, etc.

(13)*pH value*: It is the negative logarithm of the effective hydrogen-ion concentration or hydrogen ion activity in gramme equivalent per litre. It is used in expressing both acidity and alkalinity on a scale whose values run from 0 to14 with 7 representing neutrality. Numbers less than 7 indicate increasing acidity and those greater than 7 increasing alkalinity.

(14)*Viscosity*: Viscosity is that property of a liquid (or a semi-solid mass) which is a measure of its internal resistance to deform under shear stress, and it is measured by the stress in dynes/cm^2 or Pascal (Pa) required to be applied to overcome that resistance and maintain a velocity of flow of one centimetre per second. This unit of measurement of viscosity is Poise which is 1 gm.cm.sec or 1 Pascal second (Pa.sec). It is often expressed in centipoise (cP). This property is often important for describing a clay when mixed with water.

(15)*Chemical composition*: A knowledge of the chemical composition of a clay provides a useful guide to the way in which it will behave in a ceramic product made from the clay. Clay is normally analyzed for the oxides of aluminium, silicon, titanium, calcium, magnesium, potassium and sodium and the loss on ignition (LOI). These analyses provide valuable guides as follows.

(i) Al_2O_3 and SiO_2: These may help in differentiation between china clay and ball clay. If a large number of samples are analyzed, then it is found that these constituents are fairly consistent in china clay, but widely variable in ball clay.

(ii) Fe_2O_3 and TiO_2: These are the colouring oxides (pure TiO_2 is very white when fresh, but over time it turns yellow), and their analyses, in general, can be used as guide to fired colour.

(iii) CaO and MgO: Analysis of these are of importance in case the types of clay are bentonite and fuller's earth.

(iv) K_2O and Na_2O: The alkali oxides derived from feldspars and micas affect vitrification behaviour since they act as fluxes.

(v) LOI: Clays are hydrates containing varying number of water molecules. So LOI generally comes from the loss of water on burning and it varies from clay to clay.

In case of lignitic bentonite, however, its value is much higher because of loss of both water and carbon.

Sometimes additional constituents like soluble salt, trace elements and carbon are done for certain clay.

(16) *Mineralogical composition*- The methods currently available for determining mineralogical composition of clay are not precise. This is largely because of the effects of particle orientation and shape which can lead to overestimation of some constituents in relation to others. But, nevertheless, certain clay minerals like kaolinite, montmorillonite, attapulgite are predominant in certain clays, and this analysis can provide useful indications to the type of clay.

2. Fired clay:

(1) *Fired clay colour*: This is important when the clay is used after firing. The whiter a clay burns, the higher its quality is supposed to be. But in potteries, etc., the pattern of colour is more important than whiteness. The fired colour depends on certain impurities present in clay.

(2) *Shrinkage*: It is due to the fact that as water is removed on drying, the solid particles approach closer to each other, the volume of the whole mass being thereby reduced. On further heating in a kiln, the particles partially vitrify and come further closer to each other thus causing further shrinkage. It is proportional to fineness of the particles. Shrinkage is non-reversible.

(3) *Thermal expansion*: Contrary to shrinkage, thermal expansion is reversible. Samples of clay which have already been fired, are re-heated to observe the reversible expansions that occur. This involves *dilatometry*, i.e. the study of size changes which occur as a material is heated. It can provide useful information about the firing behaviour of a clay-based ceramic product. Its most valuable role is in assessing glaze/body compatibility, i.e., differential expansion, if any, of glaze in relation to the glazed body.

(4) *Fusibility*: No single fusion point can be attributed to clays. They usually start fusing partially much before they are completely melted.

(5) *Refractoriness*: It denotes that a given clay is capable of retaining its shape at a given temperature under normal pressure. In other words, it is resistance of a clay to high temperature. In most of the applications, a single type of clay is seldom used, and batches consisting of mixtures of several types are fired in kilns. As such, fusion temperatures of the different types of clay do not provide any guide to the refractoriness of a composite mixture. For determining the refractoriness of a clay in relation to its actual behaviour in a kiln, therefore, standard *pyrometric cones* are used. A pyrometric cone is a pyramid with a triangular base and of a defined shape and size. It is shaped from a carefully proportioned and uniformly mixed batch of ceramic materials so that when it is heated under kiln conditions, it will bend due to softening, and at a definite temperature and after a definite time, its tip becomes level with the base. By varying the composition of the mix, a series of cones with increasing softening temperature, is made. A cone of identical shape and size made of any clay(s) is then heated and matched with one of the reference cones. The

softening temperature of the reference cone as read from a chart, can then give the softening temperature of the test cone, and the reference cone number called "*pyrometric cone equivalent*" or PCE is the expression of refractoriness of the test clay. Three standard series of pyrometric cones are in vogue – Orton in USA, Seger in Germany and Staffordshire in UK. Of these the *Orton pyrometric cone equivalent* (or simply Orton) is used in India as the measure of refractoriness of clays. This series starts with the coolest cone numbered 022 (equivalent to 586^0C when a 1.75 inches high self-supporting cone is heated at the rate of 60^0C/hour) and the most resistant cone numbered 42 (equivalent to 2015^0C when a 15/16 inches high small cone is heated at a fast rate of 150^0C/hour). In between these limits, the numbers are 021, 020, 019 … 02, 01, 1, 2, 3, … 39, 40, 41. A refractory material is one of which the PCE is not less than 21, i.e., which does not fuse at less than 1566^0C temperature.

(6) *Vitrification*: It signifies the degree of fusion that has occurred under certain conditions of heating. The extent of vitrification of a clay is proportional to the amount of fluxing material it contains, and to the duration and intensity of heating.

(7) *Vitrification range*: It is the difference between the temperature at which vitrification of a clay starts and that at which the clay melts completely. Higher proportion of small particles, and larger amounts of basic compounds and fluxes tend to shorten vitrification range.

(8) *Porosity*: Porosity of raw clay is of little importance and that of fired clay can be regarded as the opposite of vitrification. In other words, vitrifiable clays burn denser.

On careful scrutiny of the above 16 properties, it will be revealed that many of them are interrelated. For example:

(1) Particle size, strength, binding power, swelling and impermeability are closely related to plasticity.
(2) Particle size and shrinkage are interrelated.
(3) Vitrification range is nothing but the difference between the fusion temperature and the vitrification temperature, fusibility is nothing but the opposite of refractoriness.
(4) Absorption is measure of porosity (partially) which is just opposite of vitrification
(5) Absorption is also partly related to swelling index.

The relationship amongst the other properties is not known for certainty. However, these properties are for preliminary investigation of a clay for the purpose of fixing its type and possible industrial use. At the stage of actual use, even after knowing the type of clay, industries may need to investigate the quality of a particular clay and this may require more detailed testing. But more importantly, industries rely on experience and judgement and, as far as possible, try to stick to a known and time-tested source of supply.

CLASSIFICATION OF INDUSTRIAL CLAY

Amongst the clay minerals, kaolinite, montmorillonite and attapulgite are the most important from the point of view of industrial classification of clay, while amongst the impurities, carbonaceous matter, sodium oxide, calcium oxide and magnesium oxide render some clays their distinct identity. But, on the whole, classification of clay into different types and their names are based on a mix of criteria related to industrial use, physical nature, ceramic property, mineralogy and the name of type area. The names traditionally used to identify or designate a particular type of clay are also based on the distinctive criteria.

The classifications of clay proposed prior to 1912 were mainly on the basis of stratigraphical position or chemical composition or uses. From 1912 onwards, some serious attempts were made. These are described and analyzed here.

1. Searle's classification (1912): This classification system was put forth with first the origin from a petrological point of view and then a limited number of physical properties and chemical composition as the basis. The properties considered were only refractoriness, fired colour and vitrification. The classification system (Source: A. B. Searle: The Natural History of Clay; Cambridge University, 1st Edition, 1912) is as follows.

(1) Primary clays:
- (a) Clays produced by weathering of silicates (e.g., some kaolins)
- (b) Clays produced by lateritic action – very rich in alumina, some of which is apparently in a free state.
- (c) Hypogenically formed clays produced by water containing active gases (e.g., Cornish china clay).

(2) Secondary clays:
- (a) Refractory clays (e.g., fire clay and some pipe clays).
- (b) Pale-burning non-refractory clays (e.g., pottery clay, ball clay and some shales)
- (c) Vitrifiable clays (e.g., stoneware clay, paving brick clay)
- (d) Red-burning non-refractory clays (e.g., brick/terracotta clays/ shales).
- (e) Calcareous clays or marls containing more than 5% calcium carbonate.

(3) Residual clays: Clays formed by any of the foregoing processes and deposited along with calcareous or other matter which have later been removed leaving behind the clay (e.g., white clays of the Derbyshire hills).

This classification suffers from several inadequacies – particularly in the present context. These are:

(i) In the first level, origin of clay has been considered, but this is still not fully understood.
(ii) In the second level, no uniform basis is discernible.
(iii) The commonly used terms are not correlatable with the types of clay and as such it is of no use to the user industries.

2. Ries' classification (1917): In this also, origin and mode of formation of clay were taken as the basis as follows.

A. Residual clays formed in locations of rock alteration due to various agents of either surface or deep-seated origin.

1. Those formed due to surface weathering by solution or disintegration or decomposition of silicates.
    - (a) Kaolin – white in colour, usually white burning. Parent rock: granite, pegmatite, rhyolite, limestone, shale, feldspathic quartzite gneiss, schist etc. Shape: blankets, tabular, steeply dipping masses, pockets or lenses.
    - (b) Ferruginous clays derived from different kinds of rock.
2. White residual clays formed by the action of ascending waters possibly of igneous origin.
    - (a) Formed by rising carbonated waters
    - (b) Ferruginous clays derived from different kinds of rock.
3. Residual clays formed by the action of downward moving sulphate solution.
4. White residual clays formed by replacement due to action of waters.

B. Colluvial clays representing deposit formed by wash from the foregoing and of either refractory or non-refractory character.

C. Transported clays

1. Deposited in water
    - (a) Marine clay or shale deposits often of great extent. White-burning clays (ball clays, fireclays or shales); Buff-burning clays (impure clays or shales – calcareous or non-calcareous)
    - (b) Lacustrine clays, deposited in lakes and swamps. Fire clay or shale – red-burning, calcareous.
    - (c) Flood plain clays usually impure and sandy.
    - (d) Estuarine clay, deposited in estuaries. Mostly impure and finely laminated.
    - (e) Delta clays
2. Glacial clays -- often stony, found in the drift; may be either red- or cream-burning.
3. Wind-formed deposits, loess.
4. Chemical deposits, some flint clays.

This classification has also not been successful from the point of view of utilization. Besides, all the currently used terms are not accommodated here. Although a few names such as ball clay, fire clay, shale, flint clay, etc. find mention, their differences have not been brought out.

3. Parmelee's classification (1921): This is probably the most elaborate classification proposed so far. In this classification (Source -- C. W. Parmelee and C. R. Schroyer: Further Investigations of Illinois Fire Clays; State Geol. Survey, Illinois, 1921), ultimate types of clay number 28, and there are as many as four levels of classification as follows.

I. Clays burning white or cream coloured, not calcareous.

A. Open burning clays, i.e. still distinctly porous at cone 15. These are of value in the manufacture of pottery because of their good colour and strength. These may also possess high degree of refractoriness and of value in manufacturing refractories.

1. Low strength, e.g. residual kaolins such as those from North Carolina
2. Medium and high strength, e.g. secondary kaolins such as those from Florida and Georgia

B. Clays burning dense, i.e., become nearly or completely nonporous between cones 10 and 15.

(a) Non-refractory clays

3. Good colour, medium to high strength, medium shrinkage. Uses: pottery, certain whiteware, porcelain, stoneware.
4. Poor colour, medium to high strength, medium shrinkage, Uses: stoneware, terracotta, abrasive wheel, zinc retort, face brick, saggars.

(b) Refractory clays

5. Good colour, medium to high strength, medium shrinkage. Uses: refractories, especially for glass (if do not over-burn seriously at 5 cones higher), and the uses stated under 3.

(C) Dense burning clays, that become nearly or completely non-porous between cones 5 and 10 and do not over-burn seriously at 5 cones higher than the temperature at which minimum porosity is reached.

(a) Non-refractory clays

6. Good colour, medium to high strength, medium shrinkage, usually reach minimum porosity between cones 5 and 8. Type: ball clay. Uses: pottery, whiteware, porcelain and stoneware.
7. Poor colour, medium to high strength, medium shrinkage. Uses: stoneware, terracotta, abrasive wheel, zinc retort, face brick, saggars.

(b) Refractory clays

8. Non-porous or practically so at cone 5, do not seriously over- burn at 12 cones higher, highly refractory (softening point at cone 31 or higher), bonding strength minimum 325 pounds per square inch. Uses: component in graphite crucibles for melting brass.
9. Non-porous at about 1275^0C (cone 8), not over-firing at 1400^0 C or higher, strength and softening point as above. Uses: glass pots.
10. Become dense at about 1275^0C (cone 8), do not over-burn below 1425^0C, bonding strength minimum 325 pounds per square inch or higher, softening point cone 29 or higher. Uses: glass pots.

II. Buff-burning clays

A. Refractory clays

(a) Open burning, i.e. having porosity 5% or more at cone 15 or above; indurated, non-plastic or slightly plastic unless it has been weathered. Type: flint clay.

  11. Normally aluminous, maximum alumina 40 per cent. Use: refractories.
  12. Highly aluminous, alumina exceeds 40 per cent. Use: refractories, abrasives.

(b) Open burning, i.e. having porosity 5% or more at cone 15 or above; plastic.

  13. Normally siliceous, maximum silica 65 percent. Uses: fire bricks and other efractories, terracotta, sanitary ware, glazed and enameled brick.
  14. Siliceous, silica content above 65 percent. Type: many of the New Jersey fire clays. Uses: fire brick and other refractories.

(c) Dense burning between cones 10 and 15, i.e. attains a minimum porosity of 5% or less within that range.

  15. Medium to high strength, do not over-burn for 5 cones higher than point of minimum porosity. Uses: glass pots, fire brick, saggars, architectural terracotta, sanitary ware, enameled and face brick.

(d) Dense burning attaining porosity of 5% or less at cone 10 or lower.

  16. Non-porous or practically so at cone 5, do not seriously over-burn at 12 cones higher, highly refractory (softening point at cone 31 or higher), bonding strength minimum 325 pounds per square inch. Uses: component in graphite crucibles for melting brass, architectural terracotta, sanitary ware, enameled and face brick.
  17. Non-porous at about 1275^0C (cone 8), not over-firing at 1400^0 C or higher, strength and softening point as above. Uses: glass pots, architectural terracotta, sanitary ware, enameled and face brick.
  18. Become dense at about 1275^0C (cone 8), do not over-burn below 1425^0C, bonding strength minimum 325 pounds per square inch or higher, softening point cone 29 or higher. Uses: glass pots, architectural terracotta, sanitary ware, enameled and face brick.

B. Non-refractory clays

(a) Open burning, not attaining porosity of 5% or less at any cone lower than 10.

  19. High or medium strength. Uses: architectural terracotta, stoneware, yellow ware, face brick, sanitary ware.
  20. Low strength. Use: brick.

(b) Dense burning, attaining less than 5% porosity at cones lower than 10.

  21. High or medium strength. Uses: architectural terracotta, stoneware, abrasive wheels, sanitary ware, face brick, paving brick.

III. Clays burning red, brown or other dark colours

A. Open burning clays, i.e. those which do not attain low porosity at any temperature short of actual fusion.

  22. Medium or high strength. Uses: brick, drain tile, hollow blocks, flower pots, pencil clays, ballast.

23. Low strength. Use: brick.

B. Dense burning

(a) Having a long vitrification range (5 cones)

24. High or medium strength. Uses: conduits, sewer pipe, paving brick, floor tile, electrical porcelain, cooking ware, silo block, art ware face brick, architectural terracotta, roofing tile.

25. Low strength. Uses: as dust body in the manufacture of electrical porcelain, floor tile, building brick.

(b) Having a short vitrification range

26. High or medium strength. Uses: building brick, face brick, hollow block, flower pot

(c) Fusing at low temperature — approximately cone 5, to form glass.

27. Slip clays.

IV. Clays burning dirty white, cream white or yellowish white.

28. Contain calcium or magnesium carbonate or both, never reach very low porosity, have a very short heat range. Use: common brick.

A very careful analysis of the classification system will bring to light many demerits as below.

(i) The classification is too complex for any practical application.
(ii) There are too many bases in the same level which will involve too many tests for defining the position of an unknown clay.
(iii) The interrelationship of various parameters have not been taken into account (e.g. porosity and vitrification range, strength and plasticity).
(iv) In some places, colour and plasticity of raw clay has formed the basis after the clay has already been classified on the basis of fired colour; this defies logic because colour and plasticity of a clay are examined before it is fired.
(v) The classification applies to use of clays by firing only, but many clays are used without firing.
(vi) Some common types of clays like shale, bentonite, fuller's earth etc. cannot be fitted in this system.
(vii) The interrelationship amongst the different types of clay like china clay, ball clay, brick clay etc. have not been brought out.
(viii) The position of some of the clays (e.g., terracotta clay) is not unique, and they find place in more than one position in the system.

3. **Bateman's classification (1942):** This classification (Source – Allan M. Bateman: Economic Mineral Deposits, 1st edition, 1942) is as follows:

Type	Chief Use	Chief characteristics
1. Kaoline		High grade, fine-grained, white burning
(a) China clay	White ware, porcelain	
(b) Paper clay	Fillers in paper-makng	
2. Ball clay	White ware, mixing	White burning
3. Fire clay:	Refractories	High alumina
(a) Flint clay		
(b) Diasporic clay		
4. Stoneware, paving and sewer pipe clays	Stoneware, paving bricks, sewer pipes	Dense burning
5. Brick and tile clay	Brick and tile	Common clays
6. Bentonite	Iron and steel works, filtering	
7. Fuller's earth	Filtering	Absorptive qualities

In this system, all the terms in use today do not find a place. Moreover, no basis is discernible at all.

5. Rosenthal's classification(1949): The main plank of this system is the mode of formation of clays. The classification system (Source — E. Rosenthal: Pottery and Ceramics; Harmondsworth, UK, 1st edition, 1949) can be schematically represented as follows.

Clay:
(1) Primary
(2) Secondary
(a) Refractory clay
(b) Vitrifiable clay
(c) Fusible clay

This is no doubt an oversimplification of the complexity of clays and the diversity of their usage. Only three properties have been taken into account, and there is no correlation of the terms used here with those currently used by industries. As such, it does not serve any practical purpose.

6. USBM's classification (1970): The US Bureau of Mines developed a system of classification of clays, originally in 1956 and later expanded in 1970, which is schematically represented as follows.

Clay:
(1) China clay (Kaolin)
(2) Ball clay

(3) Fire clay (including stoneware clay)
  (a) Plastic
  (b) Semi-plastic
  (c) Semi-flint
  (d) Flint
(4) Bentonite
  (a) Swelling
  (b) Non-swelling
5. Fuller's earth
6. Miscellaneous clay

It is essentially a list of the names of some of the commonly used industrial clays without any basis or parameter to bring forth their interrelationships. Moreover, fire clay, stoneware clay and flint clay are distinctly different terms having distinctly different usage, and their combining together is not justifiable. The class "miscellaneous clays" is also a very general term.

7. Chatterjee's classification (1978): K. K. Chatterjee (the present author) proposed this classification in 1978 (ref.: J. Metals and Minerals Review, vol XVII, no. 2, January, 1978) after studying the steps of testing of clays by the research institutes of the Council of Scientific and Industrial Research (CSIR), India. For testing clay samples, they are first crushed and ground, then plasticity is studied and finally they are fired to study the different fired properties such as refractoriness, fired colour, vitrifiability etc. (ref. Council of Scientific and Industrial Research: Indian Clays – their Occurrence and Characteristics – Samples examined; Pt-I and II, 1958). Since hardness is directly related to grindability and the economics of grinding, it has been taken as the first criterion for classification of clay. The next criteria are the properties that can be studied immediately after grinding and without firing, i.e. base exchanging power, plasticity and swelling characteristic. Only after clay has been classified to the maximum possible extent on the basis of these four criteria, the properties that can be studied only after firing, have been considered. These properties (refractoriness, fired colour and vitrifiability) have been used to complete the classification. Thus the criteria for classification in the successive levels follow a logical order and they have been selected so as to require the minimum possible testing for fitting any unknown clay sample in the system. Also, care has been taken that the position of none of the types of clay is interchangeable, and that the interrelationship amongst the different types is clearly visible at a glance. In the original system, 15 of the 16 currently used types of clay (china clay or kaolin, ball clay, fire clay, sodium bentonite, calcium bentonite or pascalite, attapulgite or fuller's earth, brick clay, stoneware clay, pipe clay, roofing tile clay, pottery clay, terracotta clay, terracotta clay shale, brick-making clay shale, flint clay and pozzolanic clay) were accounted for. The type pozzolanic clay was at that time, not common – at least in India. Now that it has also become very common in literature, the original system has been expanded to include this type also. Besides, the name attapulgite has been gaining acceptance over fuller's earth internationally, although in India, the name fuller's earth continues to be popular. So, now both these names have been incorporated. The term "*cement clay*" has been deliberately omitted, because no natural clay can be universally marked as cement clay and any clay can be used after manipulating its composition by addition of bauxite, hematite, sand, laterite etc.

to suit the specification of the composite feed. The modified classification system is as follows.

Clay:

- I. Hard
    - A. Plastic
        - 1. Uniform and pleasing fired colour (terracotta clay shale)
        - 2. Non-uniform fired colour (brick-making clay shale)
    - B. Non-plastic
        - 1. Poor reactivity with lime (flint clay)
        - 2. Good reactivity with lime at ordinary temperature (pozzolanic clay)
- II. Soft
    - A. Clay with good base exchanging power
        - 1. Plastic
            - (1) Swelling (sodium bentonite)
            - (2) Non-swelling (calcium bentonite or pascalite)
        - 2. Non-plastic (attapulgite or fuller's earth)
    - B. Clay with poor base exchanging power
        - 1. Plastic
            - (1) Refractory
                - (a) Poorly vitrifiable (fire clay)
                - (b) Highly vitrifiable (pipe clay, stoneware clay)
            - (2) Non-refractory
                - (a) White burning (ball clay)
                - (b) Red, brown, dark burning
                    - (i) Uniform pleasing fired colour (terracotta clay)
                    - (ii) Non-uniform fired colour
                        - Highly vitrifiable (roofing tile clay, pottery clay)
                        - Poorly vitrifiable (brick clay)
        - 2. Non-plastic (china clay or kaolin)

In USA, only sodium bentonite is regarded as bentonite proper, whereas calcium bentonite or pascalite (also called in both USA and UK as "*calcium montmorillonite*") and attapulgite are referred to as two types of fuller's earth. In Brazil, the nomenclature is similar to that in India – calcium bentonite as a type of bentonite and attapulgite or fuller's earth, a separate entity.

The individual clays are dealt with in the subsequent chapters.

Chapter 7

CLAY - KAOLIN (CHINA CLAY)

Kaolinite is the dominant clay mineral in china clay or kaolin along with some other minerals of the same group namely dickite and nacrite, as well as halloisite. Kaolinite originates from feldspar contained in different rocks, by weathering and the process is called *kaolinization*. The alteration of feldspar takes place in two stages--first to montmorillonite and then to kaolinite. Kaolin deposits may be either primary (in situ) or secondary (transported), but the in situ deposits are more common. Chemically, the composition of pure china clay is dominated by SiO_2 in silicate form (47-50%), Al_2O_3 (34-37%) and water showing as loss on ignition (10-12.5%). The chemical composition shows remarkable consistency. In nature, small amounts of other constituents like free silica, mica, Fe_2O_3 , TiO_2, CaO, MgO, K_2O and Na_2O are invariably present – to a greater extent in primary deposits, and to a lesser extent in secondary ones in which, part of these impurities are removed by natural sorting. Production of modern whiteware commenced in India in the middle of 19th century at Pathargatta in Bhagalpur district, Bihar.

BENEFICIATION

China clay is valued for its purity, and the impurities are required to be removed to the maximum possible extent to convert a crude china clay to a marketable one. Some of the uses specify such a high degree of purity that the best grade deposits have to be selected and then beneficiated. There are two processes, namely dry and wet, which are described here.

1. Dry process: It is a simple and relatively inexpensive process, but its scope is limited, and only part of the relatively coarser sized and heavier impurities can be removed leaving the finer and lighter clay particles purer. The crude clay is first crushed and dried to eliminate the natural moisture. Then pulverized to very fine size to liberate the clay particles from the impurities – an operation called "*levigation*". Finally, the separation of the clay particles is done by air classification.

2. Wet process: This is a complex and widely practised process with some variations. It can refine crude china clays to high levels of purity. First the clay is made into a slurry (called "slip" in USA) and then the slurry is separated into different coarse fractions according to particle size, by treating with different reagents or by hydro-cyclones or by spiral classifiers. The coarse or the grit fraction containing (+) 45 microns sized particles is removed. The slurry containing (-) 45 micron sized particles is then separated into (-)2 micron sized and 2 micron (+) sized fractions by hydro-cyclones or de-flocculation. The former is required for certain special non-ceramic applications. But both these slurry fractions still contain TiO_2, Fe_2O_3 (both colouring matters) and mica. The two colouring matters are removed by high intensity magnetic separation method, and, if all three are present, then ultra-flotation techniques are employed. Thus purified fractions of the clay slurry is bleached to improve brightness. Finally, the slurry fractions are filtered, dried (generally sun-dried in order to keep the cost low) and pulverized (levigated).

CRITERIA OF USE

The general properties of clays have been discussed in the chapter “Clays – General”. There are some specific properties which are important from the point of view of industrial use of china clay. These properties of pure marketable grade china clay are as follows.

1. Whiteness: Both the raw and fired colours of china clay are white. The normal content of the colouring matter Fe_2O_3 is only 0.6-1.3 per cent. The colouring parameter ‘L’ value is as high as 90 -96 (cf., the value of fresh TiO_2, which is the bench mark for whiteness, is 98-100).
2. Brightness: The brightness of calibrated china clay (i.e. even-sized fine grains) as measured in terms of reflectance from blue light (wave length 457 microns) is 80-87 (cf., the value of fresh TiO_2, which is the bench mark for brightness, is 97-98).
3. Fusion point of china clay is 1785^0C.
4. Dry shrinkage (at 110^oC) is 14% (max), total fired shrinkage (at 1350^oC) is 18% (max).
5. Its plasticity is very low (almost non-plastic).
6. Its specific gravity is 2.6.
7. It is soft and can be pulverized to a fine size of less than one micron. At this size, the particles quickly disperse in water and remain in suspension for a long time.
8. Chemically, it is inert and non-toxic, but its oil absorption is fairly high (25-45%).
9. It is electrically non-conductor.
10. Its refractive index is 1.56.

These properties are standards in a marketable grade beneficial to china clay. There may, however, be variations in the contents of certain chemical impurities and in a few of the physical parameters, which are especially specified by user industries.

USES AND SPECIFICATIONS

For various purposes, china clay is used in either raw or processed form. The impurities in china clay are SiO_2, Fe_2O_3, TiO_2, CaO, MgO and Na_2O which should be kept low as per the standard specifications. Apart from these, physical properties such as plasticity, brightness, colour, grit content, particle size, conductivity, etc. play an important role in deciding about the end use of china clay.

Very often, in certain uses – particularly those requiring firing, china clay is not fired alone, and is mixed with other materials. As a result, some of the properties of pure china clay become modified in the charge, and these adjustments are made carefully to suit the specifications of some user industries.

The important uses are:

1. Ceramics and glazes (non-refractory and refractory)
2. Bone china
3. Textile
4. Paper
5. Rubber
6. Plastic
7. Paint
8. Pharmaceuticals and cosmetics
9. Insecticide
10. White cement
11. Ink
12. Ultramarine
13. Synthetic zeolite
14. Catalyst
15. Soaps and detergents
16. Fiber glass
17. Explosives and pyrotechnics
18. Adhesives and sealants
19. Metakaolin

These uses are discussed as follows:

1. Ceramics and glazes

(a) Non-refractory: The word “ceramic” derived from Greek “keramos” originally meant fired and fused common clays. The original ceramic products (e.g., bricks, potteries) made only of clay were hard and resistant to heat and chemicals, but at the same time coloured, porous and brittle. Today, the product range has gone much beyond bricks and potteries and include white wares (porcelain-wares, table wares, sanitary wares), white tiles (both glazed and non-glazed) and electrically insulating porcelain. These high quality white products are not only hard and resistant to heat and chemicals but also nonporous and strong, and to make them, china clay (with some additional materials added to it) is used.

Manufacturing process: The principle of the manufacturing process, in essence, consists in mixing china clay, quartz or silica sand, other types of clay (e.g., ball clay), feldspar and some flux (soda) with 30-40% water. This mixture is ground, thoroughly agitated, filter pressed, moulded into the required shape, dried and then fired to a temperature ranging from 1200-1500^{0}C depending on the product hardness required, but usually at a temperature of 1300^{0}C. This fired product before glazing is called *biscuit* and the firing is called *biscuit firing* (cf., baking of biscuits). Different ceramic products can be prepared by varying the types of clay and their proportion in the mixture. A special type of ceramic product used for making “*water filter candles*” contains micro-pores to arrest passage of particles suspended in water. To make these, some finely ground organic substance (wood powder) is added to the raw material mix. On firing, the organic matter burns out leaving the candle porous.

Glazing: If the product is to be a glazed one, then it is glazed before firing. The purpose of glazing is to provide a uniform firmly adhering coating on the surface of the ceramic body concealing defects such as pinholes, bubbles, etc. The glaze is made of the same ingredients but with predominance of quartz and feldspar. The ingredients are mixed, finely ground and mixed with water, and this mixture is the glaze. The moulded raw body of the product is dipped into the glaze and then fired to a temperature of about 1400^0C. Colours and decorative designing, if required, are painted after glazing and before firing.

Glaze may be “*raw glaze*” or “*fritted glaze*”. Raw glaze consists of insoluble material applied as such (soluble components crystallize in the mixture and cause blemishes on the treated surface), while fritted glaze is heated beforehand to cause chemical change in the components. Glaze should not only melt but also spread uniformly.

Specifications: Certain desirable properties like white fired colour, low shrinkage, softness and poor electrical conductivity are intrinsic in a marketable grade beneficial to china clay. But the most disadvantageous properties are low plasticity and higher-than-firing-temperature fusion point. The former will not make it amenable to moulding whereas the latter will unnecessarily raise the manufacturing cost. Certain other materials, are therefore added to improve the plasticity and to reduce the fusion temperature, and in the process, some other properties may have to be compromised. So a careful balancing of the proportions of different materials has to be done.

Optimum range of particle size is important. Too coarse a size increases the porosity of the product whereas very fine particles create problems in squeezing out of the water during filter pressing.

Colour of china clay after firing is very important and that should be as white as possible. Shrinkage should be as low as possible, because otherwise cracks may develop after firing. The clay must not fuse at or below the firing temperature, i.e. 1300^0C. Fe_2O_3 and TiO_2 form low-melting iron-titanate glass causing blisters in the products and consequent increase in porosity. Besides, Fe_2O_3 makes the product coloured. TiO_2 has also a high melting point and it will unnecessarily increase the firing temperature. Both these constituents are therefore objectionable.

Alkalis are deleterious. Sodium and potassium in the form of carbonates combine with silica at the firing temperature to form silicates which are water soluble. Presence of these silicates in the ceramic product, obviously, will not be desirable. Moreover, alkalis have fluxing property and they get into the raw material mix through the feldspar and soda. So their presence in the china clay may create problems of managing the chemistry of the mix.

MgO is highly refractory in nature and so is undesirable in white ware, because white wares, by definition, are non-refractory in nature. Besides, it is hygroscopic, absorbing 120% of its volume of water slowly over a period of time.

Grit is not very harmful, but still too much grit increases porosity of the product and also the grinding cost. Quartz or free silica (i.e., other than the silica present in the form of aluminium silicate) changes into different polymorphs with rise in temperature such as beta-quartz at 574^0C, tridymite at 870^0C and crystobalite at 1400^0C. Although, the final form crystobalite is thermally stable, it is most often not reached below the firing temperature. Each of the other forms tend to change over to low-temperature forms and each change is accompanied with change in volume – expansion when the change is to high temperature forms and contraction when the change is to low temperature forms. Consequently, clays containing high percentage of quartz tend to expand on heating and contract on cooling, and the ceramic products made out of such clay tend to develop cracks (only flint is transformed to crystobalite readily, and hence this variety of quartz is preferred for mixing with china clay in the feed). The silica in the form of silicate is an integral constituent of all clays, and it is not harmful (on the contrary, it adds to the strength of the product).

Alumina, which is also an integral constituent of the clay minerals, has some advantages. China clay consists of a number of clay minerals, and hence the percentage alumina in it may vary from one china clay to another. Besides, it gets into the mix through the feldspar also. As such, alumina has a high melting point, but at even below the firing temperature (1300^0C) it melts imperfectly to become a highly viscous fluid, facilitating a coherently bonded non-porous product. Alumina also gets added to the mix through feldspar.

Lime (CaO) is highly hygroscopic. So, if it is present in clay, the product will absorb water in course of time on exposure, and ultimately, crumble. Also, at 1100^0C (i.e. below the firing temperature), CaO reacts with alumina and silica and forms new compounds, mostly silicates. Some of these silicates lower the fusion point of clay. Also, if lime is present in the form of $CaCO_3$ or $CaSO_4$, then CO_2 or SO_3 is expelled on heating, and the ware is left more porous. Finally, lime makes the melt more fluid and it reduces the range between softening and flowing temperature. Sometimes this range may be as short as 40^0C only. The result is that it becomes difficult to control the temperature of the furnace to remain within this range. For these reasons, lime is very objectionable in china clay.

Loss on ignition or LOI may be on account of water, and the carbonate and sulphate of calcium. While the latter is not desirable, the water is necessary to render plasticity to the china clay (in fact, plasticity of the mix is enhanced by adding some plastic clay).

Amongst the clay minerals, montmorillonite is the most detrimental to the china clay. Montmorillonite has high water absorption and high swelling power, which increase the filter pressing time for the clay during mould preparation. Even 1% content of this mineral is not acceptable.

The Bureau of Indian Standards (BIS), in 1993, has considered three grades–(I, II and III depending on the quality of the ceramic product to be manufactured) and has prescribed specifications in terms of certain parameters, some of which are applicable only to the finished ceramic product and not to china clay. The important parameters that are relevant to china clay for use in non-refractory ceramics are: *60-70% of particles less than 2 micron size and the rest coarser up to 44 micron; 10.5-13.0% (minimum) LOI; 32-37% (minimum)* Al_2O_3*; 1.8-0.5% (maximum)* Fe_2O_3*; 1.0 -0.7% (minimum)* TiO_2*; 8-6% (minmum) dry shrinkage at* 110^0*C; 18-16% (minimum) fired shrinkage at* 1350^0*C; 10-14 (minimum) Attenberg number for plasticity.* Out of these parameters the last one is not very critical for pure china clay. The Attenberg number can be modified by adding some other plastic material.

(b) Refractory: Refractory materials are defined as those resistant to heat and having a melting temperature of not less than 1580^0C. The function of refractory lining on a furnace wall is not only to withstand high temperature, but also to withstand temperature fluctuation, and to resist penetration, abrasion, and erosion by hot gases and molten materials in the furnace, and over and above, it should not chemically react with those materials.

China clay has limited use in the refractory industry because the refractory products are not suitable for use under conditions where they are expected to withstand repeated thermal shocks, and its main application is in the production of insulation bricks in combination with talc. So far as the specifications are concerned, the higher the fusion temperature, the better. In this case, MgO is favourable on account of its high fusion temperature. The hygroscopic nature of the MgO does not come in the way, because the product is used under conditions of high temperature and is not supposed to be exposed to water. Silica (free silica as quartz) increases the refractoriness of the clay on account of its high melting point (1700^0C). The problem of differential expansion of quartz due to change in form with increase in temperature is not relevant, because, at about 1500^0C, the quartz grains fuse together in the form of cristobalite which is a stable phase of silica, and no further deformation takes place during exposure of the bricks to the conditions in the furnace. So, free silica content in the clay is not objectionable.

Fe_2O_3 melts at a relatively lower temperature, and if, in addition, TiO_2 is also present then at the high temperature in furnaces where the refractory products are used, they form low-melting iron-titanate glass causing blisters in the refractory bricks and consequent increase in porosity. The Indian industries prefer less than 1% Fe_2O_3 in the china clay. Alkalis and lime lower the fusion temperature, and hence are deleterious.

Particle size is not of any critical consequence, and relatively coarse particles can be used because, on firing, they will fuse together to form a compact mass. Orton PCE should be 28-34, but it can be modified by addition of some other refractory material (china clay does not possess such high values).

2. Bone china

Bone china is a special translucent variety of porcelain first introduced in England in 1794. It is a sophisticated fine product using tri-calcium phosphate [$Ca_3(PO)_2$] obtained by burning bone, as the most fundamental raw material. The industry prefers the ash of cattle bone because it is iron-free. The raw material mix consisting of 45-50% bone ash, 25-30% china clay, 25-30% feldspar (flux) and about 5% ball clay (plasticizer) is first mixed with water and ground; then the slurry is de-watered by filter-pressing, shaped according to the product desired and slowly dried, and finally biscuit fired at a temperature lying within a carefully controlled short range of $1250\text{-}1300^0$C. The firing temperature is very critical in the case of bone china. Under-firing leaves open pores and cannot bring the all-important translucency, while over-firing produces blisters on the surface.

The biscuit is then glazed using colourless transparent glaze. The glazing material consists of borosilicate and white-burning china clay with some feldspar to act as a flux. China clay helps the glaze to remain in suspension. Glaze is applied to the biscuit by either dipping or spraying, and then fired at a temperature $1050\text{-}1100^0$ C, i.e., lower than the biscuit firing temperature. This firing of a glazed product which has previously been fired at a higher temperature is called *glost firing*.

The bone ash in the right proportion acts as a flux, but when in excess, it increases refractoriness. Some of the lime of bone first reacts with china clay to form anorthite, while the P_2O_5 reacts with other compounds to form glass. For making bone ash, cattle bone is first crushed, washed and then subjected to heating in a highly oxidized condition by slowly increasing the temperature to $900\text{-}1000^0$ C, whereby most of the organic matter is removed. The calcined bone is ground with water to very fine size, allowed to age for a few days, and then dried to a moisture content of 10-15 per cent. This bone ash contains a little organic matter which, combined with fine size, gives it some plasticity.

So far as china clay is concerned, it should be white-burning, and for that iron content should be as low as possible. The industry generally accepts up to around 3-5% of Fe_2O_3.

3. Textile

China clay is used here as a filler to give weight and strength to the body of cloths. Its inertness, fine particle size, moderately high specific gravity, softness, high dispersion, white colour and high reflectivity are the properties utilized. Very fine particle size ranging from 2 to 5 micron is preferred because this ensures very high dispersion and uniform spread of the clay in the body of the textile. Freedom from grit is of critical importance because they cut the reeds and threads. Since whiteness is important, all colouring matters are objectionable. MgO and CaO, by virtue of their being hygroscopic, result in crumbling of the clay body of the textile product on exposure to water, and so both are objectionable.

The BIS, in 1995, has recommended a set of specifications for china clay to be used as a filler in different products which also applies to textile. According to those specifications, some of the more important parameters are: *particle size below 53 micron and mostly below 10 micron; the colouring substances CuO, As_2O_3, MnO and Fe_2O_3 maximum 70 ppm, 10 ppm, 0.013% and 0.75% respectively; matter soluble in water 0.5% (max); matter soluble in HCl 2.5% (max).*

4. Paper

In paper, china clay is used both as a filler and as a surface coating material.

(a) *Filler*: It is used in varieties of papers, cardboards, hard boards etc. to impart evenness to the surface by occupying the interstices between cellulose fibers. Particle size is the most critical parameter. Levigated china clay of less than 2 micron particle size that facilitate a very high degree of dispersion so as to spread uniformly and fill up the ultra-fine pores in the cellulose, is specified. Matter soluble in water should be 0.5% (max) and that in HCl 2.5% (max). Colouring matters are also undesirable. An average daily news paper contains 10% of its weight of china clay.

(b) *Coating*: China clay is used as a coating material in high quality white paper to make the surface glazed. It is obvious that china clay should be as white as possible. Fe_2O_3 imparts colour and hence is objectionable. Grit is highly objectionable as it will spoil the smoothness of the surface of the paper. CaO will absorb water and will result in crumbling of clayey ingredient of the finished paper on exposure to air. So, both are objectionable. Grain size should be ultra-fine (for very high quality paper below 2 micron size is preferable), and more important is the uniformity of the size, because, otherwise, surface of the paper will not be smooth. Besides, fine particles provide a very large surface area which facilitates retention of the clay (i.e., the ratio of the clay added during manufacture to the clay which remains in the finished paper). The combination of fine particle size and moderate specific gravity gives to the china clay excellent rheological properties enabling it to be easily dispersed in water and produce slurries with low viscosity and high solids content--a factor of immense importance in the paper coating industry. If a glazed surface of the finished paper is desired, then brightness of the clay will also be a critically important factor. Chemical inertness of china clay is also an advantage.

The BIS, in 1995, has recommended a set of specifications for china clay to be used as a paper-coating material. According to those specifications, some of the more important parameters are: *particle size below 10 micron;* Fe_2O_3 *maximum 0.6%; matter soluble in HCl 1.0% (max); reflectance in blue light wave length 80.0-85.5; and loss on drying i.e. water absorption of finely ground china clay 2% (max).*

5. Rubber

China clay is mixed with rubber as a filler before its casting. Rubber molecules consist principally of flat platelets, which accounts for its elasticity and hardness. The effect varies considerably with different clays. Hard clays reinforces the stiffness of rubber in a greater degree than soft clays. Both hard and soft clays improve acid resistance of rubber when used in acid tank lining. China clay has proved very suitable as a reinforcing and stiffening material, particularly where resistance to abrasion is an important requirement as in the case of footwear. Low shrinkage, fine size of particles which consist of flat platelets, light weight, high dispersion, and chemical inertness of china clay are the main criteria.

As the clay is intimately mixed with the molten rubber, high LOI (i.e. shrinkage) will result in cracking. Grit is objectionable because it will not facilitate intimate mixing. For the same reason, particle size of the clay should be very fine (preferably less than 10 micron) with good dispersion so that the lightweight particles can uniformly disperse in the medium of the molten rubber. Lime is objectionable because it is hygroscopic and will cause crumbling of the rubber product on exposure to air. Colour is not very critical, and off colour is acceptable.

6. Plastic

In the plastic industry, china clay is used as a functional extender for imparting strength, electrical resistance (important in PVC cable sheaths), gloss and low water absorption. Low specific gravity, fine particle size, high dispersion, poor electrical conductivity, high reflectivity, low water absorption (i.e. low shrinkage on drying) and inertness are the important criteria for this application of china clay. In polythene film, filler where it can enhance the absorption characteristics. During the curing of polyester resin the intensity of the exothermic reaction is to some extent contained by china clay by virtue of its water content.

7. Paint

China clay was known to the prehistoric man for its use as a white paint as has been discovered from the 8,000-year-old rock art found in the caves of Mirzapur district of Uttar Pradesh, India. Nowadays, it is not used much as a pigment in oil paints owing to its high oil absorption and its poor opacity in oil due to its refractive index (1.56) being very close to that of linseed oil. It is, however, used as an extender or suspending agent in oil paints, and as a pigment in water paints or in distempers. White colour, easy dispersion with anti-settling properties and chemical inertness are the main criteria for use of china clay in the paint industry.

When it is used as a suspending agent in oil paints, obviously, the colour should be white, and for this, Fe_2O_3 should be low. Grit is objectionable as it may abrade the surface on which the paint will be applied. The most important are good dispersion and anti-settling property, because the purpose of using china clay is to keep the paint in suspension in oil medium and for this reason, grain size should be fine and uniform. Moreover, very fine sized particles can scatter both visible and ultraviolet light, thus increasing the value of the paint. However, relatively coarser china clay, which gives paint a matte finish, can also be used. MgO and volatile matter should be low. MgO is hygroscopic and slowly absorbs water resulting in volume increase (120%) and crumbling of the paint, while in case of the volatile matter its escape after applying the paint on a surface may leave pits and holes on the coating. Oil absorption should obviously be as low as possible.

Whether used as an extender or a pigment, matter soluble in water should be low, otherwise, the paint may easily be washed by water after application.

The BIS in 1997, has prescribed specifications of a few parameters, some of which are: *volatile matter 2% (max), particle size less than 63 micron(for coarse china clay) and less than 40 micron(for fine china clay), matter soluble in water 1.0% (max).*

8. Pharmaceuticals and cosmetics

China clay is used for the manufacture of cosmetics and pharmaceutical products like face powder, talcum powder, toothpaste, tooth powder, adhesives, surgical plaster, lotion and ointment for external use and porcelain in the dental preparation. In the earlier times, china clay used to be prescribed by physicians of Europe and America for treatment of cholera and as an absorbent of toxins in the alimentary canal, but for this use very careful sterilization is necessary as china clay is generally heavily contaminated with pathogenic micro-organisms. It is also used in 53% concentration for making morphin poultice. Very fine size and good plasticity are obviously necessary as these will afford a good paste and will offer a fine poultice. Since china clay is non-plastic, addition of some other plastic material is necessary. Grit is undoubtedly not tolerable because it does not go with these basic criteria., and the china clay must be superfine. Besides, china clay for medicinal purpose must be free from the toxic substances like lead, arsenic and other heavy metals.

The BIS in 1995, has prescribed specifications of a few parameters, some of which are: *particle size less than 45 micron, matter soluble in HCl acid 2.0% (max), Pb 5% (max),* As_2O_3 *2% (max).*

9. Insecticide

It is used as a distributing agent on account of its fineness, non-abrasive properties, dispersion and chemical inertness. Particle size should be mostly 10 micron. Substances toxic to plants, etc. (e.g., arsenic) are highly deleterious and should be very low (less than 10 ppm).

10. White cement

White cement is made of 65% CaO, 24% SiO_2 and only 5.9% Al_2O_3 which form an aggregate generally consisting of 46% di-calcium silicate, 33% tri-calcium silicate and only 14% tri-calcium aluminate. White cement is manufactured by burning a mixture of high grade low-alumina limestone and pure white silica sand along with certain other materials in a kiln at 1400-1500^0 C to form "*clinker*" which is cooled, mixed with a little pure gypsum to slow down the rate of setting, and ground to ultra-fine size (300-350 nanometre or 40000 mesh). The main constituents in the raw material mix are lime and silica. Sometimes clay is added to balance the composition. While in the ordinary portland cement which is a comparatively low-value commodity, locally available low cost clay is used, in white cement pure and white china clay is required. China clay must be free from any colouring substance like Fe_2O_3, MnO, CuO etc. and must be fine grained.

Some of the white cement manufacturers using raw china clay specify china clay containing 15 to 32% Al_2O_3 and 1.5% Fe_2O_3.

11. Ink

China clay is used here as an extender or suspending agent. Water-washed and chemically bleached china clay is used largely in printing inks. In letter press carbon inks, china clay with a particle size smaller than two microns is used. China clay for this application should be free from grit.

12. Ultramarine

The purer type of china clay forms the essential raw material for the manufacture of ultramarine. For making it, a mixture containing 80% china clay and the rest sulphur, silica and soda ash (Na_2CO_3) is heated and maintained at a temperature of 1500^0C for 24 hours. The ideal composition for manufacture of ultramarine is Al_2O_3-39.4%, SiO_2-46.7% and H_2O-13.9%. It should be free from free silica and low in iron.

13. Synthetic zeolite

New uses of china clay are in the manufacture of synthetic zeolites. It is a major breakthrough in the industrial application of china clay. Calcined china clay is used as a source of alumina and silica to produce synthetic zeolites. Synthetic zeolites are used in the refineries and petrochemical industries as molecular sieves which are becoming widely used.

14. Catalyst

The relatively new field is the chemical modification of china clay to make it an effective catalyst for use in petroleum refining. China clay is treated with sulphuric acid and calcined to produce the catalyst.

15. Soaps and detergents

In the manufacture of soaps and detergents the role of china clay is as a dehydrating agent. The china clay should be in the form of free flowing powder with Al_2O_3 30 to 35% and Fe_2O_3 1 to 1.5%. Water absorption capacity should be 40 to 60 ml per 100 gm or approximately 40-60 percent.

16. Fiber glass

Dried china clay is used in the fiber glass manufacture as a filler. China clay should have high alumina and low iron content. It should be water-washed and spray dried to ensure that the moisture content is low, and then ground to a fine size. The typical grade of china clay for fiber glass consists of 44% SiO_2, 37% Al_2O_3, 0.6% CaO, 2% (max) Na_2O, 0.5% Fe_2O_3 and 1% H_2O.

17. Explosives and pyrotechnics

An explosive mixture essentially contains an oxidizer and a fuel. Some pyrotechnic devices are meant to produce moderate heat in circumstances where building a fire would be inconvenient (e.g., self-heating food cans). They need a quick, short-lived, moderate and small initial fire, like lighting a match, for activating the main device. For this initial firing, a sensitive mixture containing calcium silicide ($CaSi_2$), iron oxide (Fe_2O_3), Pb_3O_4 and a little china clay is used. The role of china clay in this and other similar kinds of explosives and pyrotechnics is to act as a filler to moderate the intensity of the fire. The most critically deleterious constituents are grit and water. The former would hinder fine homogeneous mixing of the ingredients and also, on explosion, spatter and cause violence, while the latter would consume part of the heat energy. As per the specifications of the BIS in 1998, loss on drying should be 1.5% (max), loss on ignition should be 14% (max) and grit should be 0.001% (max), while the particle size should be less than 63 micron.

18. Adhesives and sealants

Adhesive is an organic or inorganic substance capable of bonding together other substances by surface attachment. On the other hand, sealant is an organic substance soft enough to pour or extrude and capable of subsequent hardening to form a permanent bond with the substance. One of the components in these is some pigment which is added for performing certain functions. China clay is the source of aluminium silicate pigment (ASP). ASP provides to an adhesive or sealant hiding ability, whiteness and thixotropy, increases viscosity and reduces drying time (due to higher solids). ASP-bearing adhesives are suitable for application in plywood because it does not cause wear and tear of sawblades.

19. Metakaolin

In the industrial circle it is referred to as “highly reactive metakaolin or HRM”. It is a powerful pozzolan manufactured from kaolin and used for making “white concrete”. Metakaolin literally means changed kaolin, and it is a change of kaolinite crystals into a disordered amorphous state. This is effected by dehydroxylization (calcining) i.e. removal of the water by application of heat over a defined period of time. At $100\text{-}200^0$C, most of the clay minerals lose their adsorbed water, but the temperature at which kaolinite loses water is $500\text{-}1000^0$C. Beyond this temperature, sintering takes place and finally dead-burnt mullite is formed which is not reactive. Mortar based on metakaolin has the advantages of high early strength, reduced permeability, greater durability, less efflorescence, resistance to degradation caused by alkali-silica reaction (ASM). But it also has the disadvantage of high heat of hydration with reduced workability. This necessitates use of some super-plasticizer and chilled water for preparing the admixture.

20. Other uses

(a) Audio and video cassettes: There is possible application of china clay for audio and video cassettes where it serves as a blocking agent.
(b) Electrical industry: It is used in high voltage insulation compounds for electrical wires.
(c) Filler in plaster products, toilet and tooth powders, crayons and matches.

Chapter 8

CLAY - BALL CLAY

Ball clay is a transported type of secondary sedimentary clay containing mainly kaolinite, but differing from kaolin in the content of impurities that include higher contents of SiO_2, TiO_2, CaO and Na_2O and lower content of alumina and also in higher plasticity. In addition to kaolinite, it may contain illite and montmorillonite. Besides, unlike the well developed crystals of kaolinite of china clay, those of ball clay are poorly developed. Most commercial deposits of ball clay are associated with lignite, and in that case it is characterized by organic matter as an impurity. It may also be non-lignitic, occurring as lenses associated with other clays. It owes its name to the general practice in English quarries of recovering it in the form of ball-shaped chunks weighing 30-35 lbs for the purpose of convenience of loading, and this practice was due to its high plasticity. But its identity is often blurred and there is often a tendency to confuse it with kaolin or other clays.

Analyses of non-lignitic and lignitic ball clays show some differences in chemical composition. Typical values of some chemical constituents in them are:

Constituent	Non-lignitic	Lignitic
SiO2	49-75%	42-52%
Al2O3	16-34%	31-32%
Fe2O3	0.8-2.5%	1.1-1
TiO2	0.9-1.6%	0.7-1
CaO	0.2-0.3%	0.2-0
MgO	0.3-0.5%	0.2-0
K2O	.2-3.3%	1.0-2
Na2O	0.2-0.7%	0.1-0
LOI	5-12%	12-23%

The high LOI in lignitic ball clay is largely due to presence of organic matter which, on firing, burns out as CO_2.

CRITERIA OF USE

The most strikingly characteristic properties of ball clay that make it stand apart from other clays are:

(1) Plasticity: It is very high and due to this, shrinkage after firing is also very high. The very high plasticity renders ball clay very sticky and difficult to handle. The high plasticity is due to prolonged hydrolysis during formation and transportation, during which the colloidal particles bound together the coarser particles.

(2) White to light brown fired colour: Although the raw colour may be dark due to the presence of carbon, it becomes lighter on firing as the carbon burns out.

(3) Refractoriness: It is in the range of 26-32 Orton PCE, i.e., 1600-1750^{0}C. It is less than that of china clay (PCE 35, i.e., 1785^{0}C).

(4) Vitrifiability: The typical English ball clay starts partially fusing at 1200^{0}C. At this temperature, due to high shrinkage, it vitrifies to a very dense mass. This early start of fusion ensures a long vitrification range (1200-1600^{0}C or longer).

(5) Carbonaceous matter: High content of carbonaceous matter hinders flocculation around it when the ball clay is treated with water. As a result, inside the plastic mass of clay, deflocculated zones are formed. Along such zones, the plastic mass tends to slip when pressed during moulding creating planes of weakness in the product.

USES

1. Fired product:

(a) Blending with other clays: Ball clay is not used alone due, particularly, to its low refractoriness and unmanageably high plasticity. But it is invariably used as an additive to other types of clay like china clay, fire clay, etc. (which are nonplastic) to adjust the plasticity of the raw material mix so as to facilitate moulding into desired shapes. Besides, its acceptable fired colour and its ability to vitrify relatively easily into a dense mass add to the advantages if the use is for fired products. In this way, it may find application in the manufacturing of any of the fired products based primarily on these nonplastic clays—ceramics, porcelain, bone china, refractories, etc. The percentage of ball clay added is carefully controlled so as to achieve optimum properties—both physical and chemical—in the raw material mix. Among the deleterious constituents mica and free quartz or grit are particularly objectionable. So far as carbonaceous matter is concerned, the black colour is of no concern as it gets eliminated during firing. But too high a content creates problem during mould preparation because deflocculated slip planes give rise to zones of weakness. Generally 0.5% and more is undesirable. However, less than 0.5% carbonaceous matter is considered desirable because then the clay becomes thixotropic, and the slip planes, while aiding flow of the plastic mass and mouldability, do not affect the quality of the product.

(b) Earthenware wall tile: This is a product (perhaps the only one) in which the only type of clay used is ball clay. Glazed earthenware wall tiles are used for the surface of walls where cleanliness is an important factor as in hospitals, kitchens, bathrooms, chemical laboratories etc. The standard size of the tiles is [14.5 cm X 14.5 cm X 4.5 mm], but other sizes are also customized. To make such tiles, a mixture consisting of ball clay, dolomite, wollastonite, talc and slate pencil powder is wet ground to 120 mesh size, passed through a magnetic separator to remove iron particles, agitated and filter-pressed by which water is driven away and cakes are formed. The cakes are dried, powdered, mixed with some binder and then tile-pressed. The tiles are first biscuit fired (ceramic engineers' term for firing before glazing like baking of biscuits), cooled, glazed on the top surface and glost fired (ceramic engineers' term for post-glazing firing) up to 1050^0C temperature.

2. Cold uses: Ball clay is used as an additive to bentonite in animal feed pellets and for lining of toxic waste dumps. It is also used as a filler in rubber and plastic.

Chapter 9

CLAY - FIRECLAY

Fireclay is that type of clay which can withstand fire without cracking or vitrifying. The "fire" is the fire of a furnace and the minimum temperature of this fire specified as the international standard in order that a clay can qualify to be fireclay is 1500^0C (Orton PCE 18). In practice, however, the fireclays used in industries are required to withstand not only high temperature once but also repeated heating and cooling, i.e., thermal shocks. As a cushion, therefore, their tolerance temperature specified is much higher, about 1600^0C or 26 PCE. It contains at least 18% and generally 30% or above Al_2O_3, and combines the properties of clay (fine grain size, softness, compactness, etc.) with those of alumina (resistance to high temperature). The product made of fireclays is called firebrick which constitutes one of the main planks on which many high-temperature-process industries stand. Worldwide, fireclay occurs as sedimentary beds associated with coal seams. Typical fireclay is plastic, but generally, the nonplastic/semiplastic flint clay is clubbed with it because both are used for making firebricks.

HISTORY

Industrialists recognized the importance of durable and refractory firebricks for carrying out various metallurgical processes as early as during the early stages of industrial revolution or even before. In India, till the mid-19th century, firebricks used to be imported. Although in 1859, Burn and Co. Ltd started making firebricks at its pottery factory in Raniganj, West Bengal, they did not become popular till 1875 when, for the first time, they were used in the blast furnace of Bengal Iron Works Co. with good results. Thereafter, the firebricks produced by this factory were in demand by other blast furnaces, foundries, railway workshops, etc. It was only after the establishment of Tata Iron and Steel Works at Jamshedpur that more number units came up (most of them in the Raniganj and Jharia coalfields of the Jharkhand-West Bengal Gondwana basin) for meeting the growing demand of firebricks. With the growth of firebrick industry grew mining of the fireclay beds occurring in these coalfields. In due course, both fireclay mining and firebrick manufacturing spread to other parts of the country — Madhya Pradesh, Orissa, etc. During the 3-year period 1944-1946, the average annual production in India as reported by the mines was about 82,000 tons which rose to 100,000 tons in 1947, to 125,000 tons in 1950, to 275,000 tons in 1960, to 584,000 tons in 1970, to 762,000 tons in 1980 and to 878,000 tons in 1982. After this consistent rise, the production declined reaching 522,000 tons in 1990 and to 463,000 tons in the year ending March, 2003. Subsequently, it registered nominal increases and has been hovering around 600,000 tons. The downturn since 1982 has been due to the development of superior refractory bricks to meet the demands of new generation iron-making and other industries employing high temperature processes.

CRITERIA OF USE

Fireclay is made up mainly of kaolinite mixed with crude vegetable matter, pyrites, lime, magnesia, alkalis, titanium and ferric oxide, and it has widely varying colours — white, grey, brown, black. But the mineralogy or both the raw and fired colours are of little importance for its uses. The most important properties that set it apart from other minerals are as follows:

(1) Plasticity: Fireclay is generally plastic, unlike china clay, which is also predominantly kaolinitic. But the special variety of fireclay, i.e., flint clay is semiplastic to nonplastic.
(2) Shrinkage: In spite of high plasticity, its shrinkage on drying or firing is low.
(3) Refractoriness: It is highly refractory. The Orton PCE may go up to beyond 33 (+1740^{0}C).
(4) Vitrifiability: It does not vitrify even at very high temperatures.
(5) Chemical composition: The beneficial constituents are Al_2O_3 (18-40%), SiO_2 and MgO. The alumina content tends to be higher in flint clay. Also, the fluxes like the oxides of sodium, potassium and calcium are low. This is due to their leaching away in a reducing atmosphere that was prevalent in flowing water and under coal beds.

USES AND SPECIFICATIONS

(1) Firebrick: The combination of high refractoriness and poor vitrifiability make it a suitable raw material for refractory firebricks. Firebricks find application in linings of boilers, cement kilns, blast furnaces, glass-making furnaces, etc. The function of refractory lining on a furnace wall is not only to withstand high temperature, but also to withstand temperature fluctuation, and to resist penetration, abrasion, and erosion by hot gases and molten materials in the furnace, and over and above, it should not chemically react with those materials. The life of the refractory lining is increasingly becoming a critical parameter in the productivity of a furnace and economics of a plant, because each time the lining fails and needs replacement, the furnace has to be shut down.

For making fire brick, the fireclay mixed with aluminous materials like kyanite, sillimanite or bauxite is first crushed and ground. Water is added in suitable proportion, and the mass is left for aging. The aged mass is then extruded in the form of a dense cake which is moulded into shapes of brick, dried and fired at 1200-1400^{0}C temperature.

The low shrinkage helps the fired brick to retain its shape and also to resist high temperature without cracking. Plasticity is an important criterion inasmuch as the fireclay will not need much of any plastic clay (ball clay) to be blended with it. But flint clays will need such blending. The poor vitrifiability enables the firebrick to effectively withstand the high furnace temperatures without partial fusion. For very high temperature applications, the alumina content of fireclay may be increased by adding some high-alumina material like bauxite to it, but in that case, the firing temperature will have to be higher.

Al_2O_3 is refractory, and higher its content, higher is the refractoriness. But high Al_2O_3 also means high firing temperature and high cost of manufacturing. So high-alumina fireclay is preferred for making firebricks for use under very high temperature conditions. MgO contributes to refractoriness on account of its high fusion temperature. The hygroscopic nature of the MgO does not come in the way, because the product is used under conditions of high temperature and is not supposed to be exposed to water.

Fe_2O_3 melts at a relatively lower temperature, and if, in addition, TiO_2 is also present then at the high temperature in furnaces where the refractory products are used, they form low-melting iron-titanate glass causing blisters in the refractory bricks and consequent increase in porosity. The Indian industries prefer less than 1-3% Fe_2O_3 in the fireclay depending on the quality of firebrick to be produced. Alkalis and lime lower the fusion temperature, and hence are deleterious.

Particle size is not of any critical consequence, and relatively coarse particles can be used because, on firing, they will fuse together to form a compact mass.

(2) Cordierite saggars: A comparatively recent development is a material called *"cordierite saggar"*, made from artificial cordierite. Saggars are trays used as kiln furniture and shelves for firing powders or components in porcelain and ceramic manufacturing. Artificial cordierite has the composition $Mg_2Al_4Si_5O_{18}$. It has the same characteristics as natural cordierite, which is formed due to contact metamorphism. It crystallizes above 950^0 C and remains stable over a considerable range of temperature, i.e., up to 1750^0C. It has low linear expansion, low coefficient of thermal expansion, excellent resistance to thermal shock, high mechanical strength, ability to work in both oxidizing and reducing atmospheres and to withstand rapid temperature changes without breakage. Saggars made of artificial cordierite have long lives of 10-15 firing cycles. Artificial cordierite is made from an admixture of fireclay, grog, bauxite powder and talc.

(3) Sialon: It is an advance material comprising a mixture of silicon, aluminium, oxygen, and nitrogen (i.e. Si-Al-O-N). Sialon is suitable for applications requiring high mechanical strength at elevated temperatures, high specific strength (for weight saving without sacrificing strength), high hardness and toughness, low coefficient of friction and good thermal shock resistance. Possible uses may include refractory brick or material for resisting molten metal, heat engines welding shrouds, gas turbine engines, metal cutting etc. Ordinary sialon can be made by reacting a mixture of fireclay and coal in a nitrogen atmosphere.

(4) Graphite bricks: During earlier times, graphite refractory bricks used to be made using a mix of graphite and plastic fireclay, mainly for use in areas of much heat and corrosion. These are no longer popular.

(5) Clay-bonded crucible: Compared to furnaces, crucibles are smaller in size. They are advantageous when mixing small quantities of different products requiring different alloys. It is also easier to change a damaged crucible, as opposed to a furnace lining. The main uses of crucibles are for foundry melting of steel, in nonferrous metallurgy (brass, aluminium) and in precious metal metallurgy. The life of crucible is highly sensitive to the type of metal involved. For example, each heat cycle of nonferrous metal melting takes days and each time, the temperature rises from normal to as high as 1500^0C, and the crucible is frequently subjected to rigorous thermal shocks.

There are two types of graphite crucibles namely clay-bonded crucible and silicon carbide crucible. It is the clay-bonded type of crucible that fireclay finds use in. For making such crucibles, graphite (40-50%), plastic fireclay (20-30%), crucible scrap (25%) and sand (5%) are first mixed, then moulded into the desired shape and size, dried and finally fired in a reducing atmosphere. The graphite for this purpose should contain about 90% FC and flake size should be +150 micron.

However, in the early 1950s, consumer preference started shifting from the former towards the latter type.

Chapter 10

CLAY - BENTONITE

Bentonite is essentially a clay with predominance (75-85%) of the clay mineral montmorillonite (a complex hydrate of aluminium, magnesium and silicon) and containing an exchangeable base — sodium or calcium. Depending on whether sodium or calcium is the dominant exchangeable base, bentonite is called sodium bentonite or calcium bentonite. The former is also called swelling type or (sometimes) true bentonite and the latter non-swelling type or pascalite or (sometimes) sub-bentonite. But transitional types between these two are also found in nature. Bentonite is believed to have been formed by the alteration of volcanic ash deposits mostly of Upper Cretaceous age.

In India, the record of the earliest mining of bentonite dates back to pre-independence period when it was mined in Kashmir. But now, the most important mining and processing centre is in the region comprising Kheda, Sabarkantha, Bharuch, Jamnagar, Amreli, Bhavnagar and Kutch districts of Gujarat from where 50,000-120,000 tons of bentonite are mined annually. Some mining is also carried out in the Barmer district of Rajasthan. Its occurrence is reported in Bhagalpur district of Bihar, but there is no significant mining/processing activity.

PROCESSING

Processing of bentonite involves simple techniques of removal of water (drying) and CO_2 (if present), chemical treatment with soda ash for adjusting some properties, and pulverizing. Drying is done by leaving it under the sun for 2-4 weeks, and simultaneously, visible impurities like grits are removed by hand-picking. A solution of soda ash is then added to increase the swelling power depending on requirement. The norm of its addition generally varies in India from 5 to 15 kg per ton. Afterwards, the bentonite is pulverized to (-) 200 mesh size.

Sometimes, bentonite is activated for increasing the efficiency of its swelling and base-exchanging capabilities. There are three common processes:

1. In an earlier practised process in Germany, dried bentonite was mixed with soda ash. The product was known as *toxoton* or *tonsil*. Now, this process is followed in South Africa. Instead of soda ash various long-chain synthetic polymers like carboxy methyl cellulose (CMC), starch (poly-phosphates) etc. can also be added. But these

organic materials become ineffective under the high-temperature and high-stress conditions of drilling due to action of hard water and attack by bacteria.

2. Bentonite is dried at 110^0 C, finely ground, then digested with 96% sulphuric acid for several hours, and finally washed and dried.
3. Bentonite is sun-dried, crushed to 100 mesh size, heated with a 25% solution of sulphuric acid, and then washed, dried and crushed to 200 mesh.

By activation, some of the alumina and combined water are removed, thus reducing the colloidal condition of the bentonite (alumina combined with the water being itself colloidal, tends to make the bentonite more colloidal).

CRITERIA OF USE

Pure bentonite is a creamy yellowish to pale buff or grayish coloured mineral with specific gravity 2.0-2.2. Its refractive index is 1.447-1.550. The important criteria determining its industrial uses are as follows:

1. *Chemical composition:* The approximate chemical composition of bentonite is: 45-65% SiO_2, 14-25% Al_2O_3, 3-9% $FeO+Fe_2O_3$, 2.0-3.5% MgO, 1-5% CaO, 0.40-2.51% Na_2O, 0.5-1.5% K_2O, 0.8-2.0% TiO_2, and Na/Ca 4.55-2.50 (Na-bentonite) or 0.16-0.0001 (Calcium bentonite).
2. *pH value:* Presence of sodium/calcium ensures that bentonite is alkaline, i.e., its pH value is above 7.
3. *Plasticity:* Bentonite is highly plastic, and consequently it has high viscosity.
4. *Swelling/adsorptive power:* Bentonite has marked swelling and adsorptive properties. The high adsorption is due to the 3-layered structure of montmorillonite. The sodium bentonite is more swelling than the calcium bentonite. The former may absorb up to 5 times its weight of water, and increase in volume by up to 15 times its dry bulk (or may even be higher after processing). The swelling/adsorptive power of calcium bentonite can also be raised to this level by activating it with acid. When mixed with water, it forms into a viscous and highly plastic gel. This property is measured and expressed in terms of four parameters, namely: (i) swelling capacity, (ii) swelling index of gel value, (iii) gelling time, and (iv) gel formation index. Specific testing procedures for bentonite have been standardized. For testing swelling capacity, 2 gm of bentonite is slowly poured into 100 ml of distilled water and allowed to remain for 24 hours after which the volume of the gel formed in millilitres is measured. To test swelling index, the minimum weight of bentonite that will form gel in 10 ml of distilled water in 24 hours is determined by trial, and the swelling index is the number obtained after dividing 10 by the weight in gramme. Gelling time is tested by the time in minutes taken by 2.5 gm of dried bentonite to form gel in 25 ml of distilled water. For testing gel formation index, 1.4 gm of dried bentonite, 0.2 gm of MgO and 2.6 gm of alumina are first thoroughly mixed, then 100 ml of distilled water is added and again thoroughly shaken for 1 hour to ensure complete suspension

of the particles. After allowing the suspended particles to settle for 24 hours, the volume of gel formed is measured which is the gel formation index.

5. *Permeability:* Because of its surface properties of water-binding, it has very low permeability. This is so because it adsorbs water and does not allow the water to penetrate into it.
6. *Dispersion:* When dispersed in water, bentonite rapidly breaks down into miniscule particles, even up to 0.1 micron size. The particles of sodium bentonite are smaller and they remain in suspension practically indefinitely, while those of calcium bentonite are a little coarser and they settle down after some time. The mechanism of this breaking down is not clearly known, but it is believed to have some connection with the silicon, aluminium and magnesium contents of montmorillonite. The tetravalent Si^{++++} ion is replaced by the trivalent Al^{+++} ion which, in its turn, is replaced by divalent Mg^{++} ion resulting in weakening of the charge and consequently the bond.
7. *Base/cation exchange capacity:* It means the quantity of positively charged ions (cations) that a clay mineral can accommodate on its negatively charged surface, and it is expressed as milli-equivalents per 100 gm (*equivalent weight* is the molecular weight of an element divided by its valency). Bentonite in general, and sodium bentonite in particular, possesses excellent base exchanging property. Sodium or potassium is exchanged readily for calcium or magnesium. The base exchanging power is further increased because bentonite breaks down readily into small particles in a liquid, thus making available a very large surface area for adsorption by virtue of which the exchange of ions takes place. The methylene blue (MB) test measures the active clay present by determining the cation exchange capacity of a sample of bentonite. The number of exchangeable ions present are determined by replacing these ions with methylene blue dye.
8. *Viscosity:* Viscosity is that property of a liquid which is a measure of its internal resistance to deform under shear stress, and it is measured by the stress in $dynes/cm^2$ or Pascal (Pa) required to be applied to overcome that resistance and maintain a velocity of flow of one centimetre per second. This unit of measurement of viscosity is Poise which is 1 gm.cm.sec or 1 Pascal second (Pa.sec). It is often expressed in centipoise (cP). It is sometimes specified for bentonite meant for use as a suspension in water.
9. *Toxicity:* Bentonite is non-poisonous and harmless.
10. *Fusibility:* The fusion temperature of bentonite ranges between 1330^0C and 1430^0C.

USES AND SPECIFICATIONS

The important industrial uses of bentonite are:

1. Oil well drilling
2. Foundry
3. Refining of oils and fats
4. Construction

5. Ceramics
6. Refractories and abrasive wheels
7. Pelletizing of iron ore
8. Cosmetics and pharmaceuticals
9. Detergents and soaps
10. Insecticide and fungicide
11. Paints and polishes
12. Paper, oil cloth and linoleum
13. Sealant
14. Animal and poultry feed

These uses are discussed as follows:

1. Oil well drilling: Sodium bentonite is used as an additive to the drilling mud to the extent of 20-30% depending on the drilling conditions and the quality of bentonite. Drilling mud serves to lubricate and cool the rotary cutting bits and also to bring the chips and powders up from the bore hole. The purpose of adding bentonite is threefold:

(i) It should increase viscosity of the drilling mud.
(ii) It should increase water suspension of mud.
(iii) It should seal the wall of the hole to prevent fluid loss.
(iv) It should condition the wall rocks to prevent caving.

Approximately 15 tons of bentonite is required for drilling 1000 m. of well.

Sodium bentonite satisfies all the requirements. Its swelling is high and, consequently, it forms a highly viscous mass with water. When in the form of fine particles, it remains in suspension almost indefinitely. Further, being highly impermeable, it is an effective sealing agent.

For indigenous use in India, the Oil and Natural Gas Corporation (ONGC) has its own specifications and testing procedures, whereas for exports, those standardized by the American Petroleum Institute (API) are followed. The two standards prescribed (i.e. ONGC and API) are mostly similar. Fine particle size, high viscosity (minimum 15 centipoises) and low yield point (i.e., the point where a stressed material no longer deforms elastically, but begins to inelastically deform or, in other words, plasticity) are the key parameters in these specifications. Once the bentonite is confirmed to be of sodium type, these specifications are by and large taken care of.

2. Foundry: The whole system of mould-making, melting of metals, casting of the melt in mould, solidifying the cast metal to produce an object in the form of the mould, and final dressing and finishing of the object is called foundry. Moulds may be of two types:

(i) Those made of some metal (e.g., zinc) in which case the mould is called "*die*" and it is permanent; the casting operation is called "*die casting*".
(ii) Those made of sand which are called "*sand mould*" or simply "*mould*", and they are generally of the "use-and-throw" kind. The casting operation is called "*sand casting*".

A sand mould (hereinafter referred to as mould) for solid cast is made with moist well-bonded sand rammed into the desired pattern by hand or machine, and is suited to casting of metals or alloys. Bentonite is used as a binding agent in casting of both ferrous and nonferrous metals, but more particularly iron. Plasticity when wet, and fusion are the key criteria. High plasticity ensures good binding power, while high fusion point is necessary to ensure that the molten metal/alloy cast does not melt it. Both sodium and calcium types of bentonite can be used.

Depending on the quality of casting, the Indian foundry industries use bentonite with varying physical characteristics depending on the final product, by and large following the specifications of the American Foundrymen's Association. Nevertheless, sodium bentonite is preferred to calcium bentonite. The parameters specified by them are: *swelling capacity 12-45 ml; gel time instant to 10 minutes; gel index 20-72; base-exchange capacity 60-100 milli-equivalents per 100 gm; green compressive strength 7-12 psi.*

3. Refining of oils and fats: In this application, bentonite is used for decolourizing purpose. Both swelling and non-swelling varieties are used for this. Non-swelling bentonite is required to be activated. By virtue of its base-exchanging property and ability to swell, it absorbs colouring matter. So, its base exchanging power as well as swelling index should be high. It should be fine-sized, because greater the fineness, larger is the available surface area, and consequently, more will be the efficiency of decolourization. But at the same time, it should not be highly colloidal and should settle down after doing its job. For this matter, content of alumina should be within some optimum limits and that of other water-soluble salts which may be present in the combined water, should be as low as possible.

The industry generally specifies 200 mesh (approximately 50 micron) size, SiO_2/Al_2O_3 ratio between 3.5 and 4.5, base-exchanging power 70 milli-equivalents per 100 gm, and swelling index above 8.

4. Construction: The purpose is to render a porous surface impermeable with a view to both preventing fluid loss through percolation and preventing caving of wall rock during excavation and drilling. Examples are sealing of water tanks, dams, canals, water wells etc. So, sodium bentonite, being highly impermeable, is preferred. The Indian industries specify some parameters, the important ones of which are: *swelling capacity 16-20 ml; gel time instant to 5-7 minutes; gel index 35-45; base-exchange capacity 65-70 milli-equivalents per 100 gm; green compressive strength 8-9.5 psi.*

However, bentonite is not suitable where the water level is fluctuating. As long as it is submerged under water, it absorbs water, swells and plugs the pores. But as soon as it is out of water, it begins to dry up, shrink and crack.

5. Ceramics: Bentonite is highly objectionable in the raw material mix for white ware because due to its high water absorption and high swelling power, it increases the filter pressing time for the raw material mix during mould preparation, and only a very small quantity (less than 1%) is sometimes added to the raw material mix for white ware, mainly with a view to improving plasticity. But, sodium bentonite is used in the glazing mixture. The semi-finished ceramic bodies are dipped in the glaze and fired at 100-1300^{0}C. The glaze should be deposited on the surface of the body uniformly, and for this purpose it is necessary that the ingredients of the mixture do not settle down but remain in suspension for a long time. The role of bentonite is to help in this by virtue of its high dispersion.

In 1988, the Bureau of Indian Standards (BIS) has prescribed a set of specifications the critical parameters of which are: *size: (-) 45 micron;* Fe_2O_3*: 4% (max);* TiO_2*: 3%(max);* Fe_2O_3*+* TiO_2*: 6% (max); CaO: 3% (max); MgO: 3% (max); CaO+MgO: 5% (max).*

Fe_2O_3 has a colouring effect. TiO_2 (over a period of time) makes the product coloured and so they are objectionable. Besides, TiO_2 has a high melting point and it will unnecessarily increase the firing temperature.

Lime (CaO) is highly hygroscopic. So, if it is present in clay, the product will absorb water over the course of time on exposure, and ultimately, crumble. Also, at 1100^0 C (i.e. below the firing temperature), CaO reacts with alumina and silica and forms new compounds, mostly silicates. Some of these silicates lower the fusion point of clay. Also, if lime is present in the form of $CaCO_3$ or $CaSO_4$, then CO_2 or SO_3 is expelled on heating, and the ware is left more porous. Finally, lime makes the melt more fluid and it reduces the range between softening and flowing temperature. Sometimes this range may be as short as 40^0C only. The result is that it becomes difficult to control the temperature of the furnace to remain within this range. For these reasons, lime is very objectionable in bentonite. MgO is also highly refractory in nature and so is undesirable in white ware, because white wares, by definition, are non-refractory in nature. Besides, it is hygroscopic, absorbing 120% of its volume of water slowly over a period of time.

6. Refractories and abrasive wheels: In alumina refractories which are otherwise not plastic, bentonite is used as a binder for imparting green strength. For the same reason, it is also used in crucibles and abrasive wheels. Fe_2O_3 and TiO_2 are objectionable because, when exposed to high operational temperatures to which the refractories are exposed, they may combine to form low-melting iron-titanate glass causing blisters on the refractory body and consequent increase in porosity. High green strength of bentonite is a necessary criterion for use in both refractories and abrasive wheels.

7. Pelletizing of iron ore: Loose fines of very small particle size (les than 325 mesh) of iron ore that cannot be sintered are formed into pellets. To the iron ore fines, 0.5-3.0% bentonite is added as a binder. Coke breeze and some flux (limestone) may also be added. The mixture is placed in cones, drums or discs, out of which discs are relatively more flexible with regard to types of ore and they can be controlled better. A disc pelletizer is a rotating inclined flat plate table. The particles gradually coalesce first, into very small pellets, which go on taking more and more particles and keep enlarging in size till they attain specified sizes. Water is sprayed as required. These are called green pellets, and the operation is called *balling*. The control is effected by changing the angle ($20\text{-}80^0$) and the rpm. of the disc (+8) of the disc. The green pellets are then heat treated at a temperature of above 1200^0 C – generally around 1315^0C – in grate kilns, followed by air cooling with a view to obtaining necessary strength.

The role of bentonite is as a binder to impart enough bonding strength to the pellets for withstanding the stress of rotation and heat treatment. The parameters of significance include swelling capacity, gelling index, gel time, base exchange capacity and green compressive strength. The values for these parameters as preferred by industries are: gelling Index 20-25; gel time 7-10 minutes; base exchange capacity 60-65 milli-equivalents per 100 gm; green compressive strength 7-8 psi. Sodium bentonite which satisfy these specifications, is preferred.

8. Cosmetics and pharmaceuticals: In both applications, the purpose is to make a paste. Bentonite increases viscosity and also, it is non-toxic and harmless. It is especially suitable for use in the therapeutic intestinal absorbent preparation. Liquid bentonite (1-2% concentration) containing its minerals absorbs toxins and bacteria responsible for various types of intestinal infections and, being inert, it passes through the body undigested after delivering mineral nutrients. In naturopathy it is used in mud packs. Due to its non-toxicity and high absorption, it is can be applied for a smoothening effect in skin diseases. The therapeutic use of a type of clay believed to be bentonite was in vogue amongst the aboriginal people in many countries since centuries.

In the field of pediatric and geriatric healthcare (where patients have difficulty in swallowing tablets), liquid bentonite (0.5-5.0% concentration) finds use as a gelling agent in the manufacture of suspensions. The criteria are low solubility and good rheological property. But the disadvantage of using bentonite is that the drug is bonded tightly and is trapped, causing its rate of release to slow down.

9. Detergents, soaps and purification of sewerage water: Sodium bentonite is the constituent of many detergents used in UK, USA and Germany for scouring textiles. The role of bentonite is to adsorb the dirt particles through exchange of cations. Besides the type of bentonite, swelling capacity, fineness of size, pH and content of grit particles are important criteria. The industries specify 10 ml swelling capacity, (-) 240 mesh size, neutral to slightly alkaline solution (pH 8-9) and freedom from grit. The sodium type of bentonite and the swelling capacity ensure good cation-exchanging and adsorptive capacities. Fine size means longer duration of suspension and larger availability of surface area for adsorption. Acidic or strongly alkaline solution may corrode the textile and grit will tend to damage the threads while scouring.

Bentonite is used in certain soaps to the extent of 25 percent.

Bentonite is effective in purification of sewage and turbid water. Here again, the criteria are its base-exchanging capacity, fine particle size with large available surface area and ability to remain in suspension for a long time.

10. Insecticide and fungicide: In this application, the role of bentonite is as a carrier. There are two types of carriers — liquid for spraying and granules for sprinkling. Due to non-toxicity, bentonite does not increase the poisonous effects of the insecticide and fungicide. In the liquid type, its role is to emulsify the powders for spraying (an emulsion is a dispersion of liquid in another immiscible liquid). Since it is to be sprayed, specific gravity (2.3-2.6) and bulk density (27-31 lb/cu.ft.) are very important.

So as far as granules are concerned, the neutral to slightly acidic non-swelling calcium bentonite with high water-holding capacity (25%) and pH 6-7 is preferred, and the bentonite is used in calcined form (bentonite clay black granules). For making this product, crushed bentonite is subjected to heat in an oil-fired rotary kiln, cooled and again crushed. The specifications of calcined bentonite stipulated by industries for this use are: *size (+) 52 to (-) 22 mesh; bulk density 0.8 gm/ml (min); pH in 10% aqueous solution 5-7; attrition 0.25%; adsorptive capacity 18% (min); practically free from dust and other foreign matter.*

11. Paints and polishes: In the case of emulsion paints, the role of bentonite is as an emulsifying agent (as above) to prevent settling of pigment. In water paints and polishes, it is used to increase viscosity and to make pastes.

12. Paper, oil cloth and linoleum: Where off-colour is acceptable or where colour is not important, calcium bentonite can be used in the manufacture of paper, oil cloth (smooth paper thickly coated with linseed oil) and linoleum (floor-covering canvas thickly coated with linseed oil). Addition of 10% bentonite, by virtue of its bonding power, helps to improve the retention of china clay (used as a coating material in high quality paper to make the surface glazed) from 45% to 84%. In addition, bentonite increases the smooth feel of the surface.

13. Sealants: Sealant is an organic substance soft enough to pour or extrude and capable of subsequent hardening to form a permanent bond with the substance. One of the components of a sealant is what is called pigment, which performs various functions like acting as a filler, colouring, shielding ultraviolet light, etc. Bentonite acts as an excellent thickener for water emulsion type sealants. Montmorillonite particles exist in the form agglomerates up to several millimetres in size, but in 5-6% concentration in water, they break down to less than 0.1 micrometer. These nano-sized particles enable even the heaviest of the pigments to remain in suspension.

14. Animal and poultry feed: Bentonite is used as a pellet-binder. Besides, it provides additional mineral nutrients. Its use increases egg size and shell hormones.

15. Others:

(i) Rubber (as a reinforcing and stiffening agent).
(ii) Welding rod (as a binder for the coating).

Chapter 11

CLAY - ATTAPULGITE (FULLER'S EARTH)

In some earlier literature, the non-swelling type calcium bentonite made up predominantly of montmorillonite and containing overwhelmingly more of alumina (14-25%) than magnesia (2.0-3.5%) was referred to as attapulgite or fuller's earth because of some commonality in their properties and usage — particularly after the former is acid-activated. This is still so in the UK. But now, in many countries including India, attapulgite is recognized as a distinct type of clay made up of a different group of clay minerals namely, palygorskite (of which the important member minerals, are sepiolite and attapulgite) and in which magnesia (11-18%) instead of alumina is predominant. Its other name, fuller's earth, owes its origin to the popular practice of the old-time washer men who used this material for removing oily dirt from woolen garments by first kneading the latter with this material and then shaking and fluffing it. The process was called "fulling" and the washer men, "fullers". It is believed that this practice was in vogue in Cyprus as early as in 5000 BC, and the clay was then known by the name "*cymolean earth*". According to the definition proposed by Ladoo R.B. and Myers W.M in 1953, fuller's earth is an inexact term applied to certain natural clays that have an ability to absorb colouring materials from oils of animal, vegetable and mineral origin. This definition is followed in certain countries like Brazil. In some parts of India, particularly Rajasthan, it is locally known by the name "*Multani Mitti*" because traditionally, it used to be sent to and marketed in Multan, Pakistan. Geologically, attapulgite occurs in association with dolomitic limestone.

As per the records, the production of attapulgite in India (then combined with Pakistan) was about 3,000 tons in 1924 which rose to about 12,000 tons in 1946. In 1949, the productions in India and Pakistan were about 4,640 and 5,050 tons respectively. In India it has been notified as a minor mineral and the Union Government does not publish its production statistics.

CRITERIA OF USE

Attapulgite is soft and dirty white to buff in colour. It is not used for making any fired product and its firing characteristics are not relevant. But the most important properties are:

1. Chemical composition: Theoretically, attapulgite is a compound consisting of magnesia, alumina, silica and 5-7% water. But the commercially important

attapulgite as found in nature contains varying amounts of calcium, alkalis and iron. It is the alkalis (sodium and potassium) that is important from the point of view of industrial usage.

2. pH value: It is slightly acidic having pH of 6.5-7.
3. Plasticity: It is nonplastic with low water retention.
4. Structure: Attapulgite has a unique acicular (needlelike) structure comprising three-dimensional chains made of hollow fibers. This prevents it from swelling like montmorillonite (bentonite) which is made up of two-dimensional platelets. But when attapulgite is treated with a liquid, the needles tend to interlock and this gives it strengthening and thickening or thixotropic property. This is not plasticity, but pseudoplasticity. Unlike other thickeners, the strength makes attapulgite a stable thickener.
5. Specific gravity: It is very light having specific gravity of only 0.6-0.7, and being nonplastic, it can remain in suspension in oil and water.
6. Base exchanging power: The base-exchanging power (also known as cation-exchanging power) means the quantity of positively charged ions (cations) that it can accommodate on its negatively charged surface, and it is expressed as milli-equivalents per 100 gm (*equivalent weight* is the molecular weight of an element divided by its valency). Sodium or potassium is exchanged readily for calcium or magnesium. Attapulgite possesses good base exchanging power due to the alkalis present in it and also the hollow fibers. The charged ions inside the hollow fibers can trap impurities of oils etc. This power can be enhanced by activation and activated attapulgite is sometimes loosely equated with calcium bentonite.
7. Catalytic power: This can be enhanced by activation.
8. Oil retention: It can retain oil to the extent of 55-72% depending on the type of oil; but after air and steam blowing, it comes down to only 20-25 percent.

ACTIVATION

Before use, attapulgite is generally activated for increasing the efficiency of its base-exchanging capabilities. There are three common processes:

1. In an earlier practiced process in Germany, dried bentonite was mixed with soda ash. The product was known as *toxoton* or *tonsil*. Instead of soda ash various long-chain synthetic polymers like carboxy methyl cellulose (CMC), starch (poly-phosphates), etc. can also be added.
2. Attapulgite is dried at 110^0C, finely ground, then digested with 96% sulphuric acid or hydrochloric acid for several hours, and finally washed and dried.
3. Attapulgite is sun-dried, crushed to 100 mesh size, heated with a 25% solution of sulphuric acid or hydrochloric acid, and then washed, dried and crushed to 200 mesh.

Activation aims at producing modifications on the surface of the clay mineral crystals and at developing a capacity to adsorb colouring matter and other impurities in oils through increased surface area of the clay particles and increased catalytic power.

USES

After activation, attapulgite is used for the following industrial purposes.

1. *Bleaching and purification:* It is used for removing colouring matter and other impurities from vegetable, animal and mineral oils, wine, fruit juice, saccharine juice, vinegar, sulphur, waxes, etc. This is done by the base-exchanging ability of attapulgite — specially activated attapulgite. In addition, its lightness combined with nonplastic nature enables it to remain in suspension in the liquid for a long time facilitating efficient interaction. Slight acidity prevents it from chemically reacting with acids of fruit juice, vinegar, etc. Relatively low oil retention after air and stem blowing keeps the loss of oil within limits.
2. *Cleaning*: Due to its strong base-exchanging power, catalytic power, nonplastic nature and high oil retention, attapulgite (activated) can be used for removing oil spillage from factory floors, for absorbing excess oil and grease off the brake bands on the winches of cranes and for cleaning oily dirt from woolen clothes. The latter use has been the oldest one as explained in the first paragraph, and in this, the nonplastic nature enables it to be shaken off easily. Attapulgite is also used for cleaning soldiers who are contaminated with chemical weapons. There is record of its widespread use in the 16th century by women as mud-pack for facial application. Now, archeologists are treating the marble surface of Tajmahal with fuller's earth for getting rid of the yellow patches caused by the action of suspended particulate matter (SPM) and bringing back the original shine. A pack of fuller's earth is first applied on the surface, left for a few days and then dusted off. The oily pollutants are taken away by the fuller's earth by virtue of its base exchanging power and hollow fibers while at the same time its nonplasticity does not allow it to stick to the surface.
3. *Simulation of explosion:* Fine grained attapulgite produces a much larger plume than ordinary dirt due to nonplastic nature and low specific gravity. Thus, special effects can be produced with a small and safe charge of explosive.
4. *Oil well drilling:* Drilling mud serves to lubricate and cool the rotary cutting bits and also to bring the chips and powders up from the bore hole. Generally, bentonite is preferred as an additive to the mud. But in some cases where the water in the rock is acidic, attapulgite is used. On account of its slightly acidic nature, it does not react with the water. Also, its lightness helps it to keep the mud particles in suspension.
5. *Insecticide carrier:* Lightness and nonplastic nature are the criteria.
6. *Pharmaceuticals:* In this application, it is mixed with bentonite to adjust the latter's plasticity and specific gravity (see chapter on bentonite). It can remain in suspension both in water and in alcohol. Its concentration varies depending on the purpose to be served as follows:

i. Adsorbent---10-50% concentration
ii. Viscosity modifier----------------------------------- 2-10% concentration
iii. Binding agent--- 2-10% concentration
iv. Suspending agent in creams, ointments, etc.------- 1-10% concentration
v. Suspending agent in oral medicine---------------- 0.5-2.5% concentration

vi. Emulsion stabilizer in creams, ointments, etc. ----- 2-5% concentration
vii. Emulsion stabilizer in oral medicine ----------------1-5% concentration
viii. Stabilizing agent---------------------------------------0.5-2.5% concentration

(1) *Petrochemicals:* Used as a catalyst for oil cracking (in 'cracking', molecules are broken down under high temperature (with or without a catalyst) into smaller units, and a new type of hydrocarbon, namely, olefin is produced. By cracking, light gases, petroleum coke, fuel oil, etc. can also be produced).
(2) *Adhesives and sealants:* Adhesive is an organic or inorganic substance capable of bonding together other substances by surface attachment. On the other hand, sealant is an organic substance soft enough to pour or extrude and capable of subsequent hardening to form a permanent bond with the substance. In sealants, addition of attapulgite gives a non-sag property due to its unique structure and strengthening power. Besides, it acts as a thixotropic modifier.

In an adhesive, one of the components is what is called pigment which performs various functions like improving certain properties, colouring, etc. When fine-grained attapulgite (grain size 0.12-0.14 micrometer) is added to water- and solvent-based adhesive preparations, its functions are as follows:

i. It provides both thixotropy and suspending properties for pigments.
ii. It improves whiteness.

(*9) Cement grouting:* When attapulgite is used in cement grouting applied to the porous surface of a dry tile, the quantity of water within the grouting composition is maintained for a sufficient time so as to allow the cement to cure adequately.

Chapter 12

CLAY - POZZOLANIC CLAY

True "*pozzolana*" is a fine, sandy volcanic ash and "*pozzolan*" is an acidic alumino-siliceous material. Thus, pozzolanic clay (also called 'pozzolanic ash') has the chemical composition essentially similar to that of clay, but if the original meaning of the term clay is considered, then it is an exception. As per the classical meaning, clays are essentially ceramic materials, and the word "ceramic" derived from Greek originally meant fired and fused common clays (see the chapter Clays—General). Pozzolanic clay is not used in any kind of ceramics.

HISTORY

It was originally discovered and dug at Pozzuoli near Visuvius, Italy Subsequently, it has been found at a number of other sites. The Romans mixed it with lime and water and used for making concrete structures, including underwater ones, in 100 BC. The Roman port Cosa was built of pozzolana that was poured underwater using a long tube to avoid its mixing with sea water.

CRITERIA OF USE

The colour of pozzolana may be white, black, grey or red. But the main criteria of its industrial use are chemical. Pozzolana reacts at room temperature with calcium hydroxide in presence of water to form calcium silico-aluminium hydrate compounds (C-S-H) which is a compact substance with low porosity and having cement-like properties at room temperature. Further, due to the acidic nature of pozzolan, the C-S-H produced from it is resistant to corrosion by sulphates and it is also resistant to water leakage and spalling due to low porosity.

USES

1. *Mortar:* Finely ground and mixed with lime and water, pozzolanic clay acts like Portland cement and makes a strong mortar that can set under water. It is therefore suited for use in underwater structures like dams, pillars of bridges, etc.
2. *Portland cement-pozzolan (pozzolanic cement):* Modern pozzolans are actually a mix of pozzolana and portland cement which is called portland cement-pozzolan or pozzolanic cement. This can also be used underwater, and in addition, its high acidity makes it especially resistant to corrosion from sulphates. Fully set pozzolanic cement is stronger than portland cement alone due to it being less porous. Low porosity also makes it resistant to water leakage and spalling. These advantages make it most suited for use underwater in oil wells as well as offshore oil wells.

SUBSTITUTES

There are other substances which possess pozzolanic properties and are used for making pozzolanic cement. These are:

(1) Fly ash: Fly ash is a waste generated in thermal power plants. As per American Standard for Testing material (ASTM), there are two classes of fly ash — class-F and class-C. Class-F fly ash is generated from burning of anthracite and bituminous coal, and it has strong pozzolanic property and practically no cementing ability alone. Class-C fly ash, on the other hand, is generated from burning of lignite and sub-bituminous coal, and it has self-cementing properties with moderate pozzolanic power. Compared to class-C fly ash, which is also used for mixing with cement, class-C fly ash has slower setting rate with easier workability. Consequently, this fly ash is preferred as a pozzolanic material to make concrete admixture. The concrete based on this fly ash is called "green concrete" because it mitigates environmental problem by making use of an environmentally hazardous industrial waste. However, according to the American Concrete Institute, both classes of fly ash can be used — class-F to the extent of 15-25% and class-C, 20-35 percent.

(2) Highly reactive metakaolin (HRM) : It is a powerful pozzolan manufactured from kaolin and used for making "white concrete". Metakaolin literally means changed kaolin, and it is the change of kaolinite crystals into a disordered amorphous state. This is effected by dehydroxylization (calcining), i.e. removal of the water of the kaolinite crystals by heating at 500-1000^{0}C over a defined period of time.

(3) Silica fume or micro-silica or fluffy silica or simply silica dust: It is the waste material generated as smoke or fume from ferrosilicon, semiconductor and other industries. It is amorphous, lightweight, nanometre-sized, fluffy and free-flowing silica powder having specific surface area of the order of 22000 m^2/kg.

(4) Rice husk ash: It is obtained from paddy fields.

Class-F fly ash has the advantage of low heat of hydration facilitating easy workability, but it also suffers from the disadvantage of low early strength. On the other hand mortar based on micro-silica, metakaolin and rice husk ash has high early strength, reduced permeability, greater durability, less efflorescence, resistance to degradation caused by alkali-silica reaction (ASM), but it also has the disadvantage of high heat of hydration with reduced workability. This necessitates use of some super-plasticizer and chilled water for preparing the admixture. Sometimes, a mixture of this fly ash and micro-silica is used in order to combine the advantages of both.

Chapter 13

CLAY - OTHERS

Stoneware Clay

Stoneware clay is similar to fireclay, with the most important difference being in vitrifiability. While fireclay is poorly vitrifiable, stoneware clay has strong vitrifiability. It starts fusing at 1250^0C. A minor difference lies in the mineralogy. In addition to kaolinite (fireclay), montmorillonite is also present in stoneware clay. Plasticity is high, it is a good conductor of heat and is strongly resistant to acids and alkalis. Raw and fired colours are not of any relevance. The main uses of stoneware clay are as follows:

1. Chemical stoneware: Chemical stoneware and chemical porcelain (both glazed and unglazed) are used in chemical industries for holding chemicals. High plasticity facilitates moulding into shapes, and due to strong vitrifiability, it completely fuses at 1280^0C to a solid, compact and impervious mass. The charge consists of stoneware clay, quartz, ball clay and feldspar.
2. Ceramic tower packing material: Cooling towers are used in plants requiring heat transfer as in the case of the spent steam in thermal power plants. They are also used in chemical industries engaged in the manufacture of organic chemicals, petrochemicals, alkalis, acids, etc. and also in room heaters. The packing materials include partition rings, saddles, honeycombs, etc. made in various shapes and sizes. The good heat conductivity is the key criterion. The other criteria and the charge are the same as for chemical stoneware.
3. Stoneware crockery: They are used in kitchens, hotels, etc. as kitchenware. The charge and the criteria are the same as for chemical stoneware. Moderate heat resistance, easy cleanability, nontoxicity are important advantages.
4. Sewerage pipes: Such pipes are made from impure stoneware clay having lower plasticity, which can be made up by blending with some plastic clay. After moulding, the pipes of required diameters are fired. On firing, the pipes vitrify into solid, compact and impervious products. Fired colour is no criterion.

Pipe Clay

Pipe clay is an exceptionally pure, white, siliceous type of ball clay. Like ball clay, it is also highly plastic. Smoking pipes made of this clay were once very popular, and to that it owed its name.

Brick Clay and Brick Shale

The differences between brick clay (also called *brick earth*) and brick shale lie mainly in hardness and mineralogy. The former is soft while the latter is hard and indurated. Mineralogically, the former is composed predominantly of kaolinite and montmorillonite and the latter of illite. The hardness of the brick shale may render it somewhat less plastic than the brick clay. But both are used for making common bricks.

Manufacturing process: Brick is an artificial stone made by forming clay into rectangular blocks which are hardened either by burning in kiln or by sun-drying. For ease of handling and laying, bricks must be small and light. The effective limit on the width of a brick is set by the distance which can conveniently be spanned between the thumb and the fingers of one hand — normally about 4 inches.

History: The history of bricks dates back to at least 3000 BC, when Babylonians and Egyptians used them in construction works. During those times, raw clay or shale was crushed, mixed with water, kneaded manually, made into different shapes and sizes with hand and then dried in the sun. These sun-dried bricks served the purpose in the dry climate of the Middle East. But later on, in damp places like England, they were found to be inadequate, and the technique of burning the clay with fire was invented. Nowadays, coal-fired brick kilns are employed. Such coal-fired bricks are strong with compressive strength varying from 35-125 kg/cm^2 depending on the quality of the brick and its purpose of use.

Criteria of use: The clay or shale for this purpose is generally impure — (calcareous, ferruginous, etc)-occurring near the surface and is low-cost to support the low-investment brick industry. The properties particularly looked for in the clay are plasticity, low shrinkage on cooling after firing and poor vitrifiability. Plasticity facilitates moulding into desired shapes and sizes; and low shrinkage ensures retention of the shape and size after firing without cracking. Poor vitrifiability prevents the brick from forming into a very hard solid mass that cannot be easily broken to suit the different spaces, and it also makes the brick porous and rough. Porosity helps it to trap air pockets that serves to insulate the building, and both the porosity and roughness together help it to bond with the mortar better by soaking water (up to 20%). Fired colour may be anything and usually not uniform. Refractoriness is not at all required.

Substitution:

(1) *Fly ash brick*: Nowadays *fly ash bricks* are gaining acceptance as a substitute of clay bricks. Since use of fly ash will mitigate the environmental problem of disposal created by its huge accumulation in power plants, governments are encouraging its

use in brick-making. For making fly ash bricks, a new technology called “Fal-G” using fly ash, lime and gypsum is being popularized. In this technology, the raw materials are ground, and water is added to obtain a semi-dry mass. The mass so obtained is shaped into bricks by machine moulding, and then the pressed bricks are subjected to specific curing cycle in sun or in air and steam to gain the required strength. Now, the thrust is on the use of more and more fly ash in the mix and for this purpose technology is constantly being improved.

(2) *Sand-lime brick*: Another substitute is s*and-lime brick* (also called “*calcium silicate* bricks”). These are used particularly where clay bricks are scarce or where consistently high-strength bricks are required. Sand-lime bricks are compact with water absorption less than 7.15% by weight after 24 hours. Here, calcium hydroxide [$Ca(OH)_2$], instead of cement, is mixed with sand and water to form a paste which is then pressed into solid, perforated or hollow bricks and hardened under high-pressure steam whereby calcium hydroxide and silica combine to yield calcium hydrosilicate, and strongly bonded bricks become ready. These are ordinarily off-white in colour, but pigments can be added to make coloured bricks.

(3) *Concrete hollow brick*: An aggregate is made up of sand, fly ash dust, gravel and clay and the aggregate should be a mix of different sizes such as +10-12.5 mm (15%), +4.75-10mm (40%), 300 micron -4.75 mm (35%) and (-)300 micron (10%). This aggregate is thoroughly mixed with water in 1:6 ratio so as to obtain a mixture of uniform colour and consistency, and then pressed into bricks, cured for 70-80 hours and sun- or steam-dried.

(4) *Kimberlite tailings*: Kimberlite is the host rock for diamond. After mining kimberlite and processing it for recovering the diamonds, huge quantities of kimberlite tailings are generated. Hollow bricks experimentally made of 70% kimberlite and 30% clay have been reported to be promising.

Terracotta Clay and Terracotta Shale

Terracotta articles are fired products used mainly for decorative purpose (e.g., flower vase, toys, show pieces). The clay and shale suitable for making terracotta articles are generally impure (ferruginous) and are similar in properties (e.g., good plasticity, low shrinkage, poor vitrifiability) to brick clay and brick shale except that the fired colour should be uniform and pleasing. Mineralogy is also similar, i.e., the shale is mainly composed of illite and the clay, of kaolinite and montmorillonite.

Roofing Tile Clay

Clay roofing tiles are popular in certain regions and amongst certain sections of people. They are low-cost roofing materials, give good insulation against heat, have aesthetic appeal and the damaged portions are easily replaceable. The clay suitable for making such tiles are, like brick and terracotta clays, composed of kaolinite and montmorillonite.

For making roofing tiles the clays collected from the deposits are stored and allowed to weather for a period of about 6 months and then mixed with water. The mixture is left to age for a week. This aged clay is then crushed, extruded cut into slabs, stored overnight, pressed into tiles, sun-dried and then finally fired at 800-900^{0}C under oxidizing conditions. At this temperature, only partial vitrification takes place.

The clay should be soft, plastic and easily vitrifiable and should have low shrinkage. Softness and plasticity facilitate moulding and cutting into shapes and sizes. Vitrifiability will tend to reduce porosity of the fired tile so that there should not be leakage of rain water, although complete vitrification is not allowed so as to maintain a little porosity which can trap air and provide thermal insulation. Low shrinkage helps retention of size after firing. In roofing tile clays, contents of 20% sand and 5-6% Fe_2O_3 are desirable. The former tends to regulate the degree of vitrification and impart the desired porosity, while the latter gives a pleasing red colour after firing because, at the firing temperature and in the oxidizing conditions, it does neither melt nor is reduced to iron (its melting temperature is 1100^{0}C).

Pottery Clay

The clay used for making ordinary pottery is also referred to in literature as *ordinary clay* and *common clay*. It is probably the oldest use of clay. Ancient men living as early as 10,000 years ago knew how to make not only fired potteries, but even painted ones. So much evidence of such painted potteries belonging to the period 8000-4000 BC have been found, that some historians have described the civilization during that whole period as "*Painted Pottery Civilization*". Artifacts comprising potteries with attractive designs painted on them have been dug out from the ruins of ancient civilizations like Mohenjo Daro and Harappa (Indus Valley), Nile Valley, Hoang-Ho (China), Turkestan (Central Asia), Chaldea (Mesopotamia), Parsepolis (Iran) that flourished during the period 5000-3000 BC. This long tradition has made pottery-making develop more as a folk art than an industry.

Potters make use of the locally available clay, and the product range is as wide as the variations in the nature of clay and in the craftsmanship of people from place to place. As a result, the art of pottery has become very location-specific — some particular place having become famous for a specific type of product. But generally, a few characteristics stand out as common amongst all pottery clays. They should be coarse, soft, plastic, low-shrinkage and non-refractory. Vitrification is regulated through the duration of firing and depending on the requirements, a product can be made to be a high-porosity one or a solid impervious one. In the manufacture of pottery, iron content (Fe_2O_3) of 0.6 – 0.7% can be tolerated — more particularly because the firing temperature is too low to melt and reduce the oxide to iron, and also because colour is not a criterion.

Besides pottery, the ordinary clay also finds some special industrial uses after processing. These are as follows:

1. Filler in rubber: Rubber clays consist principally of flat platelets, which accounts for its elasticity and hardness. The effect varies considerably with different clays. Hard clays reinforces the stiffness of rubber in a greater degree than soft clays. Stiffened rubber is suited to the requirement abrasion-resistant products like footwear. Both hard and soft clays improve acid resistance of rubber when used in acid tank lining. Ordinary clay acts as a good reinforcing agent after regeneration. Regenerated clay is produced by decomposing ordinary clay with sulphuric acid and then treating the resulting aluminium sulphate solution containing silica with sodium silicate solution. The precipitate formed is filtered, washed, dried and ground. Regenerated clay has smaller particle size.

2. Glazed tile: A process to manufacture low-cost glazed tiles from common clay was developed by the Central Glass and Ceramic Research Institute (CGCRI), India, way back in 1984. The process required comparatively low firing temperature of 950^0C for a comparatively short duration of 4-6 hours.

Chapter 14

CORUNDUM - RUBY - SAPPHIRES

The name corundum is derived from the Tamil (India) "kurundam". Corundum is the species name for all three subspecies – the industrial type corundum and the gem types ruby ("Manik" in Hindi) and sapphires, the most well known of which are the blue sapphire ("Neelam" in Hindi) and the yellow sapphire ("Pukhraj" in Hindi). These subspecies are commonly regarded as individual minerals and in mines and in commerce, the name corundum is used to mean only the industrial type. But actually they differ only in the degrees of purity and crystallization. Chemically, all of them are natural oxide of aluminium (Al_2O_3) theoretically containing 47.1% oxygen and 52.9% aluminium, but there are varying amounts of some impurities in the different subspecies giving them their distinct characteristics and identities. Some deposits of ruby and sapphires were formed in the molten magma at depths of about 100 km from the earth's surface (cf. diamond, 150-200 km depth) and then transported up by lava, and several major corundum and ruby deposits including those of India were formed due to low temperature regional metamorphism and are found in basic rocks containing pyroxene as a predominant constituent. All through its formation and transportation, the environment should be totally silica-free (otherwise the aluminium oxide would tend to become silicate). Corundum occurs in basic rocks, nepheline syenites (e.g., Canadian deposits). Rubies and sapphires are found in limestone (as in Myanmar, Afganistan, Thailand, Cambodia) and sapphires of Kashmir are found in pegmatite dykes. Both of them are also found in alluvium.

Commercial deposits of corundum contain 20-40% corundum grains, and are known in Canada, USA, South Africa, India, Madagaskar and Russia. The best rubies are concentrated in Myanmar. In India, corundum and ruby occur in several districts of Andhra Pradesh, southern Karnataka and Tamil Nadu while sapphire is reported in Kashmir and in Visakhapatnam district of Andhra Pradesh some corundum production was also reported in the past from Rewa district of Madhya Pradesh.

HISTORY

Corundum: The very name derived from a Tamil term suggests its prevalence in the South India from where it used to be exported to Europe and thus the Europeans came to know about it for the first time. But the earliest recorded production of corundum in India, was from Rewa district of Madhya Pradesh where the mineral was produced as early as in

1814 or even earlier. Now it is mined in only three states, namely, Andhra Pradesh, Chhattisgarh and Maharashtra. Annual production statistics during the pre-independence period (i.e. before 1947) were not systematic or reliable. The post-independence production history of corundum is as follows.

Year	Production (tons)
1947	182
1950	303
1960	250
1970	411
1980	1454
1990	414
Year ending March,2001	6.71

After 1990, corundum mining has dwindled mainly because of preference of the consumers (abrasive industries) for substitutes and imported materials. By the turn of the century, the number of mines came down to hardly one or two.

Ruby and sapphire: As far as rubies and sapphires are concerned, they were mined in Sri Lanka around 500 BC, and still are being mined. Myanmar is known for the best rubies. The earliest recorded history of ruby mines there dates back to the royal edicts of 1597, but before that references to ruby mines were made by European adventurers of the 15th and 16th centuries. The main areas are Mogok and Kathe. Sapphires are also mined along with rubies in Myanmar, but the best known sapphires in the world were from the southern slope of the snow-clad 5000 m high locations in the Zanskar Range in Kashmir, India, which were discovered in 1881 and initially worked till the end of the 19th century, only to be restarted in 1906 by the Kashmir Mineral Company and several valuable stones were recovered. Mining closed once again in 1908 due to difficult climate and inaccessible location. Though sporadic illegal mining was reported during the period 1927-1930, systematic mining commenced again in 1933. According to the official records of the Kashmir royalty, a total of 3.8 million carats (19000 tons) of sapphire roughs were produced during the period 1933-1938.

In the recent times, however, the productions of ruby and sapphire in India have been rather erratic, although it is known that much of the production carried out by local villagers goes unreported and unpublished. According to what has been reported and published, there was some sporadic production reported for sapphire in the past during the period 1964-1972 and recently for ruby. The reported production of raw sapphire varied between 140 kg and 214 kg during 1964-1970, and by 1972 it dwindled to a mere 85 kg. The production of ruby was first reported in July,1993, and its reported production rose from 29 kg in 1993-1994 to 400 kg in 1997-1998, after which the mine became closed.

RECOVERY

For a concentration of corundum, a process known as *Muller process* is employed. In this process, the corundum-bearing rock is first crushed and ground. Then it is fed into a mill fitted with light wooden rollers. By attrition, the hard corundum grains wear off the softer grains of talc, chlorite, mica etc. Simultaneously a current of water is passed through it which washes off those powdered grains.

CRITERIA OF USE

The unique mineralogical, physical and optical properties, besides some peculiar psychological factors, go into the usage of corundum, ruby and sapphires. These are as follows.

A. Corundum: This is for industrial use only. Colour, clarity and degree of development of crystal structure are all irrelevant (they are often dark or smoky brown coloured, opaque and with dull lustre). Only the criteria of hardness, melting point, fracture pattern and availability in small grains are important. Its hardness (i.e. abrasion resistance) is 9 in the Mohs scale, and it is the second hardest natural mineral after diamond. Its melting point is high – 2050^0C. Corundum is subconchoidal to uneven fracture pattern.

B. Ruby and sapphires: These are the gem varieties of corundum. According to Webster's Second Edition Unabridged Dictionary, gem means any jewel having value and beauty that is intrinsic and not derived from its setting; and gemstones or gem materials are stones or materials from which a gem may be cut. By popular perception, a gem is a rarely encountered hard, durable, brilliantly shining and beautiful natural mineral which has high intrinsic value. Three characteristics of a gem stand out persistently. These are: rarity, durability and beauty. Rarity is an economic function of supply and durability is a measurable physical attribute, but beauty is person-specific carrying different meanings to different individuals, and may include properties like colour, ability to take polish, sheen, size, shape etc.

(1) *Rarity:* The mode of transportation of rubies from the depths of the earth' crust for long distances up the difficult paths make them scarce. By the law of demand-supply, the scarcer a commodity is, the higher is its value. This is one of the important reasons why high values are attached to gems, and ruby and sapphires are no exception to this rule. Generally, sapphires are more widely distributed than rubies and hence the latter are more valuable in comparison to the former. But there are exceptions due to some other optical criteria like colour.

(2) *Durability*: The hardness makes them durable and indestructible. Besides, they are resistant to acids. Further, rubies and sapphires are more durable than diamonds because they have no cleavage and unlike diamonds, they do not break under pounding or shearing force.

(3) *Friction*: Both of them have a low coefficient of friction when polished.

(4) *Chemical reactivity*: They are chemically inert.

(5) *Colour and optical properties:* Unlike in the diamonds, colour is the most important parameter of beauty in rubies and sapphires, because they, being translucent, have considerably lower refractive index (about 1.76 compared to 2.42 of diamond) and lower dispersive power, and consequently less sparkle. But the translucence renders a soft milky appearance and a unique charm to look at. Their attractive colours are due to some impurities or foreign elements (not only their natures but also their

concentrations and manners of distribution) which have entered the crystals during their crystallization from molten magma and which are excited differently by different wave lengths of light rays. While the name ruby is applied to only the typical red-coloured (the blood red colour of a living pigeon) crystals of corundum, sapphires may have any colour other than red. Different fancy names are used for sapphires of different colours (e.g., oriental topaz for yellow sapphire, oriental emerald for green sapphire, oriental amethyst for purple sapphire, 'Kashmir' for a typically intense cornflower blue sapphire originally from Kashmir and now from anywhere else). The red colour of ruby is due to inclusion of traces of chromium. The blue colour of Kashmir sapphire is due to presence of titanium while the other colours of sapphire are due to the inclusion of varying amounts of magnesium, bromine, etc. Colourless or white sapphire is devoid of any impurity. The presence of minute cylindrical cavities in what is called 'star sapphire' gives a rare star-like appearance to an exquisite class of sapphire showing a peculiar optical effect of six rays radiating from the centre.

(6) *Clarity:* Small bubbles and cracks reduce the clarity of a ruby or a sapphire, and consequently, its value. But inclusions, which also affect the clarity, do not always reduce their value, because they owe their fancy colours due to them.

(7) *Cut:* Natural rubies and sapphires need to be cut into well defined faces and the faces are polished to produce their characteristic sheens and optical effects. The cutting requires a very high degree of skill – particularly when the individual pieces are very small. Minimum loss of stone is to be ensured during cutting.

(8) *Specific gravity:* Both ruby and sapphire are moderately heavy, their specific gravity varying from 3.95-4.10. The value/volume ratio is very high for them.

(9) *Caratage:* Rubies and sapphires, and for that matter any gem, are bought and used as individual pieces. So the individual weights of the pieces are important for determining their values. Moreover, the larger a gem is, the rarer and, hence, more valuable it is. Between these two, large-sized perfect rubies are very rare – even rarer than large diamonds (10 carat size is quite abundant), and, hence, if and when a large ruby is found, it may fetch an even higher price than a diamond. It has been seen that price of a fine ruby is cheaper than or equal to a similar class of diamond up to 2 carats weight, but beyond this the price of ruby tends to exceed that of diamond. While a diamond of over 3,000 carats has been found, the largest known rough ruby was only 77 carats size mined in Myanmar in 1889. Sapphires, on the other hand, are often found in large sizes. The largest size sapphire weighing 958 carats was found in 1929. It was cut into 9 gems varying in weight from 4.33-66.50 carats.

(10) *Certification:* For a common retail buyer, the physical and optical properties of rubies and sapphires carry little sense, and he is most concerned, besides size, with the colour and sheen as judged with naked eyes. But both these characteristics can be replicated by unscrupulous people. So for him certification by some trusted authority or agency assumes importance.

(11) *Aggressive marketing:* Almost any gemstone can be sold irrespective of colour and cost, provided the basic criterion of rarity is met. Economically, demand of gems is by and large elastic, i.e., they are luxury items, and not essential in our lives. Consequently, gems do not follow the conventional law of demand and supply according to which, demand generates first and supply follows. On the other hand, in

case of gems, supply comes first and demand generates later in response to that. Rubies and sapphires are no exception.

(12) *Therapeutic value*: Both rubies and sapphires are traditionally believed to possess some indirect beneficial effects on body and mind if worn on the body. This branch of therapy known as gemmotherapy works on the hypothesis that different gems, when worn by a man on his body, react differently to different kinds of cosmic rays having different effects on the health of his mind and body. It is a scientific fact that mesons produce cosmic rays which come from outside the earth in varied intensities every minute, and day and night about 600 rays pass through our body. Gemmotherapists believe that each kind of cosmic ray has some specific effect on human health, and each gem modifies these effects by preferentially absorbing or transmitting specific rays.

(13) *Beliefs and superstitions:* Both these gems, many people believe, bring luck or misery to lives.

(14) *Stability of value*: Economic phenomena like inflation, stagflation, recession and even political instability which exercise adverse impact on other manufacturing and processing sectors, do not affect adversely the demand of these gems.

USES

A. Corundum:

(a) Abrasive: Corundum grains are mounted on grinding wheels for polishing other objects. Generally, the grain sizes preferred are around 8 mesh. Papers and cloths coated with a paste of corundum flour are used for precision grinding. The most important use of corundum is in coarse and fine polishing of optical lenses. For coarse polishing, 60-220 mesh and for fine polishing, 500-2600 mesh grain sizes are required. Earlier, lac was used as the bonding material for mounting the grains on discs, but now sodium silicate is often used. A mixture of corundum, clay and feldspar may be calcined to form a bonded mass used for this purpose. Hardness and availability in small grain size are the key.

(b) Refractory: Due to its high melting point, low-iron corundum is used for special high alumina refractory materials like spark plugs, pyrometer tubes, crucibles, etc. and also for thrusting the charge into electric furnaces.

(c) Artificial emery: Emery is a natural mineral comprising an intimate mixture of magnetite and corundum used in powder form for polishing, smoothing and grinding purposes. On an average, emery contains Al_2O_3 65% min, magnetite 22% max and SiO_2 10% max. Artificial emery powder is prepared by mixing corundum and magnetite grains. The ratio between the very hard corundum and the relatively softer magnetite is varied to suit the hardness required for the surface to be polished. For example, glass may require a less hard abrasive substance than metals or alloys. The softer version containing more magnetite can be made into a paste and used in emery cloth. For this application, the grains of emery should be hard enough, should be able to withstand intense heat of friction, and should not be conchoidal (in that case, the sharp edges of the grains will tend to scratch the surface being ground or polished). The hardness, high melting point and subconchoidal to uneven fracture

pattern are the main criteria insofar as corundum is concerned. Silica is objectionable because its fracture pattern is conchoidal.

(d) Other uses:

- Asbestos products: Corundum grains are added for reinforcing their strength and for increasing abrasion resistance.
- Foundry: Corundum sand is used.
- Toothpastes: The abrasive properties of corundum help to keep teeth clean and white.
- Fingernail polishing: The abrasive properties of corundum are made use of in making emery boards for this purpose.

B. Ruby and sapphires:

(1) Ornaments and jewelry: The main demand for these gems is for making jewelry. Colour, clarity, cut, durability and the characteristic optical properties are the most important criteria. After all these basic criteria are fulfilled, comes the question of caratage or size on which depends the price. A minor use of rubies and sapphires is in cosmetic dentistry or tooth jewelry. First patented in 1986, this may consist of gems made of gold with a little of ruby or sapphire which is fixed to the front surface of a tooth. These are the choice of singers, film stars and many others wanting their teeth to glitter while smiling or talking. In this application, caratage is not a consideration.

(2) Status symbol: Gemstones are traditionally connected with royalty and aristocracy. In fact, their high costs are a favourable factor. It is important that they should not only be costly, but also appear so. The rarity of a stone plays an important role.

(3) Value storage and liquidity: These gems are high-value low-bulk commodities. Hence, kings and aristocrats in the past, and now, common men also endeavour to acquire as many of them as they can afford with a view to storing them conveniently for re-sale in times of need. Durability and indestructibility, moderate specific gravity and high value/volume ratio, and stability of value against economic or sociopolitical uncertainties are the principal criteria besides the basic ones like colour, clarity, caratage and the optical properties that determine the value of the roughs.

(4) Therapy:

i. Gemmotherapy: A sizable section of population – elite and common—believe in an unconventional system of healing known as gemmotherapy, according to which rubies and sapphires, when worn on the body as a ring or a locket or in any other form, has a beneficial effect on persons suffering from ailments like asthma, cancer, acidity, anemia, hypertension, gout, insomnia, etc. Clarity and caratage are very important criteria in this use.

ii. Cosmetic skin care: Scrubbing with powders of these gems is claimed to help improve both the health and the cosmetic look of the skin. This has been an old practice dating back to the times of mythology and more recently to the Mughal period in India when women of the royalty and aristocracy used to apply gem powders mixed with other herbal and cosmetic materials to their skins. Rubies are supposed to increase elasticity of the skin and help it appear youthful. Sapphires are applied as eye shadow, and also to maintain the pH of the skin and impart a soft look.

(5) Superstitious belief: This is a very old use, since fear and superstition have been ingrained in human beings – particularly weak-minded ones. This usage has aso been prevalent amongst the rich people and has been promoted since historical times, by astrologers.

(6) Jewel bearings: Bearings are devices to support rotating wheels and gears of machines and instruments, and those made of ruby or sapphire are called jewel bearings. A bearing must have a low coefficient of friction and resistance to shearing force besides being inert to chemicals applied as lubricants. Rubies and sapphires possess all these properties, especially after cutting and polishing, to which they are amenable. They, however, will have to be perfect and flawless crystals (otherwise they may remain vulnerable to breaking under stress). Traditionally, these natural stones were used as jewel-bearings in high-end classical Swiss watches and time pieces. In these, were used 18-21 small sized bearings that could be cut from natural rubies and sapphires.

(7) Masers and lasers: Laser is the acronym for "microwave amplification by stimulated emission of radiation" and maser is for "light amplification by stimulated emission of radiation". They differ in the wave length range of radiation emitted. It consists of light waves — 10^5 micrometers in case of microwaves and laser, and more than 1 micrometer to less than 0.4 micrometer in case of maser. The principle is based on the knowledge that light emission takes place due to spontaneous transition of electrons from higher to lower orbit (or energy state), and on Einstein's postulate (1917) that the emitted light can be intensified and concentrated if the transitions are stimulated. This led to the invention of maser which was later extended to the visible range of light and thus laser was invented in 1960. In practice, the mechanism of laser involves exciting and pushing the electrons of an atom up and down between lower and higher orbits first by what is called "pump energy" and then by what is called "excitation energy", resulting in emission of radiation. The entire process is so rapid that there is no chance for the accompanying thermal phenomena or thermal noise to interfere with these oscillating movements of the electrons from one orbit to another, and the radiation acquires an extremely constant frequency, very high intensity and sharp concentration into a beam that can be focused very accurately and pointedly. These properties of laser make it useful for measuring distances with high degrees of accuracy, for producing intense heat and for retrieving data from CDs.

An atom of a laser material should consist of 3 orbits of revolving electrons to facilitate multiple steps of oscillation between the orbits, and must possess the ability to be stimulated by some external energy to start and continue the process of rapid oscillation. An optically clear and perfectly flawless ruby crystal with its characteristic chromium inclusion is one such material. It was earlier used as a maser material also. It is the chromium atoms included within a ruby that become excited by long wave ultraviolet light rays. For producing laser for high-tech and industrial applications, the crystal must be large enough to facilitate cutting of a cylindrical laser rod out of it.

SUBSTITUTION

A. Corundum: The use of natural corundum has, during the recent times, dwindled mainly due to three reasons: (i) first, it occurs in a disseminated mode and is not very abundant, (ii) second, its granular form necessitates concentration, and (iii) third, more easily available massive bauxite, after calcination, serves as an effective substitute for corundum in at least three of its principal uses, namely abrasives, refractories and artificial emery. The bauxite-based products substituting corundum for use in refractory are calcined bauxite, sintered bauxite, calcined alumina and sintered alumina; those for use in abrasives are brown and white fused alumina and seeded alumina gel; and that for use in artificial emery is calcined bauxite.

B. Ruby and sapphires: Substitution of ruby and sapphires may be by low end cheaper semiprecious stones. This may not be the case when gems are purchased as status symbols, but it is possible if the purchase is for jewelry, for their therapeutic value, due to superstitious beliefs, etc. For high-tech industrial uses, however, the most widely used substitutes are the synthetic rubies and sapphires, the artificial stones and the imitation stones and (in lesser degrees) other synthetically made gemstones.

(a) Synthetic ruby and sapphire: A synthetic gem is made by laboratory synthesis of the same elements as in natural ones – aluminium and oxygen in the case of rubies and sapphires. A synthetic ruby was produced for the first time in 1902 by what is known as the “Verneuil flame fusion process”. Later, this process was employed for making synthetic sapphires also. In this process, a single crystal, called a “boule”, forms in the flame of a simple downward-striking oxygen-hydrogen blowtorch. Pure oxides of aluminium are poured into the top of a small furnace and melted. Other oxides (e.g., boric oxide) are added as needed for process control. Some “dope” (i.e., an element such as chromium in case of ruby, which is responsible for the characteristic colour and property) is also added. A fireclay peg is inserted into the melted material and rotated. The material starts solidifying, and as the solidification progresses, the peg is slowly withdrawn, so that by the time the peg is completely withdrawn the entire mixture grows into a solid boule of ruby or sapphire (depending on the dope added). A boule thus made is generally a cylindrical body of diameter varying from 1.25-2.50 cm and length from 5-10 cm. But by carefully controlling the process, long pencil-like boules of 0.5 cm diameter and over 90 cm length have been made.

Another melt technique called “Bridgeman-Stockbarge solidification method” was developed during the period of 1924-1936. It is mainly used for making synthetic sapphire. In this process, a crucible shaped like a cylindrical tube with a closed conical bottom is employed. The crucible is filled with powdered aluminium oxide and lowered slowly through a furnace with upper hot and lower cool zones. The entire material in the crucible first melts in the hot zone. Then the portion in the conical bottom part of the crucible, as it enters the cooler zone of the furnace, solidifies earlier than the rest of the melt. This solid portion acts as the seed around which the rest of the melt solidifies and grows into a crystal. Crystals of practically any size can be grown by this process, and small ones of 5 cm diameter to large ones of over 90 cm diameter have been made.

Later still, a third method called “Czochralski method” based on surface tension was developed, and this method is currently the most popular. The aluminium oxide is melted in a platinum or iridium or graphite or ceramic crucible. A seed crystal is attached to one end of a rotating rod which is first lowered till it just touches the surface of the melt, and then is withdrawn slowly at a rate varying from 0.1-10.0 cm per hour. The molten material gets attached to the rotating seed due to surface tension, is gradually pulled up by the seed out of the hot crucible, cools down and solidifies. This process continues till the entire molten material gets pulled up and becomes a solid single crystal. The sizes of the crystals grown by this method depend on the amount of molten material available in the crucible, and large crystals of 5 cm diameter and about 100 cm length have been made.

Synthetic rubies and sapphires resemble natural ones in hardness, absence of cleavage, ability to take polish, low coefficient of friction after polishing and chemical inertness. These, being produced in bulk and hence being relatively inexpensive, were initially in demand for substituting the natural ones in jewel bearings of watches and time pieces. But as the products became more and more perfected and as R and D works progressed, a flood gate of newer and newer applications opened up. Large sizes of flawless synthetic rubies and sapphires allowed flexibility in the shapes and sizes of pieces cut out of them and made possible expansion of their use to very sophisticated and high-tech applications of jewel bearings like the pivot supports for precision gauges and meters in aircrafts and boats, in manufacturing plants, in high-tech weaponry, and in connectors for optical fibers. The long rod-shaped synthetic rubies proved to be a boon for use as laser rods for industrial applications, because, besides the advantage of size, the amounts of dope in such rubies can also be varied to suit different requirements.

(b) Artificial stones: Artificial stones are those combinations of naturally occurring elements that are not found in nature and they are prepared in laboratories. Yttrium-aluminium-garnet or YAG is a common example. Chromium-doped YAG is sometimes used as laser rods instead of synthetic ruby. The process for making YAG is the same as that employed for a synthetic ruby and sapphire. Sometimes, neodymium (Nd) is added to YAG to customize some special properties.

(c) Imitation stones: Imitation stones only superficially look like gems without having the latter’s intrinsic characteristics (e.g., glass, polymer). The best practical application of imitation gem is in cosmetic dentistry. Tooth jewelry, is now being made of plastic to meet the demands of a large section of the population. The advantage of an imitation tooth gem over real one is that plastic does not cut a person if he accidentally swallows it.

(d) Other gemstones: Chromium-doped synthetic chrysoberyls (Cat’s Eye and alexandrite), having the chemical composition $BeAl_2O_4$, are sometimes used as laser rods instead of synthetic ruby. The process for making these synthetic gemstones is the same as that employed for synthetic ruby and sapphire.

Chapter 15

CRYOLITE

Cryolite is *sodium hexa-fluoro-aluminate* (Na_3AlF_6), an uncommon mineral of very limited natural distribution and industrial use. The name has been derived from the *Greek* words “kryos” meaning “frost” and “lithos” meaning “stone” (i.e., “ice-stone” symbolizing its ice-like appearance due to its low refractive index close to that of water). Occurrences of cryolite have been reported from Ivigtut in Greenland, Pikes Peak in Colorado in U.S.A., Mont Saint-Hilaire in Quebec in Canada, Miask in Russia, and also from Brazil, Czech Republic, Namibia, Norway, Spain and Ukraine. In all, 20-odd mines were in operation in different deposits of the world since around 1850. The most important amongst them and the last surviving one was operated in Ivigtut on the west coast of Greenland (where a cryolite-bearing pegmatite deposit was discovered in 1799) during the period of 1854-1987. Its peak annual production was in the order of 70,000 tons. However, after this deposit had been completely exhausted in *1987*, no new mine has come up and the production of natural cryolite in the world has come to a naught. But, by now a substitute of natural cryolite — synthetic cryolite — is made from fluorite (see the chapter on fluorite).

CRITERIA OF USES

Cryolite occurs as prismatic monoclinic crystals with vitreous to greasy or pearly lustre. It has Mohs hardness of 2.5 and specific gravity of 2.95-3.00. But the following properties are more important from the point of view of its industrial usage.

1. *Colour:* Cryolite is glassy, generally colourless to snow-white in colour (impure mineral may show reddish to grey-black colours).
2. *Optical properties*- It is translucent to transparent with very low refractive index of about 1.34. These RI values are very close to that of water and thus if immersed in water, cryolite becomes virtually invisible.
3. *Fusibility:* It is readily fusible. It can even be fused in the flame of a candle. When fused, it becomes a sticky mass. Cryolite completely melts at 1012^0 C (synthetic cryolite melts at 1027^0 C).
4. *Chemical composition:* Theoretically, cryolite contains 54.4% F, 12.8% Al and 32.8% Na. The common impurities are SiO_2, Fe_2O_3 and CaO. Fused cryolite has the unique ability to dissolve alumina.

USES

1. Aluminium metallurgy: This is by far the most important use of cryolite. It is used in the electrolytic processing of extraction of aluminium from alumina (Al_2O_3) by the *Hall-Heroult process*. The difficulty in the extraction of aluminium was in the high melting point of alumina (above 2000°C), which was overcome by the use of cryolite and aluminium fluoride (AlF_3). The latter is a strong flux while the role of cryolite is mainly as a solvent for alumina and also as a flux by virtue of its ready fusibility and lower-than-alumina melting point. The duo lowers the melting point to approximately 900°C. In this technology, alumina is dissolved in a fused electrolytic bath composed of aluminium fluoride and cryolite. The cryolite bath dissolves about 10% of the alumina at the operating temperature of 920-970^0 C in the electrolytic cell. When high-intensity current is applied, the alumina dissociates into positive aluminium ions and negative oxygen ions, the former depositing on the cathode and the latter reacting with the carbon of the anode forming CO and/or CO_2. The molten metal is tapped and cast into ingots. The used cryolite can be partially recycled. The consumption of cryolite varies from 50-90 kg/tonne of aluminium metal.

Very high grade cryolite containing 98% (min) Na_3AlF_6, 1.5% (max) SiO_2, 0.25% (max) Fe_2O_3 and less than 1% CaO is specified for this use. Iron oxide, silica and lime are particularly considered deleterious because they will react with alumina to form a glassy silicate.

2. Welding rod: Cryolite is used as an ingredient of the coating as a flux. Here also very high grade cryolite containing 98% (min) Na_3AlF_6, 1.5% (max) SiO_2, 0.25% (max) Fe_2O_3 and less than 1% CaO is specified.

3. Other uses: Some minor uses include:

(a) *Enamel*: Its use is as a whitener by virtue of its characteristic snow-white colour.
(b) *Glass*: It is used as an opacifier by virtue of its translucency and lower-than-glass refractive index — 1.34 compared to 1.54 of ordinary glass.
(c) *Grinding wheel*: By virtue of stickiness of the fused cryolite, it is used as a bonding agent.
(d) *Insecticide*: It is used as an active agent by virtue of the fluorine content which is poisonous for insects.

Chapter 16

DIAMOND

Diamond (called “Heerak” or “Heera” in Hindi) is popularly known as a precious (or gem) stone. In fact, it is the most important amongst the four classical and historically known precious stones (primary gems) namely, diamond, emerald, ruby and sapphire (the other popular gemstones are considered as semiprecious stones or secondary gems). Over the centuries, however, the traditional use of diamond as a gem has expanded manifold, and now it is valued equally, if not more, for various unique industrial applications including nanotechnology. So much so that nowadays, an overwhelmingly large share in the production of diamonds in the world is accounted for by its industrial variety not valued as gem. The word diamond owes its origin to the Greek word “adamas” literally meaning “unconquerable” which gradually evolved to carry the sense “very hard and indestructible”. From adamas came the Latin word adamant and then finally, by the end of 17th century, diamond.

A pure diamond is made up of a single element, namely, carbon – 98.9% C_{12} and 1.1% C_{13}, the latter often tending to be replaced partially by some foreign elements. Incidentally, it is the only gemstone which does not contain any oxygen atom, all other gemstones being either silica or metal silicate or oxide. It is distinguished from graphite which is also made up of carbon, by crystal structure. In the case of a diamond, the crystals consist of interpenetrating cubic lattices of carbon atoms arranged in hexagonal rings giving rise to a solid and compact structure, while in graphite the carbon atoms are arranged in parallel layers. The complex structure of a diamond is due to its formation at great depths ranging up to 200 km within the earth’s crust at times up to 3.3 billion years ago, i.e. at relatively early stages of the earth’s 4.5 billion year-old history, and its subsequent journey up long zigzag conduits to near-surface locations by volcanic activity. This whole process points to extremely stressful conditions of heat, pressure and different kinds of force acting on it, all of which has together resulted in the complex crystal structure of diamond as also a unique set of physical properties.

HISTORY

The original usage and popularity of diamonds was on account of its ornamental value chiefly arising out of its appearance and hardness, and, needless to say, the gem varieties were only considered to be of any value. As such, gemstones were important in human lives in the ancient period. Gemstones were mentioned in Indian mythologies as the residues left after burning of the bones of some godly saints. A gemstone deposit, turquoise, which was discovered in Sinai in 2000 BC by an Egyptian called Haraeris, is credited to be the first recorded scientific prospecting work. But diamonds came to human life much later.

Diamonds are believed to have been introduced to the world by Indian kings, whose fancy for diamond ornaments encouraged its mining. Diamond mining in India began in 800 BC. The diamonds of those times (and for a long time thereafter) were in as-mined forms i.e., uncut and unpolished (known as 'roughs' in trade circle). The nations having trade links with the Indians of the ancient period (e.g. Greeks, Romans) took to using diamond for ornamenting their gods and goddesses. In Greek mythology, diamonds were described as splinters of stars that had fallen on the earth.

Since 800 BC, for the greater part of history until the early l8th century, India was the dominant producer and supplier of diamonds to the world. The first authentic record of diamond mining in India is found in the accounts of Ptolemy, who was one of the generals of Alexander and who, after Alexander's death, became the ruler of Egypt during the last quarter of the 4th century BC. Ptolemy mentioned a "river of diamonds" in India. Much later, in the 15th century AD, an Italian traveler named Nicholi de Conti wrote about diamond mining in India. Jean Baptiste Travernier (1638-1688), a French gemmologist and trader who visited India six times gave a detailed description of diamond mining in what he called Golkonda (it is actually the area covering parts of Anantapur, Cuddapah, Kurnool, Guntur and Krishna districts in present day Andhra Pradesh). According to him, 60,000 men, women and children were engaged in digging for diamonds there.

Borneo in Indonesia joined India as a diamond-producing country in 600 AD, but India continued to dominate the world market. However, its domination gradually petered out after discovery of diamond resources in Brazil in 1725, which remained the world leader for about 150 years. Later on, diamond deposits were discovered in South Africa in 1870, followed by Tanzania, Russia and Botswana after World War II, i.e. 1945. The most recent important country to come in the diamond map is Australia in 1979. After 1725, the Indian diamond mining industry started slipping into oblivion due to exhaustion of known resources of large crystals, lack of interest of the royalty in small pieces and lack of fresh input of high technology into exploration. The history of world production of roughs during the last 75 years is as follows:

Year	Production (million carats)
1929	4.88
1930	6.46
1935	6.83
1940	13.68
1945	14.88
1950	15.61
1953	20.10
1986	99.60
2002	131.00

The general trend indicates that the gem variety of diamonds accounted, on an average, for only about 18% of the production. During 2002, the leading diamond-mining countries in order of decreasing rank were Australia, Congo, Botswana, Russia and South Africa. Other significant producers include Zaire, Namibia, Angola, Brazil, Guinea, Sierra Leone, Liberia, Ivory Coast, Ghana, Central African Republic, Tanzania, China and Indonesia.

In India, exploration efforts of the modern period has centered in the known historical occurrences concentrated in three main tracts, namely: (i) the southern tract comprising Anantapur, Cuddapah, Kurnool, Guntur and Krishna districts of Andhra Pradesh (the most notable locations are Wajra Karur, Konganapalle, Chhinur, Ramallakota, Virapalle, Kollur, Madagula, Mallavaram and Sarangapalle, Kodavatakallu, Ustapalle), (ii) the region between Mahanadi and Godavari valleys covering Sambalpur, Kalahandi, Bastar, Chandrapur and Palamou districts (the most notable locations are Hirakund, Bondesar, Deobhog) and (iii) the northern scarps of the Vindhya Range covering mainly Panna district of Madhya Pradesh. Of these, the southern tract received most attention of exploration geologists mainly due to its long mining history and also due to the fact that there were many active workings till the early years of 20th century. The exploration activities were carried out here during the period 1884-1941. In the mean time, however, the mining activity in this tract ceased completely in 1913. Since the last decade of the 20th century, many of these areas are being revisited by diamond mining companies armed with new exploration technologies. At present active mining is going on only in Panna district where a large mine namely Majhgaon mine (85 m deep opencast mine) and a number of small shallow excavations are located. The production history of roughs in India since the beginning of the 20th century is as follows.

Year	Production (carats)
1905	About 307
1910	About 84
1915	About 43
1920	About 162
1925	About 224
1930	About 1437
1935	About 1649
1940	About 2119
1945	About 1607
1950	2769
1955	1789
1960	1159
1965	4466
1970	20325
1975	19994
1980	14432
1985	16271
1990	18121
Year ending March,1995	25518
Year ending March,2001	57407
Year ending March,2006	44170

Although, by and large, India’s diamond production kept increasing since independence, its share in the world mine production of 131 million carats during the year 2002 was a miniscule 0.064 percent. In India's total mine production, the ratio of colourless gem to off coloured diamond to industrial type is roughly 30:35:35. Although the off coloured diamonds are generally regarded as industrial type, sometimes they are also purchased by processing industries for producing low value gems.

With regards to cutting and polishing, the art is believed to be long known in India but it was kept secret till it started as an industry in India and Western Europe during the middle of the 14th century, when diamond cutters learned the technique of shaping and polishing a stone by using an iron-wheel coated with diamond dust. The 58-facet style of cut called "brilliant cut" began in the 17th century. A noticeable growth in the diamond cutting and polishing industry, however, commenced only after World War II, i.e. 1945. Today, this industry is divided into specialized centers. The USA is engaged in cutting and polishing of large sized diamonds of about one carat and above. Belgium and Israel specialize in the processing of medium-sized diamonds ranging from 2 to 50 pieces per carat. In India, the industry monopolizes in the cutting and polishing of very small diamonds ranging from 50-250 pieces per carat. For processing large and medium sized diamonds a few smaller centres like Belgium, Russia, South Africa and China have also come up in the recent times.

In terms of caratage, India is the largest exporter of cut and polished diamond in 2005, while in terms of value, it ranks third after Israel and Belgium. In the global diamond market, India's share is 50% by value, 80% by caratage and 90% by the number of pieces sold. But, India is heavily dependent on import for feeding its booming processing industry. The value addition to the imported roughs after processing was about 24 percent. Consequently, the history of growth in the import of roughs and the export of cut and polished diamonds reflects the growth of Indian diamond cutting and polishing industry, and this growth has been closely and directly related to the policies of the government and to the global economic phenomena as shown in the following table.

<table>
<tr><th>Year</th><th>Value of import of roughs for processing (million rupees unless otherwise indicated)</th><th>Value of export of cut and polished diamond
(million rupees unless otherwise indicated)</th></tr>
<tr><td>1947</td><td>31.35</td><td>--</td></tr>
<tr><td colspan="3">Immediately after independence, there was some ad hoc regulatory measures and uncertainty about a policy.</td></tr>
<tr><td>1950</td><td>Rs. 12000</td><td>--</td></tr>
<tr><td>1955</td><td>0.97</td><td>--</td></tr>
<tr><td>1960</td><td>1.05</td><td>Rs. 8000</td></tr>
<tr><td>1965</td><td>1.36</td><td>41.31</td></tr>
<tr><td colspan="3">Lifting of restriction on imports of roughs followed by subsequent approval for the Diamond Trading Centre (DTC), London to commence sales to Indian manufacturers, and the policy thrust given by the government in favour of export of processed diamond to meet its overall import bills.</td></tr>
<tr><td>1970</td><td>192.66</td><td>257.42</td></tr>
<tr><td colspan="3">Oil crises of late 1973 resulting in accumulation of petro-dollars in the hands of the Arabs; shift of preference of other importing countries away from Israel and Belgium towards India (where processing cost is cheap) for compensating for the increased price of oil.</td></tr>
</table>

Year	Value of import of roughs for processing (million rupees unless otherwise indicated)	Value of export of cut and polished diamond (million rupees unless otherwise indicated)
1975	694.89	898.35
Abolition of 5% auxiliary duty and 45% import duty on the imported rough diamonds in 1978.		
April 1980-March 1981	4,024.75	5,598.77
April 1985-March 1986	10,581.18	13,744.59
April 1990-March 1991	36,600.00	52,100.00
April 1994-March 1995	49,597.36	123,571.21
Liberation and globalization of economy in India		
April,2000-March,2001	215,360.22	282,476.58
April,2002-March,2003	289,328.55	358,500.29

TYPES OF DIAMOND

Classification of diamonds can be schematically depicted as follows:

1. Gem

- Type-Ia (These contain nitrogen diffused uniformly as platelets)
- Type-Ib (These contain nitrogen as random replacement of carbon atoms)
- Type-IIa (These do not contain nitrogen)
- Type-IIb (These also do not contain nitrogen, but contain traces of boron)

2. Industrial

- Carbonado (This is a closely knit aggregate of hard, tough, black and very small diamond crystals)
- Ballas ((Globular mass of diamond crystals)
- Bort or boartz or bortz (crushed or fragmented diamonds)
  - Stones (larger than 20 mesh size)
  - Grit/dust/powder (Smaller than 20 mesh size)
  - Natural micro/nano-sized diamonds (extremely small particles — a million times smaller than 1 carat)

Approximately 98% of natural gem diamonds belong to type-I while both type-IIa and IIb diamonds are rare, the latter being extremely rare. For the purpose of sales (or 'sights' as they are called in trade), the Central Selling Organization or CSO has classified gem diamonds into 5,000 types according to size, shape, quality and colour.

TYPES OF DIAMOND DEPOSITS

The present day diamond deposits were formed in four different modes resulting in four types of deposits. These are:

(a) Primary deposits: These are the peridotitic and eclogitic diamonds. The peridotitic diamonds were formed 3,300 million years ago in the earth's mantle while the eclogitic diamonds were formed 1,000-1,600 million years ago in the earth's crust. These diamonds were formed at depths ranging from 150 km to 200 km. They were later transported to near-surface depths by volcanic activity through kimberlite and lamproite. This mode of transportation though narrow conduits in the earth's crust up to volcanic craters (diatremes) gives rise to pipe-like shape to the diamondiferous rocks, and hence they are commonly referred to as diamond pipes or kimberlite pipes or lamproite pipes. The age and depths of formation contribute to the hardness of diamonds, while the mode of transportation for long distances up the difficult paths make them scarce. Incidence of even 0.3 carats per tonne of rock is considered economic. Diamonds in Achaean kimberlite pipes are the commercial source of most of the diamonds in the world, and the Majhgaon kimberlite pipe of Panna, India also belongs to this type. Here, the incidence of diamond crystals vary from 4-20 carats (average 10 carats) per 100 tonne of rock The only important example of diamondiferous lamproite pipe is the Argyle deposit of Western Australia, which is also of Achaean age. It is one of the largest diamond mines today, but the diamonds are predominantly of industrial type.

(b) Alluvial diamond deposits: Kimberlites weather easily and release its contained diamonds which are transported down slopes by streams. Such diamonds are found as diamondiferous conglomerate and placer deposits. It is this type of shallow deposits that used to be extensively mined during the historical times. In India, even now such deposits are mined in Panna area of Madhya Pradesh, Deobhog area of Bastar district and in other places.

(c) Marine diamonds: These have been identified in the offshore areas of Namibia at 150 m below sea level and 5 m below sea bed. These were formed from the diamondiferous kimberlite rocks of South Africa, which were subjected to weathering for millions of years, washed down to Atlantic and then due to wave and wind action, deposited off the coast of Namibia. As a result of the very mode of formation by extensive natural sorting and weathering, these marine diamond deposits have become enriched in the more durable gem variety.

(d) Micro/nano-diamonds: Such diamonds are found in some meteorites, but they are not of economic significance. However, in the late 1970s, scientists found nanometre-sized diamonds in gneissic rocks being mined for uranium in Kazakhstan. Similar diamonds in gneiss have also been found in eastern China and more recently, in the early 1990s, in Norway. These rocks were never subjected to the heat and pressure normally responsible for the formation of diamonds. They are believed to be formed from carbonaceous matter due to radiation from uranium that rearranged carbon atoms – probably in a millionth of a second. Deposits containing such nanometre sized diamonds weighing a millionth of a carat are, however, considered to hold economic potentiality and research is in progress in the USA.

RECOVERY

In case of diamondiferous conglomerate, a diamond is generally separated from the gangue materials by hand-sorting. But for dressing diamondiferous kimberlite (or lamproite) mined from large mechanized mines like the Majhgaon mine of India, the typical process includes the following steps:

1. The diamondiferous rock is first crushed and as many as possible of the relatively larger pieces of diamond are separated by hand sorting.
2. Then the remaining rock is further crushed to (-) 20 mesh to (+) 80 mesh size and subjected to heavy media gravity separation by tabling. The heavy medium consists of a mixture of water (specific gravity 1), the crushed kimberlite (specific gravity 2.6), magnetite (specific gravity 5) and ferrosilicon powder (containing 84-86% Fe and 14-16% Si (specific gravity 6.5) in a ratio so as to maintain the specific gravity of the medium within the range 2.7 to 3.0. The ferrosilicon helps to reduce handling problems by lowering the bulk of the material that otherwise would increase if it is replaced by magnetite. At the end of this step, the lighter kimberlite particles float and the heavier particles comprising diamond (specific gravity 3.53), magnetite and ferrosilicon sink.
3. The sink is fed into a magnetic separator. The nonmagnetic diamonds (along with some other materials like calcite, barytes etc.) are separated from the magnetic ferrosilicon and magnetite, up to 90% of which are retrieved for recycling.
4. The nonmagnetic fraction is fed into an automatic X-ray sorter. X-rays excite the diamonds preferentially resulting in blue fluorescence. As soon as a piece of diamond is detected, automatically a gate opens and it is directed to a box. By this way, most of the diamond pieces are collected in the box.
5. The remaining potion of the nonmagnetic fraction consisting of some pieces of diamond and gangue materials is mixed with water and passed over a slanting plate coated with a special grease (this process is called ‘greasing’). This grease low hygroscopic property, i.e., it has good water-repelling ability. The surface tension and viscosity of the grease and the slant of the plate are so adjusted vis-á-vis the specific gravity of diamond that when the water containing the diamond and gangue particles flows down the plate, only the diamond particles stick to and are captured by the grease while the water along with the gangue particles flows away. The low hygroscopic property of the grease also helps this to happen. Another property of this special grease is that, on heating, it easily melts and loses its stickiness. So, when the grease with diamond particles sticking to it is heated, the latter easily separate out (this process is called ‘degreasing’) . If still any gangue gets into it, the same is sorted out.

After recovery of the diamonds from the rock, the final step consists in selecting and separating the different types of gem and industrial diamonds. This is done by trained and experienced persons by visual examination. The gems are then sold to the cutting and polishing industries.

CRITERIA OF USE

The unique mineralogical, physical and optical properties besides some peculiar psychological factors go into the usage of diamond. The criteria of use also depend on whether the diamond is of gem or of industrial type. These are as follows.

A. Gem diamond: According to Webster's Second Edition Unabridged Dictionary, gem means any jewel having value and beauty that is intrinsic and not derived from its setting; and gemstones or gem materials are stones or materials from which a gem may be cut. By popular perception, a gem is a rarely encountered hard, durable, brilliantly shining and beautiful natural mineral which has high intrinsic value. Three characteristics of a gem stand out persistently. These are: rarity, durability and beauty. Rarity is an economic function of supply and durability is a measurable physical attribute, but beauty is person-specific carrying different meanings to different individuals, and may include properties like colour, ability to take polish, sheen, size, shape, etc.

(1) *Rarity:* The mode of transportation of diamonds for long distances up the difficult paths make them scarce, and of the diamonds, the gem types are scarcer as their lower share in the total production indicates. By the law of demand-supply, the scarcer a commodity is, the higher its value. This is one of the important reasons why high values are attached to gem diamonds.

(2) *Durability:*A diamond is the hardest natural substance having a hardness of 10 in the Mohs scale. Besides, it is not affected by acids. The hardness and acid-resistance make it durable. The mode of its formation under extremely stressful conditions of heat and forces over long durations of time down in the earth's mantle and crust has contributed to this hardness. Its only weakness is that it is vulnerable to breaking with a sharp accurate blow due to its cleavage. But on its own it is indestructible.

(3) *Colour:* As has been mentioned, diamond contains 98.9% C_{12} and 1.1% C_{13} which may be partially replaced by some foreign elements. When the C_{13} is evenly dispersed without any foreign element, then the diamond is absolutely colourless (also referred to as 'white diamond'). The mystery of coloured diamonds was solved by researchers of the Bell Laboratory, USA in 1957, when they heated a diamond specimen to 2000^0C and detected the presence of nitrogen. Colours in diamond are produced due to deformity or inclusions of some foreign elements which in their turn introduce some distortions due to their differential atomic sizes vis-a-vis carbon. The commonest foreign element is nitrogen (type I) while boron (type IIb) is an extremely rare foreign element, and graphite is another. For every million carbon atoms, 1,000 may be replaced by nitrogen atoms which occur in the form of aggregates of 4-10 atoms and which are believed to have entered the diamond crystals due to prolonged exposure to high temperature and pressure during and after their formation. The nitrogen inclusion renders yellow colour to diamonds. The amount of boron when present, on the other hand, is miniscule – only one or two for every million carbon atoms. Boron causes absorption of the longer infrared rays of light and the diamond is seen as blue to bluish gray in colour. According to a report of research in the Florida University, USA and of Case Western Reserve University, Australia, the black diamonds owe their black colour to inclusion of nitrogen and

hydrogen of extra-terrestrial origin. The other colours, namely, green, red, violet, gray, brown, etc. are due to deformities of the crystal structure (e.g., displacement of some carbon atoms) caused by natural radiation in the earth (e.g., electrons, neutrons, alpha particles, gamma rays) or by nitrogen. In nature, white, green and blue diamonds are very rare and hence highly valuable. Red diamond is the rarest.

(4) *Clarity:* Small bubbles and cracks that are called ‘feathers’ by jewellers, reduce the clarity of a diamond, and consequently, its value. But inclusions, which also affect the clarity, do not always reduce the value of a diamond, because diamonds owe their fancy colours due to them.

(5) *Optical properties*: Both refractive index and dispersion are high. Refractive index is 2.42 (cf. 1.53 for ordinary glass). Dispersion is the rate of change of refractive index with change in wavelength of the incident light, and it is mainly the combination of high refractive index and high dispersive power that renders brilliance to diamonds. Type-IIa diamonds transmit both infrared and ultraviolet light (in contrast to the Type-I diamonds which absorb them).

(6) *Thermal properties*: The Type-II diamond possesses the highest thermal conductivity (5 times that of copper). The extremely rare Type-IIb diamonds are extraordinarily heat-sensitive capable of registering as small as 0.002^0C change in temperature.

(7) *Electrical properties*: Although diamonds are electrically insulating materials, the type-IIb diamonds behave as semiconductors. Semiconductors are materials with resistivity intermediate between metals (resistivity < 10^4 ohms/cm) and insulators (resistivity >10^3 ohms/cm).They contain only a small number of loosely bonded electrons at room temperature, and hence their conductivity is very poor (of the order of 100,000 times less than that of conductor metals). However, their low electrical conductivity can be substantially improved by addition of minute quantities of some foreign atoms of a different valency, one of which is boron (the process is called ‘*doping*’). The semiconductivity of the type II-b diamonds is on account of inclusion of boron atoms in them. Another characteristic of semiconductors in general is that their electrical properties can be controlled by supplying some external energy (e.g., optical energy, thermal energy). The electrical conductivity of type-IIb diamonds are extremely sensitive to changes in temperature as small as 0.002^0C.

(8) *Cut:* Natural diamonds are somewhat dull to look at. It is only when they are cut into well defined faces and the faces are polished that diamonds show their characteristic brilliance. Diamonds being the hardest substance, can only be cut by another diamond (nowadays by laser also) and can only be polished by diamond dust. The cutting requires a very high degree of skill – particularly when the individual pieces are as small as 1/250 carat or less than a milligram in weight (the size for which Indian cutting and polishing industry is famous), and that too when a large number of faces are to be developed (the highest valued ‘brilliant cut’ consists of 58 faces). More the number of faces, more will be the brilliance of the diamond.

(9) *Specific gravity:* Diamond is moderately heavy, its specific gravity being 3.53. The value/volume ratio is very high for diamond.

(10) *Caratage:* Gem diamonds, and for that matter, any gem, are bought and used as individual pieces. So the individual weights of the pieces are important for

determining their values. Moreover, the larger a diamond is, the rarer and, hence, more valuable it is. Occurrence of such diamonds is not predictable and are encountered by chance in course of mining and to give each of them a unique identity, a fancy name is given to it. Some large diamonds thus found during the nearly three millennia of history of diamond mining, have carved permanent niches in legends and literature. Initial caratage of a rough is all the more important because up to 40-50% of it may be lost during cutting and polishing in order to convert it to a gem. A few examples of famous large roughs are: Culliman (3,106 carats, found in 1905 in Premier mine of South Africa), Excelsor (995.2 carats, found in South Africa in 1893), Great Moghul (817 carats, found inKollur mine, Golkonda, India in the 17th century), Jonker (726 carats, discovered in 1934), Orloff (Russia), Koh-i-noor (original weight believed to be 800 carats and believed to be found in Golkunda, India, first recorded in 1304), Regent (India), Blue Hope (115 carats, found in India in 1668). These sizes may be compared with those generally produced from Majhgaon mine in India (0.01-0.70 carats), and the fact that hardly 400,000 pieces of the diamonds produced in the world are of more than 2 carats in size. In the recent past, notable large pieces produced from Majhgaon mine are one weighing 30.33 carats (valued Rs 9.2 million) in 2003 and another weighing 27 carats (valued Rs 9.6 million) in 2005.

(11) *Certification:* For a common retail buyer, the physical and optical properties of diamonds carry little sense, and he is most concerned, besides size, with the colour and brilliance as judged with the naked eye. But both these characteristics can be replicated by unscrupulous people. So for him certification by some trusted authority or agency assumes importance.

(12) *Aggressive marketing:* Almost any gemstone can be sold irrespective of colour and cost, provided the basic criterion of rarity is met. Economically, demand of diamonds (for that matter any gem) is by and large elastic, i.e., they are luxury items, and not essential in our lives. Consequently, gems do not follow the conventional law of demand and supply according to which, demand generates first and supply follows. On the other hand, in case of gems, supply comes first and demand generates later in response to that. A classic example is provided by what is called Champagne diamond. When Rio Tinto first came out with yellowish brown diamond from its Argyle mine, it could not find takers as it looked cheap and ordinary. Then the company got it cut into small sizes in India with cheap skilled labour, and gave it the fancy name ‘Champagne diamond’. It immediately caught the attention of designers to use them as sequins on garments. At the 2004 Oscar ceremony in Los Angeles, one actress wore a dress studded with 2,000 Champagne diamonds totaling 3,000 carats and valued at $2.5 million. It became a craze overnight – particularly a preferred choice for people with darker complexion.

(13) *Therapeutic value*: Diamond is traditionally believed to possess many direct therapeutic values for the internal functions of human body as well as for skin. Besides, it is believed by many to have some indirect beneficial effect on body and mind if worn on the body. This branch of therapy known as gemmotherapy works on the hypothesis that different gems, when worn by a man on his body, react differently to different kinds of cosmic rays having different effects on the health of his mind and body. It is a scientific fact that mesons produce cosmic rays which come from

outside the earth in varied intensities every minute, and day and night about 600 rays pass through our body. Gemmotherapists believe that each kind of cosmic ray has some specific effect on human health, and each gem modifies these effects by preferentially absorbing or transmitting specific rays.

(14) *Beliefs and superstitions:* Diamonds (for that matter, gems at large), many people believe, bring luck or misery to lives.

(15) *Stability of value*: Economic phenomena like inflation, stagflation, recession and even political instability which exercise adverse impact on other manufacturing and processing sectors, do not affect adversely the demand of diamonds.

B. Industrial diamond: So far as industrial diamonds are concerned, most of the criteria for gem diamonds are irrelevant. Only the properties of hardness (i.e. very high abrasion resistance), durability and very high thermal conductivity are important.

USES

A. Gem diamond: Of the 2,500 or so known minerals, about 200 are regarded as potential gems, and of these, as many as 84 are significant in Indian context. Diamond is the foremost amongst them. Its uses are as follows.

(1) *Ornaments and jewelry*: The main demand for gem diamonds is for making jewelry. Colour, clarity, cut, durability, refractivity and dispersion are the most important criteria. After all these basic criteria are fulfilled, comes the question of caratage or size on which depends the price. A minor use of diamond is in cosmetic dentistry or tooth jewelry. First patented in 1986, this may consist of gems made of gold with little diamonds which are fixed to the front surface of a tooth. These are the choice of singers, film stars and many others wanting their teeth to glitter while smiling or talking. In this application, caratage is not a consideration.

(2) *Status symbol:* Gemstones are traditionally connected with royalty and aristocracy. In fact, their high costs are a favourable factor. It is important that they should not only be costly, but also appear so. The rarity of a stone plays an important role.

(3) *Value storage and liquidity:* Gem diamonds are high-value low-bulk commodities. Hence, kings and aristocrats in the past, and now, common men also endeavour to acquire as many of them as they can afford with a view to storing them conveniently for re-sale in times of need. Even for meeting the expenditure of wars, etc., these are regarded as liquid assets as exemplified by the rebels of Congo who were waging a civil war against their Government, and who were fiercely fighting for keeping control over the famous diamond resources on the banks of Congo river by selling which they can purchase weapons and finance the war (these diamonds are called *blood diamond* or *conflict diamond*, and after the World Diamond Council has introduced the *Kimberly Process Certification Scheme* to discourage sale of diamonds procured from any unauthorized source, their share in the world trade has come down to 1% in 2006). Durability and indestructibility, moderate specific gravity and high value/volume ratio, and stability of value against economic or

sociopolitical uncertainties are the principal criteria besides the basic ones like colour, clarity, caratage, refractivity and dispersion that determine the value of the roughs.

(4) Therapy:

i. Ayurveda: Medicinal value of diamond have been mentioned in the 5000-year-old Indian system of medical science – Ayurveda. Powders and ashes of gem diamonds are used as ingredients of medicines. Pure white diamonds are preferred, but other criteria are not important (though the basic physical properties of diamond will in any case be there).

ii. Gemmotherapy: A sizable section of population – (elite and common)—believe in an unconventional system of healing known as Gemmotherapy, according to which gem diamonds, when worn on the body as a ring or a locket or in any other form, has a beneficial effect on persons suffering from a lack of physical and mental energy. Colour (pure white is preferable), clarity and caratage (generally 0.5-1.0 carat) of the diamonds are very important criteria in this use.

iii. Cosmetic skin care: Scrubbing with diamond powder and ash is claimed to help rough skins to become even and to glitter. This has been an old practice dating back to the times of mythology and more recently to the Mughal period in India when women of the royalty and aristocracy used to apply diamond powders mixed with other herbal and cosmetic materials to their skins for removing dead cells and for bettering health and appearance of skin.

(5) *Superstitious belief*: This is a very old use, since fear and superstition have been ingrained in human beings – particularly weak minded ones. This usage has also been prevalent amongst the rich people and has been promoted since historical times by astrologers.

(6) *Space, military and electronic applications*: The type IIa gem diamonds are important as windows in spectrophotometers and serve as lenses in many weather satellites. Their ability to transmit both infrared and ultraviolet rays is the key for this use. The type-IIb diamonds are required in space technology and military applications due to their semiconductivity and their sensitivity to very small changes of temperature (0.002^0C or even less) that can be measured with their help. Due to the same property, a possible future use of type-IIb diamonds may be to replace silicon in I-C chip as per the reports of investigations carried out in a Californian laboratory. Another future possibility is in the field of micro-engineering. Scientists in USA have been able to carve a relief prototype of a miniscule gear (300 microns diameter with 50-micron wide teeth) on the flat surface of a diamond with the help of laser beam, and such gears may be useful in robots and I-C chips as tiny cutters to slice beams of light.

B. Industrial diamond: Usage of industrial diamond is mainly based on its hardness and thermal conductivity. The stones are mainly used in:

(i) tools for cutting and boring hard metals quickly and accurately, and in drill bits taking advantage of their hardness, and also thermal conductivity that quickly dissipates the heat to their metal matrices and prevents the tools and bits from becoming hot;

(ii) dies for drawing very thin wires (e.g. tungsten filaments), for which the diamond should be flawless and its hardness helps to maintain stability of the diameter of dies;

(iii) diamond-coated reamers for penetrating blockages in human arteries (diamond-coatings can be applied to nearly any solid material at a few hundred degrees temperature);

(iv) metal wires coated with bonded beads of diamond, for quarrying and construction purposes, taking advantage of their hardness and also high thermal conductivity of diamond that quickly dissipates the heat to the metal core and prevents the beads from becoming hot;

(v) diamond stylus for use in record players.

The grits, dusts and powders find application in:

(i) grinding wheels for polishing rocks, gems, etc.;

(ii) saw blades for cutting rocks, gems, etc.;

(iii) heat sink for electronic components for which high thermal conductivity is the main criterion;

(iv) ceramic matrix composites (CMCs) as particulate reinforcing agent.

Micro/nano-diamonds are believed to hold promise for making small semiconductors by bombarding and inserting boron atoms within them. According to the present thinking, their mode of formation by radiation has made these diamonds weak electrical conductors with enormous potentiality for manufacturing small semiconductors.

WASTE UTILIZATION

Wastes are generated during both the dressing of diamondiferous rocks and cutting/polishing of roughs. Incidence of diamond in rock is very low. For example, in Majhgaon mine, India, it is only around 10 carats per 100 tons of rock. Consequently, huge tailings of rock (kimberlite in case of India and most of the other countries) are left behind after recovery of the diamonds. After cutting and polishing, the weight of the gem is about 50-60% of the rough, and the remaining 40-50% is lost in the form of diamond dust. The scope of utilizing these wastes are discussed as follows.

1. Waste kimberlite: Some research in India has been carried out in Sagar University in 1986 (Pramod O. Alexander, 2nd World Congress on Engineering and Environment, New Delhi), and more recently by the National Mineral Development Corporation. The possibilities of use that has emerged till now are:

(i) *Agriculture*: It was reported that kimberlite contained 1.65% potash, 2.69% phosphorus and also some macro-nutrients like calcium, magnesium, sulphur, and micro-nutrients like iron, copper, manganese and zinc and also higher concentration of radioactive elements that are known to stimulate crop growth. It was reported that when crushed kimberlite was spread over sandy soil in Western Australia, it supported a lush green lawn. It was also observed that the kimberlite grounds in the semiarid areas of Botswana and Russia supported dense and healthy vegetation growth. It is claimed that application of ground kimberlite in acidic soil can increase the yields of paddy (4-7%), sugar cane (6-7%), soybeans (30%), groundnut (up to 122%), wheat (11-35%) and field pea (90%).

(ii) *Bricks*: Hollow bricks experimentally made of 70% kimberlite and 30% clay have been reported to be promising.

(iii) *Tiles*: In ceramic tiles kimberlite can replace up to 60% of china clay or ball clay. In mosaic tiles cement can be substituted by kimberlite to the extent of 10 per cent. Kimberlite can also be used for glazing tiles. Powdered kimberlite can be substituted for inorganic zinc/barium salts and fired to impart a buff coloured glaze to the tiles.

(iv) *Flux for sintering iron ore*: Kimberlite is an olivine rock containing high magnesium (up to 23% MgO) and its powder can be substituted for dolomite fines for mixing with iron ore for sintering. Addition of 5% kimberlite to the mix is also claimed to improve the strength of the sinter.

(v) *Cement*: Kimberlite powder (up to 23% MgO, 32% SiO_2 and 5% FeO) can be used to substitute rice husk to the extent of 5 percent.

(vi) *Chemical products*: Kimberlite has been experimented with for production of some materials like: (a) adsorbent for de-fluoridification of water, (b) fluffy silica for use in rubber(filler), pesticide (carrier), tooth paste (bonding agent), oil-remover from spillages, (c) caustic magnesia (magnesium hydroxide) for use in fertilizers, rubber (filler), animal feeds, pulp and paper, pharmaceuticals, water effluent treatment, (d) crystalline sodium aluminium silicate called zeolite-A for substituting sodium polyphosphate in detergent powder manufacturing, (e) sodium silicate used in manufacturing soap, in brewing, in dairying, in food processing, as a deflocculating agent in cement, as an adhesive in paper and board industry, as a binder for vermiculite, in paints, for sealing pores in asbestos and fibrous glass surfaces, and (f) precipitated silica used in automobile tires, rubber and insecticides.

2. Diamond dust: Diamond dust generated during cutting and polishing is usable as an abrasive and for cosmetic skin scrubbing.

SUBSTITUTION

Substitution of diamond may take place in three ways:

1. By low end cheaper gems: Expensive gem diamond may be substituted by semiprecious stones (e.g., topaz, garnet, hessonite, zircon, tourmaline, quartz crystal, amethyst, peridote, turquoise, etc.) or by organic gemstones (e.g., pearl, coral and amber). When used in ornaments and jewelry or due to superstition, and price is the prime factor. However, this may not be the case when gem diamonds are purchased for other purposes such as for exhibiting status symbol, value storage, therapy and electronics.

2. By customized diamonds: It has long been known that by bombarding high energy particles, defects can be induced in any crystal including diamond. A transparent diamond when exposed to high energy electrons acquires a blue tinge. As it is bombarded with more electrons, the blue deepens and eventually turns green and then to black. If the copious supply of neutrons from a nuclear reactor is used in a controlled manner for irradiation, the process will become cheaper. The defects induced can be shifted around by rapid heating of the diamond at 800-900^{0}C, and various colours like orange, gold, amber and red can be produced. Thus any coloured diamond can be customized.

3. By flawed diamonds: Diamonds often contain voids which come to light once it is cut and polished. Nowadays, it is possible to repair such defects with the help of a laser beam which can be focused to a spot of less than 10 micron diameter (i.e., less than one-tenth the width of a single strand of hair). After repair, such flawed diamonds can go as substitutes of flawless ones.

4. By synthetic/artificial/imitation diamonds:

(a) *Synthetic diamond*: Synthetic diamonds are made in the laboratory out of the same elements as in natural diamond, i.e., carbon. The world's first synthetic diamond was produced by the General Electric Research Laboratory, USA by subjecting a mixture of graphite (carbon) and a metal catalyst to very high pressure (over 70,000 kg/sq.cm) and temperature(1400-1800^{0}C). These conditions are the replica of those prevailing at 150-200 km below the earth's surface, and are met using either a hydraulic press or specially contained conventional explosives. Synthetic industrial grade diamonds are routinely made today. These are generally of less than 20 mesh size and are mostly used in grinding wheels, saw blades, diamond coating of wires etc. Almost all synthetic diamonds are of the type-Ib and are yellow coloured. The first gem quality colourless synthetic diamond (type-IIa) of large size was made by the same institution in 1970. The synthetic gem diamonds are totally pure, flawless and colourless but very costly to make, their costs being much higher than their natural counterparts. They can also be converted to semiconductors by adding small quantities of boron at the time of manufacturing. The synthetic gem diamonds are very costly to make, their costs being much higher than their natural counterparts. So their use is limited only to very high-tech fields of electronics, space, defence etc. The high cost precludes them from usage in jewelry, and moreover, since they are man-made, there is no guarantee of their rarity. However, anything new can be sold by aggressive marketing, as is exemplified by what has been called "life gem" — a synthetic diamond, a 0.35-carat piece of which was initially made by a widower out of his wife's ashes for the sake of a keepsake, has, although very costly to make ($14,000 for a one carat piece made out of about 650 gm of human ash), caught the fancy of a few rich whimsical persons.

(b) *Artificial diamond*: Artificial diamonds consist of elements that are naturally occurring, but combined in forms that are not found in nature. The most common and widely used artificial diamond is American diamond (also referred to as zircon), which is cubic zirconia (ZrO_2) specially made from zircon ($ZrSiO_4$). Zirconia is monoclinic at normal temperature, becomes tetragonal when heated to above 1800^{0}C, and reverts back to monoclinic form on cooling. It melts at a high temperature of about 2700^{0}C and is reactive with certain high melting crucible materials like platinum, iridium which cannot endure this high melting temperature. By some carefully controlled special process the zirconia is melted in what is called *skull melting system*, recrystallized in cubic form and prevented from reverting back to the original form. The "skull" is a hollow-walled copper cup. Water is circulated through the hollow walls to cool the inside wall of the cup, when this skull is filled with powdered ingredients and heated by radio frequency induction until the powders melt. Because the water cools the walls of the skull, the powdered material next to the walls do not melt acting as a buffer between the wall of the container and the reactive molten material, and the latter is contained within a shell of unmelted material. When the heat source is removed and the system is allowed to cool, crystals form with nucleation and grow until the entire melt solidifies. Other examples of artificial diamond are spinel, yttrium-gallium-garnet, strontium titanate and a form of silicon carbide called mossainite (the manufacturing process of spinel and YAG is the same as that of synthetic ruby and sapphire and the details are given in the chapter on them). These can be cut and polished to look like natural gem diamonds. Due to their close resemblance to real diamonds in appearance, hardness and strength, high refractive index, high melting point, high corrosion resistance and lower cost, American diamonds have good demand for jewelry, for ornamentation of watches and for sewing sequins on garments. Their disadvantages include low density and thermal instability at elevated temperature. In India, there is a centre at Tiruchirapalli, Tamil Nadu especially for their cutting and polishing.

(c) *Imitation diamond*: Imitation diamonds only superficially look like genuine diamonds without having the latter's intrinsic characteristics. Examples are glass and polymer. The imitation diamonds serve as cheap jewelry. The best practical application of imitation diamond is in cosmetic dentistry. Tooth jewelry is now being made of plastic to meet the demands of a large section of population. The advantage of such plastics over real diamond is that plastic does not cut a person if he accidentally swallows it.

Chapter 17

DIASPORE

The name diaspore comes from the Greek word “diaspora” meaning dispersion or scattering owing to the fact that, on heating, it decrepitates into fragments that scatter all around (a characteristic feature). Its other uncommon names include *empholite, kayserite* and *tanatarite*. Diaspore is beta-monohydrate of aluminium having a chemical composition $Al_2O_3.H_2O$, and is a dimorph of boehmite (alpha monohydrate of aluminium) a source of aluminium metal along with gibbsite ($Al_2O_3.3H_2O$), and along with the latter two, is a constituent of bauxite. The difference between the two monohydrates boehmite and diaspore is that while the former is a secondary mineral formed due to dehydration of gibbsite, diaspore is a product of metamorphism and it, being difficult to be digested by caustic soda at economically viable temperature, is not commercially suitable for recovery of alumina, unlike gibbsite and boehmite.

It occurs as an alteration product of corundum (Al_2O_3) or emery (a natural mineral comprising a mixture of corundum and magnetite) in granular limestone and other crystalline rocks. Well-developed crystals are found in the emery deposits of the Urals (Russia) and Massachusetts (USA), and in kaolin deposits of Hungary.

In India it occurs as veins and geodes associated with pyrophyllite. Its deposits have been identified in Udhampur district of Jammu and Kashmir; in Hamirpur, Jhansi and lalitput districts of Uttar Pradesh and in Chhatarpur, Shivpuri and Tikamgarh districts of Madhya Pradesh. Its production has been erratic with ups and downs as shown below.

Year	Production
1963	160 tons
1970	6,172 tons
1976	10,090 tons
1980	5,928 tons
1989	15,301 tons
1990	7,810 tons
Year ending March 2001	8,849 tons
Year ending March 2006	23,719 tons

The entire production comes from Uttar Pradesh and Madhya Pradesh states.

CRITERIA OF USE

It occurs sometimes as flattened crystals, but usually as lamellar or scaly masses, the flattened surface being a direction of perfect cleavage on which the lustre is markedly pearly in character, and varies from translucent to transparent. Its hardness is 6.5-7 on Mohs scale and specific gravity is 3.4. However, the characteristics mainly determining its industrial use are as follows.

(1) *Alumina content:* Diaspore ($Al_2O_3.H_2O$) is a very high-alumina mineral containing 85% alumina and 15% water. This alumina-content is higher than another high-alumina material mullite ($Al_2O_3.SiO_2$) which is obtained by heating kyanite, sillimanite or andalusite and which contains 71.8% Al_2O_3 (see the chapter on kyanite)

(2) *Thermal behaviour:* Diaspore can withstand temperature up to around 1760^0C to over 1800^0 (c.f., melting point of pure alumina is 3700^0C and that of corundum is 2050^0C). When heated before the blowpipe, its water is dissociated and it decrepitates violently, breaking up into white pearly scales. But once the water is expelled, diaspore becomes resistant to stress, fatigue and alkali attack.

(3) *Colour:* It is colorless or greyish-white, yellowish, sometimes violet in color.

USES

1. Refractory: Refractory materials are defined as those resistant to heat and having a melting temperature of not less than 1580^0C. The function of refractory lining on a furnace wall is not only to withstand high temperature, but also to withstand temperature fluctuation, and to resist penetration, abrasion, and erosion by hot gases and molten materials in the furnace, and over and above, it should not chemically react with those materials. The life of a refractory lining has increasingly been becoming a critical parameter in the productivity of a furnace and economics of a plant, because each time the lining fails and needs replacement, the furnace has to be shut down.

Diapore is used in making high-alumina refractories as such or by bonding with flint or plastic clay, the proportion of the latter two depending on the aluminium content needed in the finished product. High heat resistance and resistance to fatigue, stress and alkali attacks make such refractories suitable for certain applications.

Fe_2O_3 melts at a relatively lower temperature and if, in addition, TiO_2 is also present then at the high temperature in furnaces where the refractory products are used, they form low-melting iron-titanate glass causing blisters in the refractory bricks and consequent increase in porosity. Hence, these are considered highly deleterious. Refractoriness is lowered by the presence of a flux like CaO and hence it is also considered highly deleterious. While, for ordinary quality refractory, the industries of India specify a minimum of 52% Al_2O_3, 2% (max) Fe_2O_3 and TiO_2 each and 1% (max) CaO, for better quality products, they prefer diaspore containing 58% Al_2O_3, 1.5% (max) Fe_2O_3, 1% (max) TiO_2 and 0.3% (max) CaO. In the first case the refractoriness achieved is 34 Orton Cone Equivalent or OCE (around 1760^0C) and in the second case, 36 OCE (over 1800^0C).

2. Ceramics: Compared to refractory, the ceramic industry consumes a negligible quantity of diaspore. It is sometimes added to the raw material mix due to its white to pale colours, scaly structure and ability to retain this structure at high temperature. The Indian industries specify its grade as containing (+) 58% Al_2O_3, 2% (max) Fe_2O_3 and 23-28% SiO_2.

3. Pesticide: It is also used as a filler in the pesticide industry, but this is a minor use. Its scales offer large surface areas for holding the particles of the chemical.

Chapter 18

DIATOMITE

Diatomite is a naturally occurring, soft, chalk-like, organic siliceous sedimentary rock consisting of the fossilized skeletons of hard-shelled unicellular microscopic aquatic plants (algae) known as *diatoms* (they are so minute that 25 millions of them can fit in a teaspoon). Diatoms live in lakes, rivers and oceans feeding on plankton which they convert to silica that forms their cell walls called *frustules*. Diatoms are photosynthetic. So, they are vital to humankind as they make up a quarter of the earth's plant life and they produce at least a quarter of the oxygen we breathe. Since diatomite forms from the remains of water-borne *diatoms,* it is found close to either current or former bodies of water.

Diatomite is also popular by its German name *kieselguhr* and is sold in the market under various trade names like *celite, diahydro, hyflosupercel, dicalite, fossil flour, sorbocel,* etc. Its loose unconsolidated variety is called *diatomaceous earth* (DE). An impure variety of diatomite mined in Denmark and containing impurities like sponge spicules, radiolarian remains, clay minerals, silica sand and alkaline earth is known as *moler earth*.

The Diatomite deposits were formed millions of years ago when volcanoes erupted, and the flowing molten lava filled up depressions on the nearby areas and shallow seas. The seawater also contained silica in the form of orthosilicic acid (H_4SiO_4), which the diatoms polymerized to biogenic silica. Diatoms flourished in the nutrient rich water under a relatively quiet environment, and billions of their shells sank and accumulated huge deposits of diatomite.

Diatomite is generally divided into two categories based upon its source: *freshwater* and *saltwater*. Freshwater diatomite is mined from dry lakebeds and is characteristically low in crystalline silica content. Saltwater diatomite contains a high crystalline silica content. It is associated with tertiary rocks of Miocene to Pliocene age.

In India, there are a few reported occurrences of impure diatomaceous earth from Gujarat. Presently workable diatomite deposits in the country are not known. However, meager productions varying from a few tons to 420 tons (1988) were occasionally reported from Gujarat during the period 1969-1992. The total world production during the year 2001 was 1.75 million tons. Currently, USA is the leading producer followed by Denmark, China and others. A single deposit in USA developed in the year 1900 (Lompoc in California) having an area of 3-4 square miles and extending to a depth of 700 feet, is believed to be the largest deposit in the world.

CRITERIA OF USE

1. *Colour and optical properties*: White to off-white, brown, black depending on impurities. It has low gloss (i.e., percentage of the incident light beam that is reflected from a surface).
2. *Strength:* Diatomite easily crumbles to fine powders, each consisting of millions of hollow frustules. But the siliceous frustules, having been matured through millions of years in nature, do not break down nor to their structure collapse. Because of the hard silica, the hardness of diatomite is 4.5-5.0 on Mohs scale, and its powders have an abrasive feel.
3. *Density:* Its specific gravity is 1.95-2.30. This is, however, no indication of its bulk density which is of the order of only 0.38 gm/cc due to high porosity.
4. *Chemical characteristics:* Each particle of diatomite contains microscopic, hollow, perforated cylindrical siliceous shells each shell of size 5 micron to 1 mm that were produced by the ancient diatoms, and silica is the main constituent for which diatomite is valued. The silica is in the form of opal or hydrous silica ($SiO_2 .nH_2O$), but it may also contain varying amounts of free silica as quartz and also shale, silt, carbonate mud, iron oxide, organic material, etc. The typical chemical composition of saltwater diatomite is 86% silica, 5% sodium, 3% magnesium and 2% iron. Freshwater diatomite mined in Australia contains lower silica and typically analyzes 65-80% SiO_2, Al_2O_3 14-18%, Fe_2O_3 2.5-4.0%, CaO 1.5-2.2%, K_2O 0.9-1.2%, TiO_2 0.65-0.85%, MnO_2 0.04-0.06%, P_2O_5 0.04-0.08%. The biogenic nature of the silica makes it available to plants as s nutrient. Diatomite does not contain silica in the form of quartz or its variations (tridymite or cristobalite), and the silica being completely biogenic and matured over millions of years, diatomite is chemically stable and inert.
5. *Porosity and liquid absorption*: Porosity is very high due to the hollow miniscule cells (frustules). It is generally 80-130%, but freshwater diatomite mined in Australia absorbs up to 150% of its own weight in fluid and slowly releases it. Further, the frustules, being interconnected, facilitate smooth movement of the absorbed liquid as well as air through a particle of diatomite even if it is pressed. The structure of diatomite does not break down and become slippery when wet like other common absorbent materials.
6. *Capillary action:* Water can be drawn up as high as 200 mm from the bottom of a vessel containing water within a short time.
7. *pH:* Diatomite is moderately alkaline with pH 7.9-9.4.
8. *Base exchanging capacity*- Base exchange is the exchange of ions in solution for those of a solid. Upon contact with a solid, the solution will undergo a change reciprocal to that of the solid. This is also known as "*cation exchange* capacity", which means the quantity of positively charged ions (cations) that a substance can accommodate on its negatively charged surface, and it is expressed as milli-equivalents per 100 gm (*equivalent weight* is the molecular weight of an element divided by its valency). The mechanism is not fully understood. The value for diatomite is fairly high at 30 meq/100gm.

9. *Thermal properties:* The microscopic porous structure of each particle provides effective thermal insulation to plants and root zones. When heated to 650^0C, diatomite becomes completely sterilized. It can withstand high temperature and retain its structure even at 1400^0C.
10. *Safety of health:* The type of hazard posed by inhalation depends on the form of the silica. Crystalline silica poses a serious inhalation hazard because it can cause *silicosis*. Amorphous silica can cause dusty lungs, but does not carry the same degree of risk as crystalline silica. Natural diatomite generally contains very low percentages of crystalline silica. However, in the diatomite processed by heat-treatment, the amorphous silica tends to assume crystalline form, and may require care while handling.

USES AND SPECIFICATIONS

Natural diatomite is normally used in processed commercial form. Processing involves calcination at 870-1100^0C as a result of which the water molecules are driven off, porosity increases and the grade improves. The industries generally specify the chemical grade as: *85-94%* SiO_2*, 1-7%* Al_2O_3*, 0.4-2.5%* Fe_2O_3*, 0.1-0.5%* TiO_2*, 0.03-0.5%* P_2O_5*, 0.3-3.0% CaO, 0.3-1.0% MgO, 0.2-0.5%* Na_2O*, 0.3-0.9%* K_2O*, 0.1-0.2% organic matter and soluble salt.* Processed diatomite finds a wide range of uses particularly those requiring high porosity and high silica. The principal uses of diatomite are:

1. Filtration
2. Abrasive
3. Insecticide
4. Cleaning absorbent
5. Fire-resistant safes
6. Horticulture and hydroponics
7. Dynamite
8. Building material
9. Paper
10. Rubber
11. Paint
12. Fertilizer
13. Refractories
14. Sodium silicate
15. Sealant
16. Climatology

These are discussed as follows.

1. Filtration: The most common use (68%) of diatomaceous earth is as a *filter* medium. Saltwater diatomite contains a high silica content with its characteristic high porosity, because of the microscopically small, hollow particles that give it a sieve-like structure. The other most important criterion is its chemical inertness. Processed diatomite is preferred because, on calcination, the water molecules are driven off thereby incresing the porosity further.

It is used in chemical laboratories under the name *celite* as a filtration aid, to filter very fine particles that would otherwise pass through or clog filter paper. It is also used to filter water drinking water, mine drainage water and swimming pool water, and other colloidal liquids such as beer (for sieving out unwanted protein particles), wine, beverages, fruit juice, sugar syrup, oil antibiotics, vegetable oils, animal fats, waxes, resins, gum solutions, gelatines, metal-plating solutions, acids, etc. to remove amoebic cysts and larvae. In refining of sulphur, molten sulphur is filtered through a mixture of diatomite and sulphuric acid for removing organic impurities.

Depending on the particular usage of the diatomite, its pore-space size should be between 1.50 and 7.22 micron, coefficient of permeability (Darcy's) between 0.057 and 3.0 gallons per day per square foot, pH between 7 and 10, bulk density between 7.0 lbs/ft^3 and 19.5 lbs/ft^3 and size mostly (-) 150 mesh.

Carbonates of calcium and magnesium are objectionable when the diatomite is intended for filtering acidic liquors such as lemon juice that will dissolve them, but not in the case of neutral liquors. Clay and organic matter are undesirable because they will be left in the residue blocking the pores and lowering the filtering efficiency. NaCl is objectionable because it will dissolve in the filtrate and contaminate it. Iron oxide may also react with some chemicals to be filtered and contaminate them. Industries specify not more than 6% clay, not more than 1% each of NaCl and iron oxide and as low as possible amounts for all the other deleterious constituents. Besides, the porous structure of the diatomite should be intact devoid of broken pieces.

2. Abrasive: The oldest use of diatomite is as a very mild abrasive. It has been used both in toothpaste and in metal polishes, as well as in some facial scrubs and hand soaps. The main criteria are its chemical stability and inertness. Pulverized diatomite mixed with one third of its weight of grease is moulded into bricks and sticks for making what are called *grease bricks*. These are used on polishing wheels. It is also used as a filler in safety matches for creating friction.

3. Insecticide: Diatomite is used as an insecticide due to its water-absorptive properties. The fine powder absorbs lipid (an oily organic compounds insoluble in water but soluble in organic solvents, essential structural component of living cells) from the cuticle (the waxy outer layer) of insects' exoskeletons, causing them to dehydrate. Arthropods die as a result of the water pressure deficiency. It works on slugs (gastropods) with limited efficacy because they inhabit humid environments. Diatomite powder is commonly employed in gardens, bee farms etc. It is sometimes mixed with some other additives to increase its effectiveness. Medical grade diatomite is sometimes used to de-worm both animals and humans in lieu of boric acid. It is also used to help control and eventually eliminate a cockroach infestation.

4. Cleaning absorbent: Its absorbent qualities make it useful for cleaning up toxic liquid spills. It has also been employed as a primary ingredient in a type of cat litter (material used for making bed). The type of diatomite used in cat litter comes from freshwater sources and does not pose a significant health risk to pets or humans due to its inertness.

Other industries such as paper, paints, ceramics, soap and detergents use diatomite as a fulling or washing material on account of its base-exchanging power.

5. Fire-resistant safes: Its thermal insulation properties enable it to be used as the barrier material in some fire resistant safes.

6. Horticulture and hydroponics: Processed diatomite consists of approximately 90% silica (an important ingredient of plant-bodies) in plant-available biogenic form, with the remainder being made up of some minerals like those containing Fe, Ca, Mg, K, P, etc. which are also essential nutrients for plant growth. It absorbs up to 150% of its own weight of fluids and slowly releases the fluids as well as the plant-available silica as per the requirement of plants. The silica stimulates self-acquired resistance (SAR) in plants thereby increasing their resistance to disease. Besides, diatomite is a lightweight, porous, non-toxic, non-hazardous cost effective mineral. The microscopic porous structure of each particle provides effective thermal insulation to plants and root zones. All of these unique factors make diatomite a highly efficient and cost-effective horticultural growth-promoting medium for all growing applications.

Diatomite can be used as a growing medium in *hydroponic* gardens (hydroponics is a technique of growing plants without soil, in water containing dissolved nutrients).

For such applications, the diatomite has to be of freshwater origin because the high salinity level of salt-water diatomite is not suitable for plants.

7. Dynamite: In *1867*, Alfred Nobel discovered that nitroglycerin could be made much more stable if absorbed in kieselguhr. He patented this mixture as dynamite, and the mixture is also referred to as *guhr dynamite*. Nobel's original dynamite was a mixture of 75% nitroglycerin and 25% kieselguhr. Now, various kinds of dynamite are made to suit different applications, by replacing nitroglycerin by other materials.

8. Building material: Diatomite was used by the ancient Greeks and Romans as a lightweight, building stone. Now, it is sometimes used as an admixture in cement and concrete. Its high porosity and absorptive power effect a strong bondage of the mix, and its high silica serves to supplement the sand.

9. Paper: The role of diatomite is twofold: (i) as a bulking agent in chip board and other cylinder machine products, and (ii) for pith control and overcoming stickiness in waste paper recovery. In the first case, low bulk density and white colour are the main criteria, while in the second case, the mildly abrasive effect of the hard silica and its ability to retain strength and structure are the main criteria.

10. Rubber: Diatomite powder is added to rubber for making brake linings. The millions of hollow air-filled frustules in the powder particles of diatomite give a cushioning effect and better grip to the brake when pressed. Even when the particles are subjected to high stress, they are able to retain their structure. The rubber used is invariably vulcanized by treating with sulphur (see the chapter on sulphur), and the diatomite being chemically inert, does not react with the sulphur. But copper, manganese and iron oxide are considered deleterious in the diatomite because all of them may react with the sulphur to form sulphates.

11. Paint: The main functions of diatomite as a constituent of paint are as a flattening agent and an extender in wall paints. The properties made use of are chemical inertness, low bulk density, high absorption of liquid (in this case oil), white colour and low gloss. The last-named property is particularly useful for imparting a flattening effect to the paint. CaO and MgO are considered deleterious because they have a tendency to absorb water and increase in volume thereby producing cracks in the paint film over a period of time. Iron oxide and organic matter have a colouring effect and are undesirable.

12. Fertilizer: In chemical fertilizer sprays, diatomite is added as a dusting and anti-caking agent by virtue of its low bulk density and inertness. Water is objectionable because it will inhibit spreading of the fertilizer and also add to the density.

13. Refractories:- Silica is a refractory material. Additionally, the millions of air-filled hollow strong frustules in diatomite particles make it an efficient thermal insulator. To top it all, diatomite can retain this unique structure even at 1400^0C. Hence, even as a refractory material is defined as one having a melting temperature of not less than 1580^0C and also having the abilities to resist temperature fluctuation, slag and metal penetration, abrasion, and erosion by hot gases and molten slags and metals, diatomite is useful as a lightweight siliceous thermal insulator material for industrial furnaces.

14. Sodium silicate: It is a family name and it includes sodium metasilicate (Na_2SiO_3), sodium ortho-silicate (Na_4SiO_4), sodium pyro-silicate ($Na_6Si_2O_7$), etc. They are also called "*water glass*" or "*liquid glass*". These are white, water soluble alkaline solids. They are prepared by fusing silica sand or quartz powder (20-100 mesh) containing 99% SiO_2, with soda (Na_2CO_3) at 1200^0C to 1400^0C. Diatomite is sometimes added as a source of silica. $Al_2O_{3,}$ $Fe_2O_{3,}$ CaO and MgO are undesirable as they tend to combine with silica and sodium forming water-insoluble salts. Sodium silicate is used in soaps and other cleaning compounds, sealant, cement and concrete, binder, adhesive, timber treatment, egg preservation and fire protection materials (see also chapter on silicon).

15. Sealant: Sealant is an organic substance soft enough to pour or extrude from tubes, and capable of subsequent hardening to form a permanent bond with the substance. By virtue of the shapes of the frustules (elongated, acicular or disc-like), high porosity and high absorption, diatomite provides a large surface area for bonding. Thus it imparts hardness and stiffness when used in conjunction with fine silica. Further, it holds the other ingredients of the sealant firmly and does not allow the sealant to expand and spill when extruded from a tube.

16. Climatology: The Earth's climate depends greatly on the amount of dust in the atmosphere by virtue of its ability to insulate the planet against ultraviolet rays of the sun and also to maintain balance between the heat inflow and outflow. Recent research indicates that surface deposits of diatomite play a dominant role here, a major example being the *Bodélé depression* in the part of the Sahara desert belonging to Chad, where storms push diatomite gravel over dunes, where dust is abraded, leading to the largest single influx of dust into the atmosphere.

17. Other uses:

(a) *Medical*: As an activator in blood clotting studies.
(b) *Chemical containers*: Used for safe handling and storage of chemicals like sulphuric acid, phosphoric acids, etc. due to its absorbent and thermal insulation qualities.
(c) *Animal feedstuff*: As a conditioner by adding nutrient silica.
(d) *Sound insulation*: Provides zigzag interconnected paths for the air to pass through, thus slowing down the propagation of sound waves and imparting acoustic insulation.
(e) *Water filter candle*: A kaolin-based ceramic product based mainly on kaolin or china clay, used for filtering drinking water for manufacturing of which, quartz, feldspar, plastic clays and diatomite are added to china clay (see also the chapter on kaolin).
(f) *Ceramics and glazes*: As a supplement to silica.

SUBSTITUTION

1. Natural siliceous earths: There are two common but unrelated forms of siliceous earth which have often been confused with and used as diatomite. They are *Tripoli* (or *infusorial earth*) and *radiolarite* (or *radiolarian earth*).

Tripoli is a finely divided, very porous, lightweight, friable and white- to grey- or buff-coloured siliceous sedimentary rock occurring in powdery or earthy masses and resulting from weathering of chert or siliceous limestone. The name has come from Tripoli in Libya where it was found. It has a harsh feel and is used for polishing metals and stones. A similar mineral occurs in Barmer-Jaisalmer region of Rajasthan, India, and the deposits are associated with marine Tertiary rocks underlying bentonite clays. It contains about 74.5% SiO_2, 4.5-9.1% Al_2O_3, 2.36-2.62%, Fe_2O_3, 0.65-2.71% CaO and 0.51-0.63% MgO.

Radiolarite is a consolidated rock composed predominantly of the skeletal remains of radiolaria (instead of diatoms). When in unconsolidated loose form, it is called radiolarian earth.

Both of these types of siliceous earth have many properties like density, colour, porosity and water absorption similar to those of diatomite. After some processing, they can be used much the same way as diatomite, and can be regarded as the latter's inferior substitute.

2. Anthracite-sand mix: This is a cheaper substitute of diatomite used for the refining of beer. For this purpose, a filter bed is made up of three layers consisting of a fairly coarse anthracite top layer, slightly fine beach sand middle layer and zircon sand bottom layer.

Chapter 19

DOLOMITE

Dolomite is named after the French mineralogist named Dolomieru. It is a natural double carbonate of calcium and magnesium having composition ($CaCO_3$. $MgCO_3$). It theoretically contains 54.35% $CaCO_3$ (or 30.4% CaO) and 45.65% $MgCO_3$ (or 21.7% MgO), and the two components cannot be isolated by any physical ore dressing method. In nature, a continuous transition from limestone to dolomite through dolomitic limestone and calcitic dolomite with increasing MgO-content, is encountered. As per convention the MgO-contents of these are: limestone 0-2.1%, dolomitic limestone 2.1-10.8%, calcitic dolomite 10.8-19.5% and dolomite 19.5-21.5%. However, commercial dolomite contains some impurities and, in the industrial circle, a minimum of 18% MgO is considered necessary in order to be recognized as dolomite.

It is formed in nature by action of magnesium-bearing solution (sea water, underground water or hydrothermal solution) on calcite — the process being called *dolomitization*. It was Dolomieru who studied some of its distinguishing properties for the first time in 1791. Its colour varies from white of the purest variety to reddish or greenish white depending on impurities. It is a widely occurring mineral, generally mined from shallow depths. Its production in India has increased steadily from a low of 4,000 tons in 1952 to 4.43 million tons during the year ending March 2006.

CRITERIA OF USE

The most distinguishing property of dolomite first recognized was that, although it was a carbonate, unlike limestone, it did not effervesce under the action of acid at ordinary temperature, but it did so only at elevated temperatures. Dolomite combines in itself certain properties each of limestone and magnesite. The main criteria for its industrial use are as follows:

(1) It is porous by virtue of the way it is formed from calcite. The magnesium-bearing solution acting on calcite replaces some of the molecules of $CaCO_3$ by an equal number of $MgCO_3$ molecules which are smaller in volume than the former. Consequently, the space vacated by the $CaCO_3$ molecules are not entirely filled up by the $MgCO_3$ molecules, and the resultant dolomite becomes porous.

(2) By virtue of the MgO-content, dolomite is resistant to fire.

(3) Dolomite can be calcined at 1000^0C when the CO_2 is completely driven off leaving a mixture of CaO and MgO. This calcined dolomite starts partially fusing at 1700-1800^0C (a process called sintering) by which the magnesia is converted to periclase (the crystallized form of magnesia) and a dense inert product known as *dead-burnt dolomite* or *doloma* is formed. Dead-burnt dolomite is essentially a mixture of free lime and periclase.
(4) The free lime contained in dead-burnt dolomite renders it susceptible to slaking or hydration thereby shortening the shelf-life of the latter.
(5) Chemically, it is basic in nature having pH 10, and hence resistant to basic slag.
(6) It has fluxing ability, mainly due to the contained lime.
(7) It is resistant to weathering.
(8) Its hardness is 3.5-4.0.
(9) Refractive index varies from 1.50-1.68.

But, the main advantage of using dolomite lies in its cheapness, due to wide and shallow occurrence.

USES AND SPECIFICATIONS

The principal uses of dolomite are:

1. Metallurgy (pig iron, ferromanganese, sponge iron, steel)
2. Refractory (basic)
3. Glass
4. Magnesium metal
5. Seawater magnesia
6. Soil conditioning
7. Sorel (magnesium oxychloride) cement
8. Magnesium oxysulphate cement
9. Paper
10. Leather
11. Pharmaceuticals
12. Adhesive
13. Construction aggregate
14. Sewage filter

These are elaborated as follows.

1. Metallurgy:- Dolomite is added to the raw material mix for manufacturing pig iron, sponge iron, ferromanganese and steel for fulfilling certain specific purposes.

(1) Pig iron and ferromanganese:

a) Role: In the case of pig iron, the charge consists of iron ore, coke, limestone and dolomite while in case of ferromanganese, manganese ore instead of iron ore, is used.

The charge is smelted in a blast furnace for pig iron and in an electric arc furnace (EAF) for ferromanganese manufacturing. Mainly limestone acts as the flux, but dolomite, besides supplementing the function of limestone performs certain other functions as follows:

i. It acts as a supplement to the action of limestone as a fluxing agent by virtue of its highly reactive CaO component, which combines with silica and alumina of the iron to form a strongly bonded calcium alumino-silicate slag and, at the same time, to reduce the melting temperature of the charge.
ii. By virtue of the MgO-content which is basic, it increases the basicity and, hence ,fluidity of the slag. A fluid slag is desirable for efficient removal of sulphur and phosphorus, and also for making it easy to pour out.
iii. By virtue of the basic MgO and the basicity of the slag, it extends the life of the basic refractory lining of the furnace. For this reason, around 8% MgO in the slag is considered desirable in a blast furnace.

b) Specifications: The natural porosity of dolomite is helpful. Besides, at the furnace temperature dolomite is calcined and the escaping CO_2 gas makes the residue porous. Due to porosity, larger surface area becomes available for reactions. The strength of dolomite is of importance so that it can withstand the stress of falling from the top of tall blast furnaces during charging. Crumbling will lead to generation of dusts that will tend to obstruct the passage of air. It should therefore be in the form of compact lumps.

Silica and alumina are objectionable mainly for the following three reasons:

i. The purpose of adding dolomite is to remove these impurities present in the iron ore. Their presence in the dolomite will only add to the impurities in the charge, and some lime will be consumed for reacting with its own impurities necessitating the addition of more of limestone or dolomite which, in its turn, will increase the volume of slag.
ii. Dolomite gets calcined at the temperature of the blast furnace to form a porous mass of lime and magnesia. If, however, silica and alumina are present in it, they will immediately combine with the lime to form calcium alumino-silicate which will shut the pores, thus decreasing further reactivity of the lime.
iii. Of the two, alumina is more objectionable, because it has a high melting point and it requires more heat to melt and become fluid. Imperfect melting of the alumina results in higher viscosity of the slag.

If phosphorus is carried into the final product, i.e. steel, it reduces ductility and makes the steel brittle under shocks. Sulphur, when carried to the steel, produces cracks at the edges at the time of rolling of the steel. Both these elements are highly objectionable in dolomite (or for that matter in the entire charge), because they are the most difficult deleterious elements to remove through slag, and they tend to segregate towards the border zone between the slag and iron. By increasing the slag volume and basicity of the slag (by virtue of incorporation of MgO through the dolomite), they can at best be partly removed, but invariably a part goes into the iron. So dolomite must not add to their percentage in the charge.The alkali load has an adverse effect on the reactions within the blast furnace. The alkalis (Na_2O and K_2O) combine with silica to form light fusible silicates which float toward the molten slag, and the availability of silica decreases, affecting the formation of an effective slag.

The Bureau of Indian Standards (BIS) has, in 1982, specified that dolomite for use in blast furnace (either directly or as component of sinter feed) should contain *MgO 18% (min.), CaO 28% (min.) and acid insolubles 8% (max.)*, whereas Indian steel plants in practice consume dolomite with *MgO 18-20%;* SiO_2 *6% (max);* Al_2O_3 *8.7% (max); size 6-80 mm.*

(2) Sponge iron:

In case of sponge iron manufacturing, iron ore is reduced in solid state, and there is no slag formation. In a typical Indian coal-based process, a mix of iron ore, coal and dolomite is fed into the rotary kiln and heated at a temperature of about 1100^0 C; and then the output consisting of a mix of sponge iron, char and Ca/Mg oxide is subjected to magnetic separation whereby the magnetic sponge iron is isolated. Role of dolomite is only to reduce the melting temperature of the charge—by virtue of its CaO component.

(3) Steel:

a) Role: For making steel, iron, coke and limestone are placed in the hearth and is melted at 18,000°C by a mixture of gas and air. Phosphorus and sulphur are oxidized, and these oxides react with limestone to form a slag which, being lighter, floats on the molten steel, and is drained off. Then the steel is tapped. In steel melting shop (SMS), the role of dolomite is as below.

i. It stirs the molten charge in open hearth (OH) furnace by what are called "*lime boils*" formed due to escaping CO_2 gas,
ii. It removes phosphorus and sulphur present.
iii. By virtue of the basic MgO, it not only neutralizes acidity of the melt caused by the presence of certain impurities like silica, alumina, etc., but also provides basic conditions so that removal of phosphorus and sulphur is further facilitated.

Although, the operating temperature is 1800^0 C (c.f., 1100^0 C in blast furnace), dolomite does not become periclase, because it enters into the reactions before that stage.

b) Specifications: For use of dolomite in steel making by open hearth (OH) process, SiO2, Al2O3, P and S besides being objectionable for the same reasons as in the case of pig iron, are also so because they tend to add to the acidity. Here the furnace is much smaller than blast furnace, and also, much of the P and S has already been removed there. Soda is a stronger base and should be desirable for increasing the basicity of the bath – necessary for removal of phosphorus and sulphur. But soda also tends to corrode the refractory lining.

The Bureau of Indian Standards (BIS) has, in 1982, specified that dolomite for use in steel melting shop should contain *acid insolubles 4% (max) with silica as low as 2.5%* whereas Indian steel plants in practice consume dolomite with *MgO 20% (min),* SiO_2 *3% (max),* Al_2O_3 *1.5% (max); size 25-120 mm*. In L-D converters, the specifications are more stringent and are: SiO_2 *0.4–1.8% and* Al_2O_3 *0.2- 0.6%.*

2. Refractory: Refractory materials are defined as those resistant to heat and having a melting temperature of not less than 1580^0 C. The function of refractory lining on a furnace wall is not only to withstand high temperature, but also to withstand temperature fluctuation, and to resist penetration, abrasion, and erosion by hot gases and molten materials in the furnace, and over and above, it should not chemically react with those materials.

For use as refractories, dolomite is converted to dead-burnt dolomite by sintering it at 1700-1800^{0}C (for achieving higher density, sintering can be continued up to 2000^{0}C). At this temperature the MgO (formed due to calcination of the $MgCO_3$ component) is partially fused to form periclase which is an inert dense and stable product. Dead-burnt dolomite is therefore a mixture of periclase and CaO. For making bricks, this material is crushed and mould-pressed with the help of some binder. Because of the properties of periclase, dead-burnt dolomite refractories can be used both as the initial refractory linings as well as for fettling purposes (repairing damaged patches of linings by applying it in the form of clinker). As a refractory it is inferior to magnesite-based refractories, but it is much cheaper. Moreover, use of one of the magnesium-based refractories namely, chrome-mag, is discouraged in countries like USA, Germany etc. because of environmental reasons (some of the chromites contains hexavalent chromium which is carcinogenic). However, a major disadvantage of dolomite refractories lies in the CaO-content which has a tendency to slake, i.e., form into hydrate, when exposed to moisture making the shelf-life of the refractory shorter. To overcome this problem, dolomite refractories are coated with tar (called *tar-bonded dolomite* refractories) or pitch (called *pitch-impregnated* dolomite refractories). Nowadays, *ceramic-bonded dolomite* and *magnesia-enriched dolomite* refractories are also popular.

When L-D process of steel-making was invented in Austria in the early 1950s, dolomite was chosen as a refractory lining material for L-D vessels. Its use continued till the early 1970s when magnesia-carbon refractories were developed and Japan and a few other countries switched over to them. But, in the late 1970s, with the development of continuous casting technology and secondary refining in ladles, dolomite refractories were found to be an appropriate balance between heat-life and cost per ton of steel (heat-life is the number of heats or cycles of smelting and metal-tapping, that the refractory can withstand). For the same reasons, such refractories became popular in argon-oxygen decarburization (AOD) and vacuum-oxygen decarburization (VOD) processes of stainless steel making and also in rotary kilns for dry processing of cement. Nowadays, pitch-impregnated dolomite refractories are used for lining walls of electric arc furnaces (EAFs) employed for direct reduction of iron.

Specifications:

Quartz changes to beta-quartz at 574^{0}C, then to beta-tridymite (870^{0}C) and finally to cristobalite (1470^{0}C), these changes being accompanied by volume expansion. Each of these forms have their low-temperature forms, and on cooling, changes to the low-temperature forms take place again accompanied by further volume changes. Thus repeated heating and cooling of the refractories containing silica result in cracks. Moreover, at the furnace temperature to which these refractories are subjected, silica reacts with CaO to form beta di-calcium silicate which may undergo rapid inversion to gamma form with considerable expansion and thus reduce the refractory to dust. If, in addition, alumina is also present, then low-melting calcium alumino-silicate is formed at 1100^{0}C temperature itself. Besides, alumina forms silicates (kyanite, andalusite or sillimanite) with increase in specific gravity (from 2.7 of silica to 3.2-3.7 of the silicates) and then mullite at temperatures 1200-1600^0 C, with disturbance of the eutectics and resultant deformation of texture and weakening of the refractory. Hence both silica and alumina are objectionable in both DBM and fused magnesia.

So far as Fe_2O_3 is considered, although it melts at a relatively lower temperature of 1100^0C, a little of it is desirable because it combines with MgO to form magnesium ferrite ($2MgO.Fe_2O_3$) which is a binding agent.

The Bureau of Indian Standards (BIS) has, in 1982, specified two grades of dolomitegrade-I for making tar-bonded dolomite brick for LD converters and grade-II for making tar-bonded dolomite brick for use in blast furnaces and sintering plants and for fettling purpose in open hearth (OH) furnaces. According to the BIS specifications, the grade-I dolomite should contain *CaO 30% (min), MgO 20% (min), SiO_2 2% (max), total acid-insoluble matter 4.5% (max) and size 50-80 mm* while the grade-II dolomite should contain *CaO 28% (min), MgO 1% (min), SiO_2 2% (max), total acid-insoluble matter 8% (max) and size 70-80 mm*. But the specifications of Indian industries with respect to a silica and alumina contents are more stringent. They specify dolomite containing SiO_2 1.7% (max) and Al_2O_3 2.5% (max) and with size-ranges varying from 5-25 mm to 50-80 mm. By using high-purity lumpy dolomite containing less than 3% impurities, as many as 800 heats have been achieved.

3. Glass: Chemically, glass is a mixture of the silicates of sodium, calcium and magnesium. The composition of typical ordinary glass is [$18Na_2O.2MgO.8CaO.72SiO_2$]. Ordinary glass contains 4-5% magnesia and some special glasses may contain up to 15% of it. The magnesium is contributed by dolomite.

Essentially, the manufacturing process of glass consists of melting a mixture of 47% silica sand, 14% soda (Na_2CO_3), 12% dolomite ($CaCO_3.MgCO_3$), 3.5% limestone ($CaCO_3$), 2.5% carbon (coke) and the balance broken waste glass (called cullet) at 1400-1500^0 C, and then cooling it first to a thick viscous liquid at 800-900^0 C. After first neutralizing the original colouring substances present in the charge by adding MnO_2, Sb_2O_3, As, etc., and then forming it into different desired shapes, colours and types, this thick liquid is rapidly quenched so as to prevent devitification to a solid glass product. The CO_2 of the carbonates of calcium and magnesium are expelled at the melting temperature reducing dolomite to CaO and MgO, but at this temperature the MgO does not become inert periclase, and it takes part in the reactions (also see the chapter on silicon).

The role of dolomite is as follows.

(a) The function of the soda, lime and broken glass is to act as fluxes lowering the melting point of silica from 1580^0 C to 1400^0 C. Dolomite provides additional CaO for fluxing purposes.
(b) Lime has a tendency to form crystals and the addition of magnesia lowers the settling rate and thus helps prevention of this devitrification.
(c) Due to the lowering of the settling rate, the change in viscosity is gradual and this facilitates the colouring matters to disperse evenly throughout the melt.
(d) It inhibits chemical attack by atmospheric gases and moisture.
(e) Dolomite imparts resistance to thermal shock and resultant fracturing in the glass.
(f) Dolomite is easier to handle than CaO because in it, CaO and MgO form a strong bond and it is, therefore, more stable than CaO alone.

The most objectionable matter is iron oxide which has a colouring effect. The Bureau of Indian Standards (BIS) has, in 1973, stipulated 0.15% (max) Fe_2O_3, but the industries usually specify a maximum of 0.04% Fe_2O_3, and in some cases even 0.025 percent. The other undesirable impurities are chromium, manganese, vanadium, lead, all of which colour the glass.

4. Magnesium metal: Magnesium metal can be recovered from this calcined dolomite by silico-thermic process. In this process, a mixture of calcined dolomite and 75%-grade ferrosilicon is briquetted and heated in a retort. The magnesium oxide in the calcined dolomite is reduced by silicon, producing magnesium vapour, which is condensed to crystals of 99.8% purity magnesium. The reaction is as follows:

$$2MgO.CaO + FeSi \rightarrow 2Mg + Fe(CaO)_2.SiO_2$$

These magnesium crystals are melted, refined and formed into ingots. For this purpose, the calcined dolomite should be of 200 mesh size and it must contain MgO 40.5%, CaO 58.10% and Fe_2O_3+Al_2O_3 0.8%.

5. Seawater magnesia : Sea water, which contains 0.2 % MgO (equivalent to 1.3 gm per litre of magnesium metal), is a source of high-purity MgO from which both refractory grade dead-burnt magnesite (see chapter on magnesite) and magnesium metal can be obtained (it has been the major source of magnesium since 1937). For recovering MgO, sea water is first treated with calcined dolomite (or calcined limestone). The CaO (from dolomite or limestone) forms $Ca(OH)_2$ and, then, the latter is reacted with the sea water to form $Mg(OH)_2$ which is precipitated using a seed. This $Mg(OH)_2$ cake can be dried at 1000^0 C to get MgO or can be treated with HCl acid to form a 15% $MgCl_2$ solution, which, on electrolysis, yields magnesium metal.

The MgO of the dolomite also contributes to the yield of $Mg(OH)_2$. The essential requirements of dolomite raw material for this purpose are that impurities like iron oxide and alumina in particular are kept to a minimum. They will get carried to the MgO and their presence will create the same problems as explained in the case of refractory.

6. Soil-conditioning: Ground dolomite is suitable for application to acidic soil by virtue of its basicity. It also improves porosity of the soil. Besides, it is a source of magnesium which is an essential element in the chlorophyll ($C_{55}H_{70}MgN_4O_{5\text{-}6}$) of the plants. For this purpose, high grade is not required, but silica is considered deleterious because it increases the grinding cost. Moisture is also objectionable because it adds to the weight. Dolomite is generally applied at the rate of 2-3 tons per acre. However, it suffers from the disadvantage of poor solubility in water.

The industries generally use dolomite containing 15-20% MgO with SiO_2 5% (max.) and with 50% smaller than 100 BS mesh (150 micron) size. However, according to the specifications laid down by the Bureau of Indian Standards (BIS) in 1985, the material should be in size smaller than 2 mm (10 mesh) with 50% smaller than even 250 micron (60 mesh) size; the neutralizing value (expressed as $CaCO_3$ percent by mass) shall not be less than 70%; the total lime and magnesia (as CaO + MgO) shall not be less than 50% by mass; and the maximum limit of moisture content should be 5 percent.

7. Sorel cement: Named after a chemist named Sorel who first invented it in 1853, *Sorel cement* (also called *magnesium oxychloride cement*) having molecular formula

$[(MgO)_2(MgCl_2)(H_2O)_{11}]$ is a rapidly setting cement (sets in 3-4 hours to a very hard cement). After setting, it becomes light and pleasingly brownish orange in appearance. It is resistant to fire and vermin. It can be used in flooring of railway carriages, kitchens and bathrooms, in false roofing, in preparation of adhesive composition and as a thickener in polyester sheet moulding materials where it forms a salt with the carboxylic end groups of the polyester molecules.

In the manufacture of Sorel cement, dolomite is used as a cheap but inferior substitute of magnesite. It is first calcined by driving off all the CO_2 at about 1000^0C, finely ground and then, 100 parts of this MgO is treated with a 100 parts of a strong solution of $MgCl_2$ in presence of 1 part of sodium hexametaphosphate. Sodium hexametaphosphate and excess MgO react to form magnesium polyphosphate complex. The latter is completely insoluble and serves to tie up CaO, which otherwise will tend to absorb water to form $Ca(OH)_2$ (i.e., slake). Thus degradation of the quality of the cement is prevented. Silica is objectionable because, at the calcination temperature, it will react with both CaO and MgO to form silicates.

8. Magnesium oxysulphate cement: *Magnesium oxysulphate cement* is a quick-drying material (hardens in 10 minutes) and is useful for mending cracks in concrete roadways. It is made by first treating the calcined dolomite with calcium sulphate and water to obtain magnesium sulphate heptahydrate ($MgSO_4.7H_2O$) then to a 50% concentrated solution of this, sodium hexametaphosphate, MgO and water are added. The $MgSO_4.7H_2O$, part of MgO and water combine to form a slurry of magnesium oxysulphate ($MgSO_4.5MgO.8H_2O$) or MOS in short. In a parallel reaction, Sodium hexametaphosphate and a part of MgO react to form magnesium polyphosphate complex. The latter is completely insoluble and serves to tie up CaO which is thus prevented from slaking and becoming expansive $Ca(OH)_2$ that tends to degrade the quality of the cement when exposed to humidity. Its properties are similar to those of Sorel cement.

9. Paper: In the sulphite process of paper manufacturing, both CaO and MgO components of dolomite are useful. By mixing water, CaO is converted to slaked lime or $Ca(OH)_2$ and MgO to $Mg(OH)_2$. Then by passing SO_2 gas, they are converted to $CaHSO_3$ and $MgHSO_3$ which are acidic in nature. They together dissolve all the constituents of wood chips except cellulose, but $MgHSO_3$ being more reactive, more soluble and more stable than $CaHSO_3$, increases the efficiency of the process.

In this process, free silica and grit are objectionable because their grindability being poor and they being insoluble, they may affect the smoothness of the finished paper. Iron oxide affects the whiteness of the product because it is a colouring substance and is carried to the final pulp.

10. Leather: In the leather industry slaked lime is used to loosen the hairs of the skin so that they can be removed easily. Lime water softens the epidermal cells and dissolves the mucous layer, thereby loosening the hairs. Dolomite can also be used as a source of lime. Fe_2O_3 is objectionable because it may stain white leather.

11. Pharmaceuticals: In this industry, dolomite is note used directly, but in the form of pure white magnesium carbonate ($MgCO_3$) prepared from it. For this purpose, first, a saturated aqueous solution of dolomite powder is made by passing CO_2 through it under high pressure and simultaneously raising the temperature. As a result, $CaCO_3$ precipitates. The dolomite solution is filtered out and heated to near boiling so that both water and CO_2 are driven out, and crystals of $MgCO_3$ precipitates. This $MgCO_3$ is pure white and it has an average refractive index of 1.5 but is optically anisotropic (i.e., refractive index changes with variations in the orientation of the crystals). Thus obtained $MgCO_3$ is used in pharmaceuticals in the following three ways:

(a) *Excipient*: In pharmaceutical technology, an inert substance added to a drug as a diluent or as a bulking agent or as a carrier is called *excipient*. Up to 45% concentration of dolomite is added to tablets as excipient.
(b) *Flavour*: It is added to medicines as an adsorbent of flavours. The $MgCO_3$ holds the flavour on the surface and slowly releases it. A concentration of 0.5-1.0% is used in this application.
(c) *Intaglio printing*: Its use is for highlighting engraved letters (name, identity, etc:) on a tablet coated with coloured polymer film. The white $MgCO_3$ is sprayed on the surface of the polymer film. While spraying, care is taken so that the crystals of $MgCO_3$ are oriented in such a manner as to match their refractive index with that of the coloured polymer and the sprayed coating appears transparent vis-à-vis the latter, but within the intaglio, the crystals are oriented in the direction of highest refractive index. As a result, the engraved letters appear opaque and prominent.

12. Adhesive: Adhesive is an organic or inorganic substance capable of bonding together other substances by surface attachment. High-purity white dolomite is added to certain adhesives with a view to: (i) adjusting the colour, (ii) reducing shrinkage due to internal stress by virtue of its moderate hardness, and (iii) maintaining flexibility by virtue of its porosity. For high-performance adhesive where even a minute shrinkage associated with cracks is not permissible, dolomite is mixed with calcite. Dolomite is, however, is not suitable to acrylic-based adhesives because the former is basic (pH 10) and latter is acidic (pH 4) and the two react.

13. Construction aggregates: Crushed dolomite is used as a component of concrete aggregates for building and road construction. The ability of CaO to bond with cement and bitumen is the key criterion. With regard to the specifications, they are as follows.

(a) Lumpy clay: In dolomite used for fine cement aggregates for building construction its content should be 1% (max), for coarse aggregates for use in unmetalled roads the limit should be 0.25%, and for aggregates intended for construction of bituminous road it should be 0.5-1 percent.
(b) Soft and unsound fragments like chert, shale, etc.: In dolomite used for building aggregates, it should be 5% (max) while that for road aggregate should be 2-4 percent.
(c) Alkalis: NaCl is hygroscopic and will tend to give off water when dried, damaging the building and road surfaces. It should be as low as possible.
(d) Opal ($SiO_2.nH_2O$): In addition to SiO_2, it also contains 3-9% water and small amounts of some impurities like ferric oxide, alumina, magnesia and alkalis. It is highly undesirable.

(e) Size: Particle-size should be non-uniform so as to form an interlocking bond with the matrix. The size should be 200 mesh-1.5 inches (75 micron-40 mm).

14. Sewage filter: Highly porous bed of dolomite is used for filtering sewage water. The surfaces of the particles should be as uneven and rough as possible because the bacteria get stuck to such surfaces. Silica is not objectionable, but clay matter is because the latter fills up and blocks the pores.

15. Other uses:

(a) *Earthenware wall tile*: This is primarily a product based on ball clay. Glazed earthenware wall tiles are used for the surface of walls where cleanliness is an important factor as in hospitals, kitchens, bathrooms, chemical laboratories, etc. Dolomite is one of the ingredients for opacifying the tiles (see the chapter on ball clay).

(b) *High-magnesium lime*: Here, $CaCO_3$ content in dolomite assumes importance. For this use, dolomite should contain $CaCO_3$ 58-75%, $MgCO_3$ 28-48% and other constituents should be less than 3 per cent.

(c) *Underground coal mine*: Dolomite is used for painting the galleries so as to reflect light and increase illumination, and for retarding coal dust explosion (by virtue of the fire-resistance of MgO). Dolomite for this purpose must be finely powdered so that at least 50% of the particles is smaller than 200 mesh (75 micron) size. Silica is objectionable because it increases grinding cost.

(d) *Filler in fertilizer*: For this purpose, dolomite must be free from colouring impurities such as oxides of iron, chromium, manganese, etc. It is added as a bulking agent and for neutralizing acidity of soil.

(e) *Foundry*: Here, it is used as flux.

WASTE UTILIZATION

Dolochar: In a typical Indian coal-based process of sponge iron manufacturing, iron ore is reduced in solid state, by a mix of coal and dolomite in a rotary kiln at a temperature of about 1100^0C. The output consists of a mix of sponge iron, char and Ca/Mg oxide which is subjected to magnetic separation whereby the magnetic sponge iron is isolated. The nonmagnetic fraction comprising a mixture of char and Ca/Mg oxide is called *dolochar* and generally regarded as waste material. But it seems to have good potentiality for use in brick-making.

Chaspter 20

EMERALD AND ITS VARIATIONS

Emerald ("Panna" in Hindi) is one of the most valuable gemstones. Chemically, it is beryllium aluminium silicate and a variety of beryl ($Be_3Al_2Si_6O_{18}$). Its variations, which are also gemstones – albeit of lesser importance – are aquamarine ("Beruj" in Hindi), heliodor ("Peet Panna" in Hindi), bixbite ("Lal Panna" in Hindi) and morganite or vorobyevite ("Sinduriya" in Hindi). Their differences lie mainly in colour and rarity. Amongst these, emerald is the most time-honoured and sought-after gem. Beryl occurs in granite and pegmatite, and it sometimes develops (as a result of low-pressure regional metamorphic activity) into its gem varieties – particularly emerald in metamorphic talc-biotite schist near its contacts with pegmatite and other acidic intrusions. Emeralds also occur in calcite veins cutting across Lower Cretaceous black shale (as in Muzo, Columbia) and in altered marble (as in the Urals, Russia). The most important sources of emerald in the world today are in Colombia, Russia, Brazil and Pakistan while the other varieties are mined mainly in Madagascar, Nigeria, India, China, Pakistan, Nigeria, Nepal and Brazil (Mainly aquamarine and morganite).

HISTORY

Emerald was known to be sold and purchased in the Babylonian gem market in 4000 BC. Most of the emeralds during the ancient times before 2000 BC were mined from two mines in Egypt, namely Jebel Sikait and Jebel Zabara near the shore of the Red Sea. But those emeralds were mostly of low quality, beset with flaws. Good quality emeralds and its other sister gems like aquamarine, it is believed, came from India as early as in 400 BC. Aquamarine ornaments are known to be in use during the 3rd century BC by the royal families belonging to the Andhra dynasty of South India. During the old civilizations of Incas in Peru and Aztecs of Central America, emerald is believed to be in circulation in barter trade throughout South America. Those stones probably came from the mines of what is now Colombia. The Spaniards rediscovered them after conquest of Mexico (1519) and Peru (1533). Most of the world's best quality emerald supply continues even today to come from Colombia.

There is no definite record of mining of emerald or its sister gems in India during the old times. Evidence of aquamarine mining has been found in Coimbatore district of Tamil Nadu during the early 1800s. Good quality aquamarines were also found in Daso area in Ladakh, Jammu and Kashmir in 1915. Emerald, morganite and heliodor – all three have been mined in Kishangarh, Mewar and Lohargal areas of Ajmer district in Rajasthan. But in the recent times, published statistics are available for only emerald mining in India. Its production has been reported from a couple of mines in Ajmer district till 1982, after which there has been no report of production. But the cutting and polishing industry is well entrenched in the export business, though a little uncut emerald is also exported. This industry depends on imports of mainly uncut emerald, although of late, cut but unpolished stones are also imported for further processing. The growth and status of Indian emerald industry including both mining and processing, are shown in the following table.

Year	Quantity of production crude emerald in carats	Value of import of emerald (mostly uncut) in million rupees	Value of export of emerald (mostly cut and polished) in million rupees
1957	342,000	0.17	Rs. 69000
1960	322,000	2.43	--
1964	553,000	6.23	--
1965	65,000	19.36	--
1970	12,000	45.76	0.68
1975	38,000	41.00	6.30
Year ending March, 1980	7,000	78.43	20.67
Year ending March,1982	8,000	150.22	34.03
Year ending March, 1985	--	143.52	19.62
Year ending March, 1988	--	493.74	555.77
Year ending March, 1995	--	667.89	2,546.47
Year ending March, 2000	--	564.63	3,068.50*
Year ending March, 2002	--	882.74	1,324.81

CRITERIA OF USE

According to Webster’s Second Edition Unabridged Dictionary, gem means any jewel having value and beauty that is intrinsic and not derived from its setting; and gemstones or gem materials are stones or materials from which a gem may be cut. By popular perception, a gem is a rarely encountered hard, durable, brilliantly shining and beautiful natural mineral which has high intrinsic value. Three characteristics of a gem stand out persistently. These are: rarity, durability and beauty. Rarity is an economic function of supply and durability is a measurable physical attribute, but beauty is person-specific carrying different meanings to different individuals, and may include properties like colour, ability to take polish, sheen, size, shape, etc. The unique mineralogical, physical and optical properties besides some peculiar psychological factors go into the usage of the gem varieties of beryl.

(*1) Rarity*: By the law of demand-supply, the scarcer a commodity is , the higher is its value. This is one of the important reasons why high values are attached to gem diamonds. While beryl is a very widespread mineral, it develops the properties of a gem only under very limited geological conditions and in only a few locations. Amongst the five gemstones, emerald is the rarest, and very perfect flawless prices of emerald are still rarer.

(2) Durability: Beryl (and so also its gem varieties) is a hard substance having hardness 7.5-8 in the Mohs scale. Besides, it is practically devoid of any cleavage. This combination of properties gives it resistance to both scratching and breakage. Also, it remains unaffected by acids. All these properties make it durable.

(3) Colour and optical properties: Unlike diamonds, colour is the most important parameter of beauty in the case of emerald and its other varieties, because they, being translucent, have considerably lower refractive index (1.56-1.60 compared to 2.42 of diamond) and lower dispersive power (dispersion is the rate of change of refractive index with change in wavelength of the incident light), and consequently less sparkle. But the translucence renders a soft milky appearance and a unique charm to look at. Their attractive colours are due to the nature, amount and manner of distribution of some impurities or foreign elements which have entered the crystals during their crystallization from molten magma and which are excited differently by different wave lengths of light rays.

The colour of emerald is bright green owing to small amounts of chromium present within it. Aquamarine is bluish green, being an extension of emerald containing greater concentration of chromium. Morganite is rose coloured due to presence of lithium in small amounts, while the red coloured bixbite is an extension of it with higher concentration of lithium. The colour of heliodor may be greenish yellow, iron-yellow, bright golden yellow or honey-yellow (due to presence of small amounts of ferric oxide).

(4) Clarity: Small bubbles, cracks and other flaws reduce the clarity of a gem, and consequently, its value. A clear, flawless emerald is very rarely found while such pieces of aquamarine, morganite, etc. are relatively more easily encountered. The high values of emerald are largely due to this factor.

(5) Cut: Natural gems are mined as rough stones. They need to be cut into well-defined faces and the faces are polished to produce their characteristic sheens and optical effects. The cutting requires a very high degree of skill – particularly when the individual pieces are small. Minimum loss of stone is to be ensured during cutting.

(6) Specific gravity: Although lighter than diamond, ruby and sapphire, nevertheless these beryl gems are moderately heavy, their specific gravity being about 2.7. The value/volume ratio is high for emerald and moderately high for its sister gems.

(7) Caratage: These beryl gems, for that matter, any gem, are bought and used as individual pieces. The larger a gem is, the rarer and, hence, more valuable it is. So the individual weights of the pieces are important for determining their values. While large flawless pieces of aquamarine are common, those of emerald are unknown. Large pieces of emerald, whenever mined, were found to be badly flawed.

(8) Certification: For a common retail buyer, the physical and optical properties of gems carry little sense, and he is most concerned, besides size, with the colour and sheen as judged with naked eyes. But both these characteristics can be replicated by unscrupulous people. So for him certification by some trusted authority or agency assumes importance.

(9) Aggressive marketing: Almost any gemstone can be sold irrespective of colour and cost, provided the basic criterion of rarity is met. Economically, demand of any gem is by and large elastic, i.e., they are luxury items, and not essential in our lives. Consequently, gems do not follow the conventional law of demand and supply according to which, demand generates first and supply follows. On the other hand, in case of gems, supply comes first and demand generates later in response to that. Emeralds and its sister gems are no exception.

(10) Therapeutic value: All these gems are traditionally believed to possess some indirect beneficial effects on body and mind if worn on the body. This branch of therapy known as gemmotherapy works on the hypothesis that different gems, when worn by a man on his body, react differently to different kinds of cosmic rays having different effects on the health of his mind and body. It is a scientific fact that mesons produce cosmic rays which come from outside the earth in varied intensities every minute, and day and night about 600 rays pass through our body. Gemmotherapists believe that each kind of cosmic ray has some specific effect on human health, and each gem modifies these effects by preferentially absorbing or transmitting specific rays. Besides, some gems have been found to produce beneficial effects on human skin.

(11) Beliefs and superstitions: Gems, many people believe, bring luck or misery to lives. Emerald in particular, have been steeped in superstition right from the historical times.

(12) Stability of value: Economic phenomena like inflation, stagflation, recession and even political instability which exercise adverse impact on other manufacturing and processing sectors, do not affect adversely the demand of gems.

USES

These beryl gems are used only as gems, there being no known industrial use for them at present. The only non-gem usage known is that of morganite. Once lenses for fancy eye glasses were made from this rose-coloured stone. But now they are no longer in vogue. The present uses of these gems are as follows.

(1) Ornaments and jewelry: The main demand for beryl gems is for making jewelry. Colour, clarity, cut and durability are the most important criteria. After all these basic criteria are fulfilled, comes the question of caratage or size on which depends the price.

(2) Status symbol: Gemstones are traditionally connected with royalty and aristocracy. In fact, their high costs are a favourable factor. It is important that they should not only be costly, but also appear so. The rarity of a stone plays an important role.

(3) Value storage and liquidity: These gems are high-value low-bulk commodities – more so the emeralds which carry high values. Hence, kings and aristocrats in the past, and now, common men also endeavour to acquire as many of them as they can afford with a view to storing them conveniently for re-sale in times of need. Durability and indestructibility, moderate specific gravity and high value/volume ratio, and stability of value against economic or sociopolitical uncertainties are the principal criteria besides the basic ones like colour, clarity and caratage that determine the value of the roughs.

(4) Therapy:

a) Gemmotherapy: A sizable section of population (elite and common) believe in an unconventional system of healing known as Gemmotherapy, according to which emeralds, when worn on the body as a ring or a locket or in any other form, has a beneficial effect on persons suffering from psychological and some physiological problems of epilepsy, digestion, ear and heart. Clarity and caratage (generally 2-8 carats) of the emerald are very important criteria for this use.

b) Cosmetic skin care: Scrubbing with emerald powder is claimed to help dry and flaky skins to look youthful. This has been an old practice dating back to the times of mythology and more recently to the Mughal period in India.

(5) Superstitious belief: This is a very old use, since fear and superstition have been ingrained in human beings – particularly weak-minded ones. This usage has also been prevalent amongst the rich people and has been promoted since historical times by astrologers.

Chapter 21

FELDSPAR (FELSPAR)

The name feldspar has come from the German “feld” meaning field and “spar” meaning stone. Feldspar is a group of minerals which are primarily high-silica aluminosilicates with varying amounts of sodium, potassium and calcium and a large number of combinations. The common feldspars are orthoclase (potassium feldspar, $K_2O.Al_2O_3.\ SiO_2$), albite (sodium feldspar, $Na_2O.Al_2O_3.6SiO_2$) and anorthite (calcium feldspar, $CaO.Al_2O_3.2SiO_2$**).** Albite and anorthite are completely miscible and one may progressively merge into the other forming an isomorphous series known as plagioclase series with each of them occupying the two end positions. Members of the plagioclase series are:

1. Albite (100-90% albite and rest anorthite)
2. Oligoclase (90-70% albite and rest anorthite)
3. Andesine (70-50% albite and rest anorthite)
4. Labradorite (50-30% albite and rest anorthite)
5. Bytownite (30-10% albite and rest anorthite)
6. Anorthite (10-0% albite and rest anorthite)

Out of the feldspar minerals, only orthoclase is monoclinic while the rest are all triclinic. But, there are two triclinic variations of orthoclase, namely, microcline and anorthoclase (contains sodium in addition to potassium). Hyalophane and celsian are two relatively rare barium-containing feldspars.

Feldspars especially orthoclase are the most abundant rock forming minerals in the earth’s crust making up about 60% of igneous, 30% of metamorphic and 10% of sedimentary rocks. The sodium- and potassium-bearing acidic feldspars are common in acidic rocks like granite, pegmatite, syenite, etc., while the basic calcium-bearing ones are found in basic rocks like basalt, gabbro, etc.

From the economic point of view, the most significant are the two potassium feldspars (orthoclase and microcline) that occur as segregations in large masses. Generally, microcline is included in orthoclase as they cannot be differentiated without microscopic examination. Some of the other varieties have only some minor uses. In the commercial circle, orthoclase (including microcline) is generally understood by the name feldspar. Massive quantities of feldspar of commercial importance are mostly found in pegmatite, which is its main source.

HISTORY

In India, the history of mining of feldspar from pegmatites of Rajasthan and Karnataka is as old as the pottery and porcelain industries of Delhi, Gwalior, Hassan, Bangalore and Mysore areas. But the first record of organized mining dates back to 1904 when Burn and Company started its quarrying operations in Lameta Ghat near Jabalpur in central India. However, official records of production are available since 1930. Since then the history of production can be tracked from the following table.

Year	Production
1930	390 tons approximately
1935	665 tons approximately
1945	950 tons approximately
1950	1,800 tons
1960	10,613 tons
1968	35,261 tons
1970	34,568 tons
1980	60,190 tons
1990	64,794 tons
Year ending March 2001	179,574 tons
Year ending March 2006	322,929 tons

World production has increased from about 600,000 tons in 1944 to tons to 13 million tons in 2000.

CRITERIA OF USE

The properties relevant to different industrial uses of feldspars are as follows.

1. *Chemical characteristics:* The potassium feldspars orthoclase and microcline ($K_2O.Al_2O_3. SiO_2$) theoretically contain 64.7% SiO_2, 18.4% Al_2O_3 and 16.9% K_2O. In nature, potassium feldspars also contain some soda. They are a ready source of alumina in certain processes. They are resistant to acids. Oil absorption is low.
2. *Colour and optical properties:* The common colours of orthoclase are white and flesh red; cream, buff brown, red , green, etc. colours are also rarely seen. Plagioclase feldspars show different colours depending on the relative amount of sodium and calcium and also inclusion of other foreign constituents like hornblende, hypersthene and magnetite; they often show a rainbow-like play of colours (e.g., albite, labradorite). Lustre is vitreous to pearly. Refractive index of orthoclase varies from 1.5194-1.525 (c.f., linseed oil 1.48, ordinary glass 1.53, diamond 2.42).
3. *Physical properties:* Specific gravity of commercial orthoclase ranges from 2.56-2.58, and hardness of all the feldspars varies from 6.0-6.5 (depending on content of soda). Orthoclase breaks in sub-conchoidal to conchoidal fracture pattern.
4. *Thermal property:* Commercial orthoclase melts at temperatures varying from 1225-1260^0C. The higher the content of soda, the lower the melting temperature (pure

albite melts at 1100^{0}C). It is an effective flux for materials melting at higher temperatures.

5. *Electrical properties:* Orthoclase, and to a lesser extent sodium feldspar, has the ability to stabilize electric arc.

USES AND SPECIFICATIONS

Before using, some of the natural feldspars are subjected to processing for removal of iron compounds, mica and quartz which are considered deleterious in many uses. The principal uses are :

1. Ceramics and glazing
2. Bone China
3. Glass
4. Enamel
5. Abrasive
6. Refractory
7. Welding electrode
8. Gem

These are discussed as follows.

1. Ceramics and glazing: The word "ceramic" derived from Greek originally meant fired and fused common clays. But in modern usage it includes some other inorganic materials mixed with clays in different forms (common clay, china clay, ball clay etc.) which are fired together and fused, though clay still remains the core component. The original ceramic products (e.g., bricks, potteries) made only of clay were hard and resistant to heat and chemicals, but at the same time porous and brittle. Today, ceramic products are not only hard and resistant to heat and chemicals but also nonporous and strong, and the product range includes stoneware crockery, vitreous tiles, sanitary ware, ceramic tower packing materials (rings, saddles, honeycombs, etc. used for processing and storing chemicals), water filter candle and porcelain.

Manufacturing process: The principle of the manufacturing process, in essence, consists of mixing quartz or silica sand, one or more types of clay, feldspar and some flux (soda) with 30-40% water. This mixture is ground, thoroughly agitated, filter pressed, moulded into the required shape, dried and then fired to a temperature ranging from 1200-1500^{0}C depending on the product hardness required. Different ceramic products can be prepared by varying the types of clay and their proportion in the mixture. The role of orthoclase feldspar is to adjust the fusion temperature of the raw material mix by virtue of its intrinsic alumina content and also its usual impurity soda.

Specifications: Alumina, which is an integral constituent of the feldspar (as also of the clay), has some advantages. Although it has a high melting point, but at even below the firing temperature (1300^0C) it melts imperfectly to become a highly viscous fluid, facilitating a coherently bonded non-porous product.

Fe_2O_3 and TiO_2 (over a period of time) make the product coloured and so they are objectionable. Besides, TiO_2 has a high melting point and it will unnecessarily increase the firing temperature.

Alkalis are deleterious. Sodium and potassium in the form of carbonates combine with silica at the firing temperature to form silicates which are water soluble. Presence of these silicates in the ceramic product, obviously, will not be desirable.

MgO is highly refractory in nature and so is undesirable in white ware, because white wares, by definition, are non-refractory in nature. Besides, it is hygroscopic, absorbing 120% of its volume of water slowly over a period of time.

Lime (CaO) is highly hygroscopic. So, if it is present in clay, the product will absorb water ourse of time on exposure, and ultimately, crumble. Also, at 1100^0 C (i.e. below the firing temperature), CaO reacts with alumina and silica and forms new compounds, mostly silicates. Some of these silicates lower the fusion point of clay. Moreover, lime makes the melt more fluid and it reduces the range between softening and flowing temperature. Sometimes this range may be as short as 40^0C only. The result is that it becomes difficult to control the temperature of the furnace to remain within this range. For these reasons, lime is very objectionable.

The Bureau of Indian Standards (BIS) has, in 1981, stipulated the specifications as: *Fe_2O_3 0.5% (max), CaO + MgO 1.0% (max), K_2O (in the form of alkalis) 9% (max), Na_2O (in the form of alkalis) 6% (max), K_2O + Na_2O (both in the form of alkalis) 13% (max), and PCE 8 to 10 (roughly equivalent to 1300^0C).* However, the Indian industries use feldspar of different qualities for different products as follows:

(a) Sanitary ware : K_2O (in the form of alkalis) 11-14%, Na_2O (in the form of alkalis) 2-7%, Fe_2O_3 0.25% (max)
(b) Insulators : K_2O (in the form of alkalis) 11-12.5%, Na_2O (in the form of alkalis) 4% (max.), Fe_2O_3 0.48% (max)
(c) Ceramic Tiles : K_2O (in the form of alkalis) 9%, Na_2O (in the form of alkalis) 4%, K_2O+Na_2O 14% (max.)(Both sodium and potassium feldspars are used)
(d) Crockery ware : K_2O (in the form of alkalis) 12.15%, Na_2O_3 3.7% , Fe_2O_3 0.10%

Glazing: If the product is to be a glazed one, then it is glazed before firing. The purpose of glazing is to provide a uniform firmly adhering coating on the surface of the ceramic body concealing defects such as pinholes, bubbles, etc. The glaze is made of the same ingredients but with a predominance of quartz and feldspar. The ingredients are mixed, finely ground and mixed with water, and this mixture is the glaze. The moulded raw body of the product is dipped into the glaze and then fired to a temperature of about 1400^0 C. Colours and decorative designing, if required, are painted after glazing and before firing.

Glaze may be "*raw glaze*" or "*fritted glaze*". Raw glaze consists of insoluble material applied as such (soluble components crystallize in the mixture and cause blemishes on the treated surface), while fritted glaze is heated beforehand to cause chemical change in the components. Glaze should not only melt but also spread uniformly.

Here also the role of feldspar is to adjust the fusion temperature of the raw material mix by virtue of its intrinsic alumina content and also its usual impurity soda. Fe_2O_3, CaO and alkalis are the most objectionable constituents for the same reason as in the case of the ceramics.

2. Bone China: Bone China is a special translucent variety of glazed porcelain first introduced in England in 1794. It is a sophisticated fine product using tri-calcium phosphate [$Ca_3(PO)_2$] obtained by burning bone, as the most fundamental raw material. The bone ash in the right proportion acts as a flux, but when in excess, it increases refractoriness. Some of the lime of bone first reacts with china clay to form anorthite, while the P_2O_5 reacts with other compounds to form glass. For making bone ash, cattle bone is first crushed, washed and then subjected to heating in a highly oxidized condition by slowly increasing the temperature to 900-1000^{0}C, whereby most of the organic matter is removed. The calcined bone is ground with water to a very fine size, allowed to age for a few days, and then dried to a moisture content of 10-15%. This bone ash contains a little organic matter which, combined with fine size, gives it some plasticity. The industry prefers the ash of cattle bone because it is iron-free.

For manufacturing Bone China, the raw material mix consisting of 45-50% bone ash, 25-30% china clay, 25-30% feldspar (flux) and about 5% ball clay (plasticizer) is first mixed with water and ground; then the slurry is de-watered by filter-pressing, shaped according to the product desired and slowly dried, and finally biscuit fired at a temperature lying within a carefully controlled short range of 1250-1300^0 C.

The biscuit is then glazed using colourless transparent glaze. The glazing material consists of borosilicate and white-burning china clay with some feldspar to act as a flux. China clay helps the glaze to remain in suspension. Glaze is applied to the biscuit by either dipping or spraying, and then fired at a temperature 1050-1100^0 C, i.e., lower than the biscuit firing temperature.

The firing temperature—both at biscuit and glazing stages—is very critical in case of Bone China. Under-firing leaves open pores and cannot bring the all-important translucency, while over-firing produces blisters on the surface. And it is for this reason that the role of feldspar becomes very important.

3. Glass: Physically, common standard glass is an amorphous, hard, brittle and transparent substance and chemically, it is a mixture of the silicates of sodium, calcium and magnesium. The composition of typical ordinary glass is [$18Na_2O.2MgO.8CaO.72SiO_2$].

Essentially, the process of manufacture of glass consists of melting a mixture of silica sand, soda (Na_2CO_3), dolomite ($CaCO_3.MgCO_3$), limestone ($CaCO_3$), carbon (coke) and broken waste glass (called cullet) at 1400-1500^{0}C, and then cooling it first to a thick viscous liquid at 800-900^0 C. The function of carbon is to combine with the excess oxygen and to provide heat while the soda, lime and broken glass act as fluxes lowering the melting point of silica from 1580^0 C to 1400^0 C. Feldspar is also added to the charge as a source of alumina for process control and for supplementing soda for fluxing. Matching of the refractive indices of feldspar and glass is an additional advantage. Green-coloured microcline is used for making green glass.

Alumina, which is an integral constituent of the feldspar, has some advantages. Although it has a high melting point, but at even below the firing temperature, it melts imperfectly to become a highly viscous fluid and, thus, prevent devitrification. However, its supply has to be carefully controlled by adjusting the total feldspar added. Similarly, though some alkali is beneficial to supplement the fluxing action of the soda in the raw material mix, excess Alkali will affect both the process and the composition of the glass and so its content beyond a limit is not desirable in the feldspar.

Lime has a tendency to form crystals, and one of the functions of MgO is to prevent this. By combining with the lime. So additional CaO getting into the melt through feldspar is undesirable, and CaO is considered a deleterious constituent in the feldspar. Excess MgO will also affect the final composition of the glass. Fe_2O_3 is a colouring matter and is also deleterious.

The specifications stipulated by the BIS in 1981 with respect to iron and alkali are: *CaO + MgO 1.0% (max), Fe_2O_3 0.5% (max), K_2O (in the form of alkalis) 9% (max), Na_2O (in the form of alkalis) 6% (max), K_2O + Na_2O (both in the form of alkalis) 13% (max)*. For high-quality glass the industries limit the Fe_2O_3 to 0.3 percent.

4. Enamel: Chemically, enamel is a complex mixture of silicates, borates and fluorides of some metals like sodium, potassium, aluminium etc. It is a glaze coating on metallic surfaces so as to give protection to the latter against high temperature and corrosion. It is prepared by mixing borax ($Na_2B_4O_7.10H_2O$), quartz, feldspar, fluorspar, soda (Na_2CO_3), sodium nitrate, oxides of cobalt, manganese and nickel and an opacifier substance (e.g., tin oxide, titanium silicate, antimony trioxide). In this mixture, borax (23-34%), quartz (5-20%) and feldspar (28-52%) are the dominant components. This mixture is ground, melted and quenched in water to yield a glassy mass. To this glass are added clay and more quartz powder and the mixture is finely ground to powder and made into a slurry with water. This is called *"enamel slip"*. Metallic objects are dipped in it and fired to about 900^0 C. Two to three such enamel coats are usually applied. Colour effects can be produced by addition of colouring oxides of metals (e.g., iron, chromium, cobalt, uranium etc.) to the melt before it is quenched. Role of feldspar is primarily as a fluxing agent and also as a source of alumina.

5. Abrasive: Hardness and sub-conchoidal to conchoidal fracture makes it suitable as a mild abrasive for use as a scouring material. An added advantage is that the silica in the powder is in a combined state (and not in a free state) which makes it health-friendly (free silica powder can cause silicosis). It is also used in vitrified grinding wheels made of clay-feldspar bond.

6. Refractory: Refractory materials are defined as those resistant to heat and having a melting temperature of not less than 1580^0 C. The function of refractory lining on a furnace wall is not only to withstand high temperature, but also to withstand temperature fluctuation, and to resist penetration, abrasion, and erosion by hot gases and molten materials in the furnace. Feldspar as such is not a refractory material, but it has strong resistance to acids, and it is added to fireclay to increase acid-resistance of firebricks.

At high temperatures, free silica reacts with CaO to form beta di-calcium silicate which may undergo rapid inversion to gamma form with considerable expansion resulting in crumbling of the refractory. Besides, lime itself lowers the fusion temperature and it also reacts with the alumina of the feldspar forming low-melting calcium alumino-silicate. Hence both free silica and alumina are objectionable. Fe_2O_3 melts at a relatively lower temperature, and hence it is also objectionable. Alkalis also lowers the fusion temperature, and hence is deleterious. The Indian industries specify less than 1.5% Fe_2O_3 and 11-12% Na_2O_3+K_2O (derived from the alkalis) in the feldspar.

7. Welding electrode: According to the definition of the American Welding Society, "Welding is a metal-joining process wherein coalescence is produced by heating to suitable temperature with or without pressure and with or without the use of filler metal". The mechanism of welding is based on electron emission. In this, the electron discharge takes place in the form of an arc. When electricity is passed though two electrodes (cathode and anode) in contact with each other, and then the contact is broken by moving them a little away, the resistance and consequently the potential, increases so much that the tips of the electrodes begin to glow. The temperature at the tips increases rapidly, and electron emission takes place. The high energy electrons associated with the temperature ionizes the air in the gap between the electrodes. This ionized air becomes an electrical conductor and current flows from one electrode to the other. This is the mechanism of arc discharge. The temperature of the arc may be of the order of thousands of degrees (20,000-50,000^{0}C). If the broken pieces of a metal are placed in the arc, then they will fuse and join together, and this process is known as welding. The most common type of welding is arc welding. In this, electrodes made of rods of covered metal are used. The covering serves both electrical and metallurgical purposes. Electrically, the covering insulates the rod from accidental contact with adjacent material; metallurgically, the covering may provide gas- and slag-forming ingredients to protect the weld from the air, and it may also supply de-oxidizers or alloying material resulting in sound welds.

The strong ability of orthoclase to stabilize electric arc and also to act as a fluxing agent are the key. In arc welding, finely ground (60-200 micron) orthoclase constitutes 5-10% of the coating mixture of the electrodes. It forms a low-melting slag, which covers the weld metal protecting it against oxidation. It also stabilizes and smoothens the electric arc. Fe_2O_3 is the most objectionable constituent, because it reduces to iron which causes generation of eddy currents, destabilizing the arc. Indian industries specify the maximum limit of 0.3% Fe_2O_3. Indian industries prefer low-soda feldspar containing 1-3% Na_2O, but in some countries sodium feldspar is used. Sodium feldspar is less effective as an arc-stabilizer, but more effective as a fluxing agent.

8. Gem: Gem includes both precious and semiprecious stones. The criteria that make a gem are:

(a) *Rarity*: By the law of demand-supply, the scarcer a commodity is, the higher is its value.
(b) *Durability*: The combination of hardness, toughness and acid-resistance makes a stone durable.
(c) *Colour and optical properties*: Colour, lustre and optical dispersion are the most important parameter of beauty.
(d) *Clarity*: Small bubbles, cracks and other flaws reduce the clarity of a gem, and consequently, its value.
(e) *Cut*: Natural gems are mined as rough stones. They need to be cut into well-defined faces and the faces are polished to produce their characteristic sheens and optical effects. The cutting requires a very high degree of skill, particularly when the individual pieces are small. Minimum loss of stone is to be ensured during cutting.
(f) *Specific gravity:* The value/volume ratio depends on this parameter.
(g) *Caratage:* The larger a gem is, the rarer and, hence, more valuable it is. So the individual weight of a piece is important for determining its value.
(h) *Certification*: For a common retail buyer, the physical and optical properties of gems make little sense, and he is most concerned, besides size, with the colour and sheen as judged with naked eyes. But both these characteristics can be replicated by

unscrupulous people. So for him certification by some trusted authority or agency assumes importance.

(i) *Aggressive marketing*: The demand of gems being elastic, almost any gemstone can be sold irrespective of colour and cost, provided the basic criterion of rarity is met.
(j) *Therapeutic value*: Gems are traditionally believed to possess some indirect beneficial effects on body and mind if worn on the body. This branch of therapy known as gemmotherapy works on the hypothesis that different gems, when worn by a man on his body, react differently to different kinds of cosmic rays having different effects on the health of his mind and body. Besides, some gems have been found to produce beneficial effects on the human skin.
(k) *Beliefs and superstitions:* Gems, many people believe, bring luck or misery to lives.
(l) *Stability of value*: Economic phenomena like inflation, stagflation, recession and even political instability which exercise adverse impact on other manufacturing and processing sectors, do not affect adversely the demand of gems, particularly the high-value ones.

Feldspar actually does not qualify to be a precious stone, but some of its varieties are marketed as semiprecious stones after cutting and polishing, the main criteria being durability due to moderate hardness and acid resistance, vitreous to pearly lustre, attractive colours and therapeutic value as claimed by gemmotherapists. The gems are:

(a) *Amazonite ("Sifri" in Indian language)*: It is the green-coloured microcline.
(b) *Moonstone ("Chandrakanta" in Indian language)*: It can be any of the plagioclase feldspars which shows rainbow-like play of colours. Gemmotherapists claim that moonstone, when worn on body, can mitigate epilepsy and heart and gastric problems.
(c) *Sunstone ("Atoshi" in Indian language)*: It can be any of the plagioclase feldspars which shows bright shining yellow colour.

9. Other uses:

(a) *Non-skid dust*: Ground feldspar is used as non-skid dust for sprinkling on oily floors.
(b) *Paint*: Feldspar is used as an extender and a filler because of its colour, lustre, refractive index (near to that of linseed oil), acid-resistance, low oil absorption and low cost.
(c) *Plastics*: The hard silicate in the form of feldspar improves abrasion resistance and weather resistance of plastics.
(d) *Battery*: Addition of a small amount of feldspar helps in stabilization of the current flow.
(e) *Coal washing*: Used as an additive to magnetite to adjust the specific gravity of the medium.
(f) *Steel alloy*: Used as a flux
(g) *Dentistry*: High-purity feldspar is used in making an artificial tooth.
(h) *Source of potash*: (Discussed in the chapter on potash).

Chapter 22

FLUORITE (FLUORSPAR)

Fluorite (also called fluorspar) is a *mineral* composed of *calcium fluoride,* CaF_2. The name is derived from the Latin word “fluere” meaning “to flow”, because it melts very easily to a free-flowing liquid. In fact, the name of the element fluorine is named so because it is a major constituent of fluorite. Fluorine is widespread in different compounds but not found in free state due to its strong chemical affinity. Its crustal incidence has been estimated to be 597 ppm and the seawater contains 1.3 mg/litre. The important minerals containing fluorine are:

(a) Fluorite (CaF_2)
(b) Fluor-apatite [$3Ca_3(PO_4)_2.Ca(Cl,F)$]
(c) Cryolite (Na_3AlF_6)

Of these, fluorite is commercially the most significant.

Fluorite is a common mineral in deposits of *hydrothermal* origin, as a primary mineral in granites and other igneous rocks and as a common minor constituent of dolomite and limestone. It may also occur as a vein deposit, especially with metallic minerals, where it often forms a part of the gangue and may be associated with galena, sphalerite, barytes, quartz, and calcite. Fluorite is a widely occurring mineral. Notable deposits occur in Germany, Austria, Switzerland, England, Norway, Mexico, Kenya, USA and Canada. At Wagon Wheel Gap, Colorado, USA, fluorite is a major constituent of hot spring deposits. It is also sometimes found in pegmatite.

HISTORY

Fluorite fascinated people all along due to its attractive colours and other optical properties. But its first practical use can be traced to 1670 when glass was etched with the help of a natural substance then called *Bohemian emerald*. Later, it was found out to be a calcium compound which was named fluorite by Scheele in 1771 due to the ability of its melt to flow freely. In 1811, Andre Marie Ampere (whose name is associated with ampere, the unit of electric current) prepared an acid analogous to HCl-acid from this compound and he named its element fluorine. Though other compounds of fluorine were prepared during the subsequent years, fluorine eluded isolation due to its strong chemical affinity. In 1869, George Gore was able to separate the gas by electrolysis of HF-acid, but the liberated fluorine and hydrogen immediately reacted explosively. A practical method of isolating fluorine was first developed in 1886 when the Nobel Laureate French chemist Ferdinand Frederic Henri Moissan successfully and safely electrolyzed a mixture of potassium fluoride (KF) and HF-acid in a platinum cell.

Until World War II (1939-1945), there was no commercial production of fluorite. It received a boost during the war due to its utility in uranium refining and enrichment. In 2001, the world production stood at 4.3 million tons with China accounting for more than half of it, other important producers being Mexico, South Africa, Mongolia and Russia.

In India, there was no record of production until 1960, when some hand-sorted or graded product started being produced. Production of beneficiated concentrate commenced later in 1970. The growth of production is as follows.

Year	Graded fluorite	Concentrate
1961	332 tons	Nil
1966	2,089 tons	Nil
1970	4,979 tons	1,528 tons
1980	4,236 tons	17,101 tonn
1990	5,715 tons	25,953 tonn
Year ending March, 2005	6,291 tons	7,717 tons

Graded fluorite is produced in Rajasthan and Maharashtra while concentrates are produced in Gujarat only. High grade fluorite is, however, not produced in India.

PROCESSED GRADES

Crude fluorite is processed by both hand-sorting and beneficiation. For hand-sorting, the mineral is crushed to around 10 mm size pieces that can be visually discerned by labourers. But this is suitable when the run-of-mine grade is relatively high to enable the workers to visually identify the mineral and a not very high grade output is desired. For getting high grade output from finely disseminated low-grade mineral, beneficiation by flotation is employed. Also, the flotation process makes it possible to recover lead and zinc values if associated with the fluorite. The chemical process involving acidulation is employed for recovering fluorite from phosphate rock.

In India, the cut-off grade for hand-sorting is 30% CaF_2 while the mill-feed grade for beneficiation is 24% ± 5% CaF_2, 3-5% $CaCO_3$, 0.7-1.7% P_2O_5 and 55-65% SiO_2. The output after processing is standardized in terms of three marketable grades as follows.

1. Acid or chemical grade: This grade of fluorite should ideally contain a minimum of 97% CaF_2 and up to 1.5% SiO_2. For ordinary products, however, 93% CaF_2 is acceptable as in India.
2. Ceramic grade: For high-quality ceramic products, fluorite containing a minimum of 95% CaF_2, up to 2.5% SiO_2 and up to 1.5% $CaCO_3$ is generally considered standard in USA. But strictly speaking, there is no standard grade and it is highly variable

depending on the quality of the finished product, and for very ordinary cheap products, low grade fluorite can also be used.

3. Metallurgical grade: This grade is expressed in terms of what is called *effective units of* CaF_2. Effective CaF_2 is determined by subtracting 2.5 units for every unit of SiO_2. Determined thus, the effective CaF_2 should be at least 60 per cent, which is the same as 80% CaF_2 and 8% SiO_2. But the maximum grade can go beyond 97% CaF_2 with maximum 1% SiO_2.

CRITERIA OF USE

1. Crystal form: Fluorite is an *isometric* mineral with a cubic habit, though octahedral and more complex isometric forms are not uncommon. Cubic crystals up to 20 cm across have been found at Dalnegorsk, Russia.

2. Thermal properties: It melts at quite a high temperature of 1360^0C, but once melted, it becomes a free-flowing low-viscosity liquid (the name “fluorite” has come from this property).

3. Physical properties: Its hardness is 4, and it is brittle. Its specific gravity 3.18.

4. Optical properties: The refractive index of fluorite is low 1.433 (c.f., ordinary glass 1.53; diamond 2.42). Fluorite is transparent to sub-translucent and has a vitreous lustre. It is characterized by very low dispersion so light diffraction is far less than ordinary glass.

5. Colour: It is found in a wide variety of colours and in different shades, so much so that some people refer to fluorite as "the most colourful mineral in the world". The range of common colours for fluorite starts from the hallmark colour purple, then includes blue, green, yellow, colourless, brown, pink, black and reddish orange. The colour in fluorite is commonly banded and is usually due to the presence of hydrocarbons (petroleum), but a study of the Ambadongar fluorite deposit of Gujarat, India has revealed that it is due to colloidal calcium activated by nuclear bombardment. The colour may fade to white if heated to 150^0C, but, on cooling, again returns to some extent. It has a distinctive iridescence. The rarer colours of pink, reddish orange (rose) and even black are usually very attractive and in demand. Most specimens of fluorite have a single colour, but a significant percentage of fluorites have multiple colours which are arranged in bands or zones that correspond to the shapes of the crystals (for example, in case of a cubic fluorite, the colour zones are in cubic arrangement). A fluorite crystal can have a clear outer zone allowing a cube of purple fluorite to be seen inside; sometimes the less common crystals such as a coloured octahedron may be seen inside a colourless cube. One crystal of fluorite may potentially have four or five different colour zones or bands.

6. Fluorescence: Many substances easily gain energy and emit light without being heated very much. They do this through a process called *luminescence*. Atoms of some luminescent materials stay excited for some time before they de-excite and consequently, they glow in the dark long after they have received extra energy. They are called *phosphorescent*, and those emitting light only during their exposure to exciting energy are called *fluorescent*. Fluorite occasionally fluoresces light blue in long-wave ultraviolet light. In fact, the phenomenon we call fluorescence was coined by George Stokes who first discovered this property in fluorite, and the word fluorescence was derived from fluorite since specimens of fluorite were some of the first fluorescent specimens ever studied (c.f., opalescence associated with opal).

Fluorescence involves the elevation of electron energy levels by quanta of ultra-violet light, followed by the progressive falling back of the electrons into their previous energy state, releasing quanta of visible light in the process. The blue fluorescence has been attributed to the presence of europium ions, yttrium is the activator for the yellow fluorescence and the green and red fluorescence are believed to be due to a combination of rare earth elements, manganese, uranium etc.

Like the normal light colours of fluorite, its fluorescent colours are extremely variable. Typically it fluoresces blue but other fluorescent colours include yellow, green, red, white and purple. Some specimens have the added effect of simultaneously having two different colours under long and short wave UV light, and some will even demonstrate *phosphorescence* in a third colour. Thus there can be four possible colour luminescence in one specimen.

A variety of rare fluorite called *chlorophane* can demonstrate another property, thermo-luminescence, which means that it will glow when heated (even if it is activated by a person's own body heat when held in hand in a dark room, its glow can be seen). The thermo-luminescence of chlorophane is green to blue-green (in fact, the word “chlorophane” means “show green”). Once seen, the glow will fade away and can no longer be seen in the same specimen again.

7. Chemical characteristics: Fluorite is a halide mineral having composition CaF_2 consisting of 51.1% Ca and 48.9% F. Yttrium and caesium may substitute calcium. Fluorite is decomposed by sulphuric acid to form free hydrofluoric acid.

8. Fluorine: Fluorine is a pale yellow, highly poisonous and violently reactive gas. It reacts with practically all inorganic and organic substances; finely divided metals, glass, ceramics, carbon and even water burns in it; its reaction with hydrogen is explosive. But, when combined with other elements, it forms useful compounds that are highly resistant to chemical and physical attacks.

USES AND SPECIFICATIONS

Fluorite has few primary uses, one of which is hydrofluoric acid. There is a number of uses of this acid and its derivatives. The principal uses are therefore grouped under those based on the primary mineral fluorite, those on its principal derivative hydrofluoric acid, those on the latter’s derivative fluorine gas and those based on a mix of these. They are:

A. Uses based directly on fluorite

1. Flux in metallurgy
2. Ceramics
3. Enamel
4. Optics
5. Cement
6. Gem
7. Hydrofluoric acid

B. Uses based on hydrofluoric acid
  1. Chemicals
    (a) Synthetic cryolite
    (b) Fluoro-silicic acid
    (c) Aluminium fluoride
    (d) Chloro-fluoro-carbons
    (e) Potassium fluoride
    (f) Fluoro-boric acid
    (g) Fluorine gas
  2. Industrial processes
    (a) Aluminium metallurgy
    (b) Niobium-tantalum metallurgy
    (c) High-octane petroleum

C. Chemicals and processes based on fluorine
  1. Potassium perchlorate
  2. Anhydrous hydrogen fluoride
  3. Sodium silico-fluoride
  4. Uranium hexafluoride
  5. Fluoro-silicates of ammonium, magnesium and zinc
  6. Fluoro-carbon
  7. Fluoro-polymer
  8. Sodium fluoride
  9. Stannous fluoride
  10. Sodium mono-fluoro-phosphate
  11. Uranium metallurgy

D. Uses based on a mix
  1. Glass

These are discussed as follows.

A. End-uses of fluorite

1. Flux: In iron- and steel-smelting, it is added to the slag with a view to increasing its liquidity so that it can flow freely. For the same reason, it is used in iron foundry industries and in welding rod coating. A liquid slag is also more efficient in the removal of sulphur and phosphorus. With regard to specifications, the Bureau of Indian Standards (BIS) has prescribed in1981 the parameters for ordinary products as: *80% (min) CaF_2, 8% (max) SiO_2, 3% (max) $CaCO_3$, 3.5% (max) R_2O_3, 0.3% (max) S and Pb each*. In case of special products, the parameters are: *85% (min) CaF_2, 6% (max) SiO_2,* the rest being same. Some of the Indian industries sometimes specify two additional parameters 1% (max) P_2O_5 and 0.5% $BaSO_4$, while some others use as low as 70% CaF_2. The consumption norms of fluorite per ton of steel are 1.6-1.8 kg in open hearth furnace and 4 kg in electric arc furnace.

2. Ceramics: Fluorite is used as an opacifying agent for glazed pottery, cooking utensils, etc. by virtue of its low refractive index (1.433). The refractive index of most glazes is around 1.5 and the covering power of an opacifier mainly depends on the difference between the refractive indices of it and that of the glaze. For this purpose, the Indian industries use low grade fluorite containing 60-80% CaF_2.

3. Enamel: Enamel coating used to be very common in earlier times, but nowadays various superior alloys like stainless steel, etc. have made it obsolete. Chemically, enamel is a complex mixture of silicates, borates and fluorides of some metals like sodium, potassium, etc. It is a glaze coating on metallic surfaces so as to give protection to the latter against high temperature and corrosion. It is prepared by mixing borax ($Na_2B_4O_7.10H_2O$), quartz, fluorite, soda (Na_2CO_3), sodium nitrate, oxides of cobalt, manganese and nickel and an opacifier substance (e.g., tin oxide, titanium silicate, antimony trioxide). In this mixture, borax (23-34%), quartz (5-20%) and feldspar (28-52%) are the dominant components. This mixture is ground, melted and quenched in water to yield a glassy mass. To this glass are added clay and more quartz powder and the mixture is finely ground to powder and made into a slurry with water. This is called *"enamel slip"*. Metallic objects are dipped in it and fired to about 900^0C. Two to three of such enamel coats are usually applied. Colour effects can be produced by addition of colouring oxides of metals (e.g., iron, chromium, cobalt, uranium, etc.) to the melt before it is quenched.

The role of fluoride is to increase the liquidity of the molten mixture and to impart opacity to the enameled surface. The specifications prescribed for it by Indian user industries are CaF_2 95% (min), SiO_2 2.5% (max), Fe_2O_3 0.12% (max) and $CaCO_3$ 1% (max).

4. Optics- Fluorite was once used for optical lenses, but these have been replaced by synthetically prepared crystals of calcium fluoride. It is used instead of glass in some high performance telescopes and camera lens elements to focus infrared light. Also, exposure tools for the semiconductor industry make use of fluorite for the optics of the 157 nm wavelength, a wavelength created by exciter laser using fluorine gas. Fluorite has uniquely high transparency at this wavelength. Fluorite has very low dispersion, and so light diffraction is far less than ordinary glass. In telescopes with even high-power fluorite lenses, images of astronomical objects are very clear and well-defined.

5. Cement:: According to research carried out by the National Council for Cement and Building Materials (NCBM), India, crushed fluorspar can be added to the cement clinker (see the chapter on limestone) and then ground to ultra-fine size along with the latter. Fluorite is used for giving colouring and fluorescing effects and iridescence. For this purpose, the Indian industries use fluorite containing as low as 20% to about 75% CaF_2 depending on the effect required.

6. Gem: Although low hardness (4 on Mohs scale), brittleness, low refractive index (1.433 compared to 2.42 of diamond), low dispersion and good cleavage that makes fluorite prone to break easily, do not go well for people to rate it as a precious stone, nevertheless, its attractive multiple colours with zoning, iridescence and fluorescence have been attracting people since long as a semiprecious gem for ornamental carvings. The green-coloured fluorite has sometimes been misleadingly called *green quartz*. Large crystals are used for carving decorative vases and dishes.

One of the most famous of the older-known localities of fluorite is Castleton in Derbyshire, England, where, under the name *Derbyshire Blue John*, purple-blue fluorite was extracted from several mines/caves, including the famous *Blue John Cavern*. During the 19th century, this attractive fluorite was mined for its ornamental value. The name is derived from French "bleu et jaune" (blue and yellow) characterizing its color. Blue John is now scarce, and only a few hundred kilograms are mined each year for ornamental and lapidary use.

Recent deposits in China have produced fluorite with coloring and banding similar to the classic Blue John stone.

The gem varieties of fluorite are also associated by some people with a kind of magical power giving relief in some psychological problems.

7. Hydrofluoric (HF) acid: This is an important industrial chemical which serves as the starting point for many downstream chemicals. The highest acid grade fluorite is used as a feedstock in its manufacture. Consumption norm of fluorite is 3 tonne per tonne of HF-acid.

Hydrofluoric acid is manufactured by reacting dilute sulphuric acid with ground fluorite (mostly of 212-500 micron size) at 300-800^{0}C. In the process, gypsum is produced as a by-product (*fluoro-gypsum*). The reaction is:

$$CaF_2 + H_2SO_4 + H_2O \rightarrow 2HF + CaSO_4.2H_2O$$

It can also be produced by reacting dilute sulphuric acid with fluor-apatite as:

$$3Ca_3(PO_4)_2.CaF_2+10H_2SO_4+20H_2O\rightarrow 6H_3PO_4+2HF+10(CaSO_4.2H_2O)$$

This process is followed by condensation and distillation. The commercial grades generally vary from 60% to 70% HF-acid and the rest water.

HF-acid is a strong acid extensively used for etching glass. Very high-purity acid is used for etching semiconductor devices. Besides, there are some important chemicals prepared from HF-acid, which, in their turn, find use in some industrial processes.

B. Products based on hydrofluoric acid and their uses

1. Chemicals:

Among the products, synthetic cryolite requires very high grade HF-acid than other chemicals. As regards the deleterious constituents, sulphur, $BaSO_4$, $CaCO_3$, oxides of iron and aluminium, phosphorus and arsenic are highly objectionable. Both S and $BaSO_4$ remain unaffected by the sulphuric acid and react with fluorine. Calcium carbonate, and the iron and aluminium oxides react with the dilute H_2SO_4 acid. Phosphorus will tend to take away some calcium from the fluorspar and form calcium phosphate, which gets mixed up with the by-product gypsum and makes the latter unfit for use in the cement industry, i.e., to slow down setting time. Hence, all these are considered deleterious. Arsenic vaporizes and corrodes the machines and also may get carried into the HF-acid and its products.

The Bureau of Indian Standards (BIS) has prescribed in 1981 the parameters for fluorite for manufacturing HF-acid meant for manufacturing synthetic cryolite as: 97*% (min)* CaF_2*, 1% (max)* SiO_2*, 1% (max)* $CaCO_3$*, 1.5% (max)* R_2O_3 *and 0.1% (max) S.*

The BIS specifications for manufacturing HF-acid meant for making other chemicals are: 96*% (min)* CaF_2*, 1% (max)* SiO_2*, 1.2% (max)* $CaCO_3$*, 1.5% (max)* R_2O_3*, 0.08% (max) S, 0.05% (max)* $BaSO_4$*, 0.2% (max)* P_2O_5*, 0.25% organic matter and 10% free moisture.*

The Indian industries, however accept lower grades containing as low as 90% CaF_2 with up to 1.5% SiO_2, 1.5% $CaCO_3$, 1.6% R_2O_3, 0.3% (max) $BaSO_4$ and 0.6% P_2O_5. The HF-acid prepared from this lower grade is eventually sweetened by blending with higher imported grade HF-acid.

(a) Synthetic cryolite: HF is first reacted with silica to produce fluoro-silicic acid [H_2SiF_6] as shown below.

$$4HF + SiO_2 \rightarrow SiF_4 + 2H_2O$$

$$3\,SiF_4 + 4H_2O \rightarrow Si(OH)_4 + 2H_2SiF_6$$

This fluoro-silicic acid is used in the manufacture of synthetic cryolite ($3NaF.AlF_3$) by treating it with clay and bauxite. Alternatively, it can be made by reacting HF-acid with soda ash (Na_2CO_3) and aluminium hydroxide (Al_2O_3). Its main use is in aluminium metallurgy.

(b) Fluoro-silicic acid: This acid [H_2SiF_6] prepared as above, is itself used for fluoridation of water, in metal finishing and in electroplating. This acid contains 80% F.

(c) Aluminium fluoride: Aluminium fluoride (AlF_3) is manufactured by treating alumina with hydrofluoric acid or fluorosilicic acid. Its main uses are in metallurgical industries as a flux for melting aluminium and for casting, soldering, welding, etc., in opacifier for optical and special glasses, enamels and ceramic products, and in the manufacture of aluminium silicate fibers.

(d) Chlorofluorocarbons: Earlier, sulphur dioxide was used as a refrigerant in home refrigerators. However, due to its irritating nature, it lost its popularity and was substituted by chlorine-containing chlorofluorocarbons or CFC (CF_2Cl_2), which were non-toxic and non-inflammable. One such compound was dichoro-difluoro-methane or *freon* came to be widely used in refrigerators, air conditioners, aerosol, sterilization, purification of graphite, etc. For preparing it, CCl_4, HF-gas and methane are reacted together. But even CFC is now banned in many countries because it is one of the five *green house gases* or *GHG* (the other four are CO_2, methane, NO_2 and water vapour) and it is largely responsible for the *ozone hole.*

(e) Potassium fluoride: Potassium fluoride (KF) is manufactured by reacting caustic potash (KOH) with HF-acid and then drying the product at 200-300^{0}C. It is used for production of fluorine gas, for synthesis of aromatic fluorides that in turn are used in agro-chemicals and pharmaceuticals.

(f) Fluoro-boric acid: It is used in electroplating, in metal finishing and in tin refining.

(g) Fluorine gas: Fluorine gas can be obtained by electrolyzing either a mixture of potassium fluoride and hydrofluoric acid or only fused potassium fluoride at 100^{0}C, in a copper vessel using graphite electrodes insulated by bakelite stoppers. The fluorine is purified by passing it through sodium fluoride. It is then compressed into cylinders under 400 psi pressure and sold.

Fluorine is a highly poisonous gas. Small amounts (1 ppm) of it to make *fluorinated water* for domestic supply, to help prevent tooth decay because it kills tooth bacteria (excess amount may cause *fluorosis* which is a disease of bones). Also, fluorine, being the most reactive gas, can combine with various inorganic and organic substances to form some useful chemicals.

2. Industrial processes:
   (a) Aluminium metallurgy:
      (i) *Primary aluminium*: For extraction of aluminium metal from alumina by the classical Hall-Heroult technology, two fluorite-based chemicals namely

synthetic cryolite and aluminium fluoride (AlF_3) are mixed and fused for use as the electrolytic bath. Synthetic cryolite is nowadays used as a substitute of natural cryolite, the only deposit of which in Ivigtut, Greenland has completely depleted. In this technology, alumina is dissolved in a fused electrolytic bath composed of aluminium fluoride and cryolite. The cryolite bath dissolves about 10% of the alumina at the operating temperature of 920-970^{0}C in the electrolytic cell. When high-intensity current is applied, the alumina dissociates into positive aluminium ions and negative oxygen ions, the former depositing on the cathode and the latter reacting with the carbon of the anode forming CO and/or CO_2. The molten metal is tapped and cast into ingots. The used cryolite can be partially recycled. The melting point of cryolite is around 1000^{0}C and that of alumina 3700^{0}C. AlF_6 acts as a flux and lowers this melting temperature to about 2000^{0}C. Cryolite actually does not lower the melting temperature of alumina, but it only melts and then dissolves the latter.T he consumption of synthetic cryolite and aluminium fluoride per tonne of aluminium works out to total equivalent fluorite of 15.45 kg. With regard to specifications of fluorite, those prescribed for manufacturing the HF-acid from which synthetic cryolite is prepared, are often referred to as the specifications for aluminium metallurgy because the role of synthetic cryolite is the most critical, i.e. for dissolving alumina.

(ii) *Recycling of aluminium*: Aluminium is a metal which can be endlessly recycled. Both aluminium fluoride and synthetic cryolite are required for each recycling.

(b) Niobium/tantalum metallurgy: Niobium and tantalum occur together and are extracted together by first fusing the ore with caustic soda and then treating the melt with hydrochloric acid to dissolve the impurities and precipitate tantalo-niobic acid crystals. This tantalo-niobic acid is dissolved in hydrofluoric acid. Potassium fluoride (KF) is added and as a result, selective precipitation of tantalum-potassium-fluoride and niobium-potassium-oxyfluoride takes place. On cooling, the former precipitates and is recovered by filtration as residue, while the latter going with the filtrate is subjected to further processing to extract niobium. The niobium compound is treated with alkali to obtain niobium oxide while pure tantalum metal is obtained by fusing and electrolyzing the tantalum-potassium fluoride.

(c) High-octane petroleum: In *cracking* petroleum, molecules are broken down under high temperature (with or without a catalyst) into smaller units, and a new type of hydrocarbons, namely olefins, are produced, and these olefins are coupled with isobutane (C_4H_{10}) in presence of HF-acid at 40^{0}C to produce isoparaffins like heptane (C_7H16) and octane (C_8H_{18}) by a process called *alkylation*. Alkylation helps in improving *Octane number* of mo-gas (octane number is a measure of *anti-knock* value of a motor fuel, i.e. the ability to resist the knock or sound produced due to its sudden and violent combustion in a spark ignition engines; for its measurement, a standard scale has been devised by assigning the value zero to heptane (C_7H_{16}) which has very poor knock resistance, and 100 to octane (C_8H_{18}) having a very high knock resistance; octane number is the percentage of this isomer of octane in its mixture with heptane, the knock resistance of which matches with the test sample; for example, if the knock resistance of the test sample matches with that of a mixture containing 75% octane isomer and 25% heptane, then the octane number of the sample 75).

C. Products and processes based on fluorine and their uses

1. Potassium perchlorate: Fluorine is a powerful oxidizing agent. When it is bubbled through a solution of potassium chlorate ($KClO_3$), the latter is oxidized to potassium perchlorate ($KClO_4$) according to the reaction

$$F_2 + 2KClO_3 + H_2O \rightarrow 2HF + KClO_4$$

2. *Anhydrous hydrogen fluoride (HF):* Fluorine reacts explosively with hydrogen even at low temperature. So much so that even water is dissociated by it as per the reaction

$$2F_2 + 2H_2O \rightarrow 4HF + O_2$$

The oxygen liberated oxygen is highly charged with ozone. The HF-gas is a powerful chemical.

3. Sodium silico-fluoride: Also called sodium fluoro-silicate or sodium hexafluorosilicate (F_6Na_2Si), it intensifies and accelerates glass-melting.

4. Uranium hexa-fluoride (UF_6): It is used for refining and enrichment of uranium.

5. Fluoro-silicates of ammonium, magnesium and zinc: These are used as preservatives for hide, wood, etc.

6. Fluoro-carbon: These are used as filter membranes in semiconductor fabrication industry.

7. Fluoro-polymer filter: These are essentially fluoro-carbons and are inert. One such compound poly-tetra-fluoro-ethylene or PTFE is an excellent material for filter membranes which are made into cartridges for operation at nano-size level. The pores of (-) 0.1 micron size are suitable for filtering high-purity aqueous chemicals which are required for etching and cleaning of ultra-high-purity semiconductor chips.

8. Sodium fluoride (NaF), Stannous fluoride (SnF_2) and Sodium monofluorophosphate (Na_2PO_3F): These are added as components of toothpastes for preventing tooth decay by virtue of the poisonous action of fluorine on bacteria.

9. Uranium metallurgy: In the process, both HF gas and fluorine are used. The uranium ore is first concentrated and the concentrate containing 50–90% U_3O_8 is refined for extraction of uranium metal. For this purpose, the concentrate is first dissolved in nitric acid, and then an aqueous solution of high purity uranium compounds is obtained by solvent extraction process using tributyl phosphate dissolved in kerosene or hexane as the solvent. The product is pure uranyl nitrate solution. This uranyl nitrate is thermally decomposed to obtain UO_3, which is then reduced to UO_2 by hydrogen. UO_2 is heated in presence of anhydrous HF gas to yield UF_4 which is reduced to metallic uranium by reacting it with either calcium metal or (more widely) magnesium metal at 600^0C according to the reaction :

$$UF_4 + 2Mg \rightarrow U + 2\,Mg\,F_2$$

Sometimes it may be necessary to enrich the concentration of U_{235} in the metallic uranium or its compounds. For this purpose UF_4 is first fluorinated further to yield UF_6. The UF_6 is subjected to differential gaseous diffusion through micro-porous filters. The lighter U_{235}-containing UF_6 (molecular weight 349) and the heavier U_{238}-containing UF_6 (molecular weight 352) are partially separated. In this way the concentration of U_{235} may increase from about 0.7% to 3 per cent. The enriched UF_6 so obtained is reduced again to UF_4 by means of hydrogen, and enriched uranium metal obtained by metallic reduction as above.

D. Uses based on a mix

1. Glass: Physically, common standard glass is an amorphous, hard, brittle and transparent substance and chemically, it is a mixture of the silicates of sodium, calcium and magnesium. The composition of typical ordinary glass is [$18Na_2O.2MgO.8CaO.72SiO_2$]. Essentially, the process of manufacture of glass consists in melting a mixture of 47% silica sand,14% soda (Na_2CO_3), 12% dolomite ($CaCO_3.MgCO_3$), 3.5% limestone ($CaCO_3$), 2.5% carbon (coke) and the balance broken waste glass (called cullet) at 1400-1500^{0}C, and then cooling it first to a thick viscous liquid at 800-900^{0}C and then rapidly quenching it to a solid glass product. The low-melting soda and broken glass become liquid first and silica (quartz) being soluble in boiling soda, dissolves in this liquid to form low-melting sodium silicate which then reacts with the CaO and MgO to form glass. So far as glass is concerned, the main uses of fluorite are as follows.

(i) The compound sodium hexafluorosilicate (F_6Na_2Si) is added to serve double purposes to supply the sodium to supplement the soda for fluxing, and to increase fluidity of the melt.

(ii) In the manufacture of float glass and fiber glass, fluorite is directly added. Float glass is a type of sheet glass (above 0.5 mm thickness) in large sizes that is exceptionally smooth on both surfaces and free from internal stress. For its manufacture, molten glass at 1100^{0}C is discharged from the furnace onto a bed of molten tin, on which it floats and spreads out freely in the form of a long strip. It is then cooled either slowly (annealed float glass) or suddenly (heat-strengthened float glass). Molten tin by virtue of its low shrinkage on solidification, higher-than-glass specific gravity, non-adherence to glass surface, and low coefficient of friction allows the molten glass to spread freely without any resistance and then solidify without any wrinkle. Fiber glass, on the other hand, is glass formed into fine fibers (thinner than human hair) by drawing molten glass through tiny holes. In both these processes, liquidity and free-flowing ability of the molten glass are very crucial, and role of fluorite assumes importance because of its ability to improve both these parameters. The Indian user industries generally use fluorite containing 90 to 98% CaF_2 with size 75 to 150 microns.

(iii) In the manufacture of opalescent glass, fluorite, by virtue of its lower refractive index (1.433) than glass (1.53) serves to opacify glass (covering power of opacifier depends on the difference between the refractive indices of it and that of the substance opacified, and also on the particle size of the opacifier).

WASTE UTILIZATION

1. Low-grade fluorite powder:- Nowadays low-grade fluorite powders are moulded and pressed into the shape of briquettes. Such *fluorite briquettes* have become popular in some European countries. For easy loading, olivine and bauxite are also mixed with the fluorite while briquetting.

2. Topaz: Chemically, topaz is aluminium fluorine hydroxyl silicate $[Al_2(SiO_4)(OHF)_2]$. It is regarded as a future source of fluorine, particularly the non-gem type which have no other industrial use.

Chapter 23

GARNET

The name garnet is derived from Latin "granatus" meaning "like a grain" (c.f., granite derived from "granum" meaning "grain"; also the fruit called pomegranate the seeds of which are similar to garnet grains). Garnet is the collective name for a group of silicates of two (one bivalent and one trivalent) of the metals calcium, aluminium, magnesium, iron, manganese and chromium. The individual minerals under this group are:

1. Aluminium garnets

    (i) Grossularite or hessonite [$Ca_3Al_2(SiO_4)_3$]
    (ii) Pyrope [$Mg_3Al_2(SiO_4)_3$]
    (iii) Almandite [$Fe_3Al_2(SiO_4)_3$]
    (iv) Spessartite [$Mn_3Al_2(SiO_4)_3$]

2. Iron garnet Andradite [$Ca_3Fe_2(SiO_4)_3$]
3. Chromium garnet Uvarovite [$Ca_3Cr_2(SiO_4)_3$]

Out of these, the iron-containing garnets, almandite and andradite are the most common. Many garnets occurring in the nature are admixtures of the various varieties .Garnet may occur as a primary mineral in schist, gneiss and pegmatite, and as a secondary mineral in beach and river placers.

HISTORY

Garnet is known and used for centuries, first, as a gem and later as an abrasive. In India the inland placer deposits of Tirunelvelli district of Tamil Nadu have an old history of mining. Records of production from this area are available since 1914. Later on, the beach sands of Tamil Nadu, Kerala and the primary deposits of Andhra Pradesh, Karnataka, Bihar and Rajasthan also have become sources of garnet albeit their contribution is insignificant. The history of production in India can be tracked from the following table.

Year	Production
1914	1,000 tons approximately
1928	490 tons approximately
1932	150 tons approximately
1938	120 tons approximately
1939-1949	4-5 tons annually
1955	150 tons
1960	469 tons
1962	428 tons
1968	1,993 tons
1970	993 tons
1980	3,753 tons
1990	4,880 tons
Year ending March 2001	232,259 tons
Year ending March 2006	679,700 tons

After 1990, there has been a phenomenal increase in the production due to recognition of its importance as an abrasive in a number of new-generation products, and India has emerged as a leading exporter. USA is the largest consumer in the world. Presently, the Tirunelveli district of Tamil Nadu account for practically the entire production.

CRITERIA OF USE

1. *Hardness:* This is the most important criterion in most of the uses. Hardness of the garnets vary from 6.5-7.5 on Mohs scale (c.f., quartz 7). Amongst the garnets, uvarovite is the hardest.
2. *Crystal form:* The common forms of garnet crystals are dodecahedron and trapezohedron and their combinations.
3. *Fracture:* Subconchoidal to uneven.
4. *Specific gravity:* Garnets are moderately heavy with specific gravity varying from 3.15-4.3—uvarovite being the lightest and almandine the heaviest amongst them.
5. *Colour:* Garnets are comprised of different metals present in varying amounts. Often one metal partially alters to another. Sometimes, there may be inclusion of a foreign matters. All these factors have resulted in an array of colours in garnets such as:
    (a) Grossularite: White, pale green, amber yellow, honey yellow, wine yellow, rose red, brown, emerald green etc. depending on degree of alteration of calcium and aluminium to ferrous and ferric irons and also inclusion of chromium.
    (b) Pyrope: Mostly deep red (the name pyrope has come from a Greek word meaning "fire-like") and sometimes blackish (due to inclusion of iron in varying amounts).
    (c) Almandite: Red, brownish red and black due to partial replacement of magnesium by iron.

(d) Spessartite: Dark red to violet due to replacement of manganese and aluminium by ferrous and ferric irons.

(e) Andradite: Different shades of yellow, green and red and also brown to black due to replacement of ferric iron by aluminium and of calcium by ferrous iron, manganese or magnesium.

(f) Uvarovite: Emerald green due to presence of chromium and its partial replacement by aluminium.

(6) Refractive index: Refractive indices of garnets vary from 1.705 (pyrope) to 1.895 (andradite). When compared with ordinary glass (1.53) and diamond (2.42), it can be surmised that the refractive index of garnet is fairly high.

(7) Transparency: Garnets are transparent to translucent. Rarely some variety may show perfect transparency (e.g., pyrope).

(8) Lustre: Vitreous to resinous.

(9) Chemical characteristics: Garnets are known for their resistance to acids. Only uvarovite is insoluble in acids.

(10) Geological mode of occurrence: Secondary garnets, which were transported by water and redeposited in the form of small grains in placers, are found with their sharp fracture edges rounded off to a greater or lesser extent. In contrast, those occurring in igneous and metamorphic rocks are in the form of coarse crystals—sometimes as large as 25 mm (one inch), which, when crushed, yield the characteristic fracture with sharp edges.

USES AND SPECIFICATIONS

The most important uses of garnet are:

1. Coarse polishing
2. Fine polishing
3. Sand blasting
4. Gem

These are discussed as follows.

1. Coarse polishing: The most important industrial use of garnet is in the manufacture of coated abrasive-like paper (garnet paper), cloth (garnet cloth) and discs for removing rust or worn-out paint of metal surfaces, sizing of metals and wood, for smoothening leather, etc. Sodium silicate, gelatin or cattle hide glue is generally used as the bonding material for mounting garnet grains on the base. For making garnet paper/cloth garnet grains are sprayed or gravity-dropped on sheets of paper/cloth coated with heated bonding material (shellac, gelatin etc.). Hardness (6.5-7.5 on Mohs scale), and subconchoidal fracture with sharp edges are the key criteria. Crushed grains of primary garnet crystals are more effective than rounded grains of secondary placer garnet, but the latter can also be used for less hard surfaces like those of wood, plastic, rubber etc.

2. Fine polishing: Micronized garnet mounted on paper/cloth is used for fine polishing of delicate surfaces like TV picture tubes (for achieving high picture resolution), for fine polishing wood surface etc. Here also, hardness (6.5-7.5 on Mohs scale), and subconchoidal fracture with sharp edges are the key criteria and crushed grains of primary garnet crystals are used. In this application, grain size, consistency of the size and angularity of the grains are the most important quality parameters. If the size is too large then the grains will be very angular and will scratch the surfaces. On the other hand, very small-sized grains will be rounded and will be ineffective. The industries use a minimum of 10 micron size, because grains finer than this tend to be too rounded. The most preferred size range, however, is 20-35 micron.

3. Sand blasting: Garnet sand is fired under pressure usually in the presence of water to suppress the dust against the material to be polished. For this purpose the chemical composition of the sand is not important, but absence of clay and other water-soluble clogging materials is very important. Moderate specific gravity of garnet contributes to the force of the blast and is an important criterion in this usage.

4. Gem: According to Webster's Second Edition Unabridged Dictionary, gem means any jewel having value and beauty that is intrinsic and not derived from its setting; and gemstones or gem materials are stones or materials from which a gem may be cut. Gem includes both precious and semiprecious stones. The criteria that make a gem are:

(a) *Rarity*: By the law of demand-supply, the scarcer a commodity is, the higher is its value.
(b) *Durability*: The combination of hardness, toughness and acid-resistance makes a stone durable. Amongst the gemstones generally those with hardness at least 8 on Mohs scale are considered as precious stone and those up to 7 as semiprecious stones.
(c) *Colour and optical properties*: Colour, lustre and optical dispersion are the most important parameter of beauty.
(d) *Clarity*: Small bubbles, cracks and other flaws reduce the clarity of a gem, and consequently, its value.
(e) *Cut*: Natural gems are mined as rough stones. They need to be cut into well defined faces and the faces are polished to produce their characteristic sheens and optical effects. The cutting requires a very high degree of skill – particularly when the individual pieces are small. Minimum loss of stone is to be ensured during cutting.
(f) *Specific gravity:* The value/volume ratio depends on this parameter.
(g) *Caratage:* Larger a gem is, rarer and hence more valuable it is. So the individual weight of a piece is important for determining its value.
(h) *Certification*: For a common retail buyer, the physical and optical properties of gems carry little sense, and he is most concerned, besides size, with the colour and sheen as judged with naked eyes. But both these characteristics can be replicated by unscrupulous people. So for him certification by some trusted authority or agency assumes importance.
(i) *Aggressive marketing*: Demand of gems being elastic, almost any gemstone can be sold irrespective of colour and cost, provided the basic criterion of rarity is met.
(j) *Therapeutic value*: Gems are traditionally believed to possess some indirect beneficial effects on body and mind if worn on the body. This branch of therapy known as gemmotherapy works on the hypothesis that different gems, when worn by a man on his body, react differently to different kinds of cosmic rays having different

effects on the health of his mind and body. Besides, some gems have been found to produce beneficial effects on human skin.

(k) *Beliefs and superstitions:* Gems, many people believe, bring luck or misery to lives.

(l) *Stability of value*: Economic phenomena like inflation, stagflation, recession and even political instability which exercise adverse impact on other manufacturing and processing sectors, do not affect adversely the demand of gems—particularly the high-value ones.

Judging from the above criteria, garnet (weak resistance to acids and hardness 6.5-7.5 on Mohs scale) is not a precious stone. But some rarely found highly transparent large flawless clear crystals of garnet exhibiting attractive colours are valued as semiprecious stones. Sometimes grossularite, pyrope and almandite (the later with compositions modified due to partial alteration) fulfil these conditions. Obviously, such crystals can only be found in primary deposits of igneous and metamorphic rocks.

There are two main gem varieties of garnet:

(a) *Gamet* (“Tamrha” in Indian language): It is a type of garnet formed by partial replacement either of magnesium by iron in pyrope [$Mg_3Al_2(SiO_4)_3$] or of iron by magnesium in almandite [$Fe_3Al_2(SiO_4)_3$], and has a general composition [$(Fe,Mg)Al_2(SiO_4)_3$]. It shows red, rose and chocolate colours and its refractive index is 1.73.

(b) *Gomed*: Mineralogically, it is grossularite or hessonite [$Ca_3Al_2(SiO_4)_3$]. It shows yellow, rose and chocolate brown colours and its refractive index is 1.74. Gemmotherapists claim that it is beneficial for digestive disorders if worn on the body.

The most important sources of gem garnets are Czechoslovakia, USA, India, Madagascar, Tanzania, Brazil and Russia.

5. Other uses

(a) *Anti-skid material*: Finely ground garnet is also used for sprinkling on slippery floor.

(b) *Spark-plug cleaning*: Hardness and fracture pattern of crushed primary garnet are the criteria.

(c) *Artificial gems*: Artificial gems consist of elements that are naturally occurring, but combined in forms that are not found in nature, and they are prepared in laboratories. Yttrium-aluminium-garnet (YAG) and gadolinium-gallium-garnet (GGG) are common examples. Chromium-doped YAG is sometimes used as laser rods instead of synthetic ruby. The process for making YAG is the same as that employed for synthetic ruby and sapphire, i.e., “Czochralski method”. Sometimes, neodymium (Nd) is added to YAG to customize some special properties (See the chapter on corundum-ruby-sapphire for details of the process).

WASTE UTILIZATION

In garnet micronizing plants, (-) 10 micron sized grains are rejected. These have been tried for utilization in making very high-strength vitrified tiles for use as pavement blocks in ports in two ways:

(a) A very hard surface has been obtained by coating the tiles with these waste garnet particles.
(b) The Central Glass and Ceramic Research Institute (CGCRI), India made very hard brown tiles by mixing this waste with china clay and feldspar and firing.

However, these applications have not become popular with the consumers.

Chapter 24

GEMSTONES - MISCELLANEOUS

A number of precious and semiprecious gemstones, the minerals of which have significant industrial uses besides uses as gems, have been dealt with under the chapters corundum, diamond, emerald, feldspar, fluorspar, garnet, kyanite-sillimanite-andalusite, phosphorus, pyrites, quartz, rutile, staurolite, tourmaline, and zircon. But there is a number of minerals and non-mineral materials of stand-alone gemstones which have either nil or negligible industrial use. The commonly talked about and traded ones amongst them are:

1. Chrysoberyl (cat's eye and alexandrite)
2. Spinel (red spinel and blue spinel)
3. Topaz
4. Cordierite (iolite)
5. Jadeite/nephrite (jade)
6. Fuchsite quartzite
7. Olivine (peridot)
8. Turquoise
9. Lazurite (lapis lazuli)
10. Malachite (kidney stone)
11. Zoisite (tanzanite)
12. Organic gems
    - (a) Pearl
    - (b) Coral
    - (c) Amber (non-mineral material)

These will be described in this chapter with reference to the criteria of their value as gems.

However, there are some other gemstones of minor importance which have been traded at one time or other as gems, mainly by virtue of their attractive colours and good marketing skill. These are axinite [Al-Ca-Fe-Mn-borosilicate, purple blue], danburite [$CaB_2(SiO_4)_2$, colourless to pale yellow], diopside [$(Ca, Mg)(SiO_3)_2$, green], enstatite [$MgSiO_3$, greenish white], epidote [$Ca_2(Al, Fe)_3(SiO_4)_3(OH)$, pistachio green], euclase [$Be(Al.OH)SiO_4$, pale, colourless to faint shades of red, yellow, green and blue], sphene [$CaTiSiO_5$, reddish brown and greenish green to blue], hambergite [$Be_2(OH)BO_3$, colourless], phenacite [Be_2SiO_4, colourless to pale blue], scapolite [mixture of $CaCO_3.3CaAl_2Si_2O_8$ and

$NaCl.3NaAlSi_3O_8$yellow], apophyllite [$KFCa_4Si_8O_{20}.H_2O$, colourless/white/yellowish /reddish/greenish], bowenite [$H_4Mg_3Si_2O_9$, green], idiocrase [$Ca_{10}Al_4(Mg,Fe)_2Si_9O_{34}(OH)_4$, brown/green/yellow/blue], prehnite [$Ca_2Al_2Si_3O_{10}(OH)_2.nH_2O$, yellowish to olive green], piedmontite [$Ca_2(Al,Fe,Mn)_3(SiO_4)_3(OH)$, yellow/orange/rose], rhodonite [$MnSiO_3$, flesh-red], sodalite [$3NaAlSiO_4.NaCl$, violet to azure blue].

CRITERIA OF USE

According to Webster’s Second Edition Unabridged Dictionary, gem means any jewel having value and beauty that is intrinsic and not derived from its setting; and gemstones or gem materials are stones or materials from which a gem may be cut. By popular perception, a gem is a rarely encountered hard, durable, brilliantly shining and beautiful natural mineral which has high intrinsic value. Three characteristics of a gem stand out persistently. These are: rarity, durability and beauty. Rarity is an economic function of supply, and durability is a measurable physical attribute, but beauty is person-specific carrying different meanings to different individuals, and may include properties like colour, ability to take polish, sheen, size, shape etc. The unique mineralogical, physical and optical properties besides some peculiar psychological factors go into the usage of the gems. The criteria that make a gem are:

1. *Rarity*: By the law of demand-supply, the scarcer a commodity is, the higher is its value.
2. *Durability*: The combination of hardness, toughness and resistance to chemical and atmospheric attack makes a stone durable.
3. *Colour and optical properties*: Colour, lustre and optical dispersion are the most important parameter of beauty.
4. *Clarity*: Small bubbles, cracks and other flaws reduce the clarity of a gem, and consequently, its value.
5. *Cut*: Natural gems are mined as rough stones. They need to be cut into well defined faces and the faces are polished to produce their characteristic sheens and optical effects. The cutting requires a very high degree of skill – particularly when the individual pieces are small. Minimum loss of stone is to be ensured during cutting.
6. *Specific gravity:* The value/volume ratio depends on this parameter.
7. *Caratage:* The larger a gem is, the rarer and, hence, more valuable it is. So the individual weight of a piece is important for determining its value.
8. *Certification*: For a common retail buyer, the physical and optical properties of gems make little sense, and he is most concerned, besides size, with the colour and sheen as judged with naked eyes. But both these characteristics can be replicated by unscrupulous people. So for him certification by some trusted authority or agency assumes importance.
9. *Aggressive marketing*: Demand of gems being elastic, almost any gemstone can be sold irrespective of colour and cost, provided the basic criterion of rarity is met.
10. *Therapeutic value*: Gems are traditionally believed to possess some indirect beneficial effects on body and mind if worn on the body. This branch of therapy known as gemmotherapy works on the hypothesis that different gems, when worn by

a man on his body, react differently to different kinds of cosmic rays having different effects on the health of his mind and body. Besides, some gems have been found to produce beneficial effects on human skin.

11. *Beliefs and superstitions:* Gems, many people believe, have some magical power bringing luck or misery to lives.
12. *Stability of value*: Economic phenomena like inflation, stagflation, recession and even political instability which exercise adverse impact on other manufacturing and processing sectors, do not affect adversely the demand of gems—particularly the high-value ones.

Gem includes both precious and semiprecious stones. The most obvious and easily measurable difference between these two classes lies in hardness. It is generally perceived that gems not harder than 8 on Mohs scale are semiprecious. But there are exceptions and gems softer than this value are traded as precious stones because they fulfill many of the other criteria (e.g., emerald, hessonite garnet, pearl, coral). The various gems not covered elsewhere in this book are described here. Hardness and durability, specific gravity and favourable density/value ratio, lustre, crystalline form, refractive index and colours are the main physical and optical criteria for all these gems, but in addition, psychological factors are of crucial importance.

CHRYSOBERYL

Its other mineralogical name is *cymophane*. Chemically it is beryllium aluminate ($BeAl_2O_4$) with hardness 8.5 on Mohs scale, specific gravity 3.7 and refractive index 1.75. It is transparent to translucent and has vitreous lustre. It occurs in orthorhombic crystalline form. Primary chrysoberyl crystals are found in granites, pegmatites and mica schists. But being hard and durable, its crystals are also found in secondary sand/gravel deposits. There are two important gem varieties, namely:

1. Cat's eye ("Lohomunya" in Indian language): It show a variety of colours like white, green, yellow and grey as seen from different angles, producing an attractive chatoyant effect.
2. Alexandrite ("Sikandara" in Indian language): It shows emerald green colour in natural light and red colour when viewed in artificial light. The green colour is due to inclusion of chromium.

Of these, cat's eye is more valued because, between the two, it is rarer in nature and more attractive due to the chatoyant effect, and it has not been made synthetically.

Alexandrite can be prepared synthetically also. The process for making these synthetic gems is the same as that employed for synthetic ruby and sapphire (see the chapter on corundum for details). Currently the most popular process is the *Czochralski method* based on surface tension. In this process, the ingredient (or nutrient as it is called) beryllium aluminate powder is melted in a platinum or iridium or graphite or ceramic crucible. A seed crystal is attached to one end of a rotating rod which is first lowered till it just touches the surface of the melt, and then is withdrawn slowly at a rate varying from 0.1-10.0 cm per hour. At this stage, the green dope chromium is introduced to the melt for producing the characteristic colour of alexandrite (*dope* is an element added to the nutrient during crystal-growing stage to achieve a particular colour). The molten material gets attached to the rotating seed due to surface tension, is gradually pulled up by the seed out of the hot crucible, cools down and solidifies. This process continues till the entire molten material gets pulled up and becomes a solid single crystal. The sizes of the crystals grown by this method depend on the amount of molten material available in the crucible, and large crystals of 5 cm diameter and about 100 cm length have been made. Such chromium-doped synthetic alexandrite is used in laser rods as a substitute of synthetic ruby. For manufacturing laser rods, large high-quality optically perfect crystalline synthetic alexandrite is preferred to natural one which is practically never found in very large size and as pure flawless optically perfect crystals, and even if found by chance, a consistent supply required by industries cannot be guaranteed.

SPINEL

Chemically, spinel is magnesium aluminate ($MgAl_2O_4$). It crystallizes in isometric form, and its hardness is 8 on Mohs scale, specific gravity 3.6, refractive index 1.71 and lustre vitreous. It is transparent to opaque and shows colours varying from red to blue through green, yellow, etc. of different shades. Crystals of spinel occurs as metamorphic minerals embedded in granular limestone and dolomite and also in gravels in association with corundum. There are two important gem varieties, namely:

(a) Red spinel (“Lalrhi” in Indian language): Red coloured
(b) Blue spinel (“Neela” in Indian language): Blue coloured

Spinel can be prepared synthetically also and the process is the same *Czochralski method* described under chrysoberyl above except that the chromium doping is not done (see the chapter on corundum for details).

TOPAZ

Chemically, topaz is aluminium fluorine hydroxyl silicate [$Al_2(SiO_4)(OHF)_2$]. Topaz crystallizes in orthorhombic form with almost perfect cleavage. Its hardness is 8 on Mohs scale, specific gravity 3.5, refractive index 1.71 and lustre vitreous. It has variable colours of white, straw yellow, wine yellow, rose-red, greenish and bluish. However it has poor toughness and can be split with a single blow. It occurs in granite, rhyolite and pegmatite.

The genesis of the name is uncertain. It might have originated from the Sanskrit word “taaposa” meaning fire or from the Greek word “topazas” meaning “to shine”. Its history is very long and beset with many superstitious beliefs. The ancient Greeks believed that topaz provided power to dispel mental depression and strength to its wearer. The romans associated it with eyesight. Ancient Egyptians wore topaz as an amulet to protect them from injury. Cleopatra is said to be especially fond of topaz, because it reminded her of honey. During the

18th and 19th centuries, the Russian Czarinas used red and pink topaz in jewelry, and for this reason, this variety of topaz acquired the name *Imperial Topaz*.

Besides as a semiprecious stone, topaz powder is also used in cosmetic skin care to impart a youthful brightness to the face.

CORDIERITE

Chemically, cordierite is magnesium aluminium silicate [$(Mg.Fe)_2Al_4Si_5O_{18}$]. It crystallizes in orthorhombic form with distinct cleavage. Its hardness is 7.0-7.5 on Mohs scale, specific gravity 2.6, refractive index 1.54 and lustre vitreous. Its colour varies from deep blue to purplish blue. It occurs in gneiss and crystalline schist, in contact metamorphic zones, in igneous rocks like granite, andesite, rhyolite etc., and sometimes in the vitrified contact zones between sandstone and basalt.

Gem variety of natural cordierite is called *iolite* (“Neeli” in Indian language).

Cordierite can now be made artificially from an admixture of fireclay, grog, bauxite powder and talc for industrial use. Artificial cordierite has the composition $Mg_2Al_4Si_5O_{18}$. It has the same characteristics as natural cordierite, which is formed due to contact metamorphism. It crystallizes above 950^0 C and remains stable over a considerable range of temperature i.e., up to 1750^0C. It has low linear expansion, low coefficient of thermal expansion, excellent resistance to thermal shock, high mechanical strength, ability to work in both oxidizing and reducing atmospheres and to withstand rapid temperature changes without breakage. Such artificial cordierite is used in making what is called *“cordierite saggar”*. Saggars are trays used as kiln furniture and shelves for firing powders or components in porcelain and ceramic manufacturing. Saggars made of artificial cordierite have long lives of 10-15 firing cycles.

JADEITE/NEPHRITE

The two minerals jadeite and nephrite belong to two different groups—pyroxene and amphibole, but their physical properties are very similar. But since ancient times, the term *jade* (“Morgaja”in Indian language) has been used loosely in southern China, Tibet and northern Myanmar (which has been its principal sources since ancient times) to denote the gem varieties of both nephrite and jadeite, and the same tradition is prevalent even now everywhere. Chemically, nephrite lies in between tremolite [$CaMg_3(SiO_3)_4$] and actinolite [$Ca(Mg.Fe)_3(SiO_3)_4$] while jadeite is sodium aluminium silicate [$NaAl(SiO_3)_2$]. However, while jadeite is now rare and found only in Uru Valley of Upper Myanmar, nephrite of gem quality is relatively more abundant, being mined in New Zealand, Siberia, Alaska, British Columbia and Wyoming state of USA.

Jadeite crystallizes in monoclinic form with difficult cleavability. Its hardness is 6.5-7.0 on Mohs scale, specific gravity 3.3, refractive index 1.66 and lustre sub-vitreous. It is extremely tough. It shows variations of green colour and is sometimes white. It is believed to have formed due to deep-seated metamorphism of igneous rocks, but its origin is controversial. The properties of nephrite are similar except that it is slightly lighter (specific gravity 3.0) and softer (6.0-6.5 on Mohs scale) than the latter.

Jade (meaning gems derived from both jadeite and nephrite) was highly valued in China for making ornaments and carving utensils in ancient times and is even now its position continues to be so. Both types of jade are aggregates of fine-grained interlocking crystals rendering them very tough and amenable to carving of intricate designs. The tough nephrite jade was used for making tools and weapons as well as for ritual objects by the ancient Chinese, the early inhabitants of the Swiss lake dwellings, the Aztecs of Central America and the Maoris of New Zealand. But the most precious of all jades is a rich emerald green coloured jadeite jade with a trace of chromium inclusion named *Imperial jade*.

A gem is also traded by the name *Indian jade*, but it is fuchsite quartzite and not jade at all (see below).

FUCHSITE QUARTZITE

Fuchsite [$H_2K(Al,Cr)_3(SiO_4)_3$] is a variation of muscovite in which part of aluminium has been replaced by chromium imparting a bright green colour to the mica. It is named after the German geologist Fuchs who studied it during 1835-1845. Fuchsite quartzite is a bright green jade-like mineral/rock in which fuchsite is thoroughly impregnated in a matrix of silica. It can take good polish and its polished form is regarded as a gem. Because of this colour, it is traded by the name *Indian jade*, and because of its typical occurrence in Greenland, it is also called *Greenlandite*.

OLIVINE

Chemically, olivine is magnesium iron silicate [$(Mg.Fe)_2SiO_4$] belonging to chrysolite group. It crystallizes in orthorhombic form. Usually, it is a transparent to translucent mineral found as an olive-green coloured mineral with hardness 6.5-7.0 on Mohs scale, specific gravity 3.3, refractive index 1.69 and lustre vitreous. But the ratio Mg/Fe varies widely from 16:1 to 2:1 forming the series forsterite, fayalite and with this variation, colour and other properties may also change slightly. It occurs in basic igneous rocks like basalt.

Its gem variety is called *peridot* (“Ghritamoni” in Indian language). Its colour is pale yellowish green and specific gravity is 3.4. Although the mineral olivine is abundant and widespread, peridot (which is transparent) is rare. It has been used as a gem since ancient times. Its important sources are the island of Zeberget in the Red Sea, Mogok in Upper Myanmar and Arizona in USA.

TURQUOISE

The name has come from Turkey from where it used to imported by the Persians. Chemically, turquoise is hydrated phosphate of copper and aluminium [$CuAl_6(PO_4)(OH)_8.5H_2O$]. It is usually a cryptocrystalline mineral with hardness 5-6 on Mohs scale, specific gravity 2.7, refractive index 1.61 and lustre vitreous. It shows sky blue, blue and even black colours and is almost opaque. It is a secondary mineral formed due to alteration and decomposition when apatite, feldspar and copper minerals were present together and occurs in the form of thin veins and small patches.

The gem varieties of turquoise also known by the same name ("Phiroja" in Indian language) are blue or bluish coloured.

LAZURITE

Chemically, lazurite is a combination of sodium-aluminium silicate and sodium sulphide ($3NaAlSiO_4.Na_2S$). It crystallizes in cubic or dodecahedral form. Its hardness is 5.0-5.5 on Mohs scale, specific gravity 2.4, refractive index 1.50 and lustre vitreous. It has rich colours varying from violet to azure blue, and is translucent. It is a product of contact metamorphism occurring in contact zones of limestone with granite.

Its gem variety is called *lapis lazuli* ("Lajwart" in Indian language). It may contain calcium and tin.

MALACHITE

Chemically it is hydrated cupric carbonate [$CuCO_3.Cu(OH)_2$]. It is a common ore of copper occurring in the weathered zones overlying copper deposits. Its hardness is 3.5-4.0 on Mohs scale, specific gravity 3.8, refractive index 1.90. Its crystals have perfect cleavage and have vitreous to adamantine lustre. Its colour is deep green

Its gem variety is called *kidney stone* ("Dane-phirong" in Indian language).

ZOISITE

Chemically, zoisite is hydrated calcium aluminium silicate ($4CaO.3Al_2O_3.6SiO_2.H_2O$). It crystallizes in orthorhombic form. Its hardness is 6.0-6.5 on Mohs scale, specific gravity 3.3, refractive index 1.71. Its crystals have perfect cleavage and have vitreous lustre. Its colours are grey, yellowish brown, greenish, apple-green and rosy. It is transparent to sub-translucent and has strong optical dispersion. It is common in some crystalline schists formed by metamorphism of igneous rocks rich in anorthite. Although zoisite is a common and widespread mineral, there are two gem varieties:

1. Thullite: Named after "Thule" the old name of Norway where it was first found. Thullite is a beautiful rose-coloured variety of zoisite. It owes its colour to the presence of manganese.
2. Tanzanite: A beautiful transparent bluish violet crystalline variety of it was found in Tanzania in 1965. It turned out to be a rare occurrence and it is valued as a gem. It has been named after Tanzania.

PEARL

Pearl (called "Moti" in India) is one of the organic gems made up of 82-88% $CaCO_3$ in the form of aragonite, 10-14% *conchiolin* (an organic horn-like substance which holds together the calcareous material) and 2-4% water. Its hardness is 2.5-4.5 on Mohs scale, specific gravity 2.8, refractive index 1.60 and lustre typical pearly. They have poor toughness and are fragile.

Pearls are inorganic materials formed biologically. The animals that produce the pearls are of the mollusk genera *Pinctada* or *pearl oyster* (invertebrate having a soft unsegmented body usually enclosed in a shell). All species of Pinctada produce pearls and they live in well-defined localities mostly the sea. There is only one freshwater pearl known—the mussel *Unio* of USA. Pearls are of three kinds as follows.

1. *Mother-of-pearl*: As part of the shell-building process, mollusks deposit continually on the inner surface of their shells, layers of aragonite platelets held together by conchiolin. This natural organic-inorganic composite of calcium carbonate and conchiolin is called *nacre* or *mother-of-pearl*. However, while all species of mollusks may secrete nacre in response to some irritant foreign substance, mother-of-pearl is produced by the epithelial cells without any irritant, in the mantle tissue. Nevertheless, mother-of-pearl is iridescent due to the fact that the thickness of the aragonite platelets is about 0.5 micrometre which is comparable to the wavelength of visible length. This results in absorptive and reflective effects on different wavelengths of light resulting in different colours of light being reflected when viewed at different angles (*pseudochromatic colouration*). Hence, though mother-of-pearl is generally irregular shaped (it takes the shape of the shell) and is far more abundant and far less valued than pearls, it has been a prized semiprecious gem since ancient times and has been a major component of jewelry and decorative arts in Egypt, Persia and China for thousands of years. Since the early 20th century, the coastal area of Western Australia has emerged as the leading producer of mother-of-pearl.
2. *Natural pearl*: Peals are formed when some irritant—usually a parasite—enters the mantle of the mollusk which, unable to get rid of it, secretes the pearly substance *nacre* to shield the shell from the irritant. This irritant forms the nucleus around which layers of nacreous substance is deposited. This deposition later hardens to form a pearl. It takes upward of seven years for a standard sized pearl to develop. But it is a matter of one-in-several-thousand chance that an irritant would enter the right kind of shell and consequently, it is also extremely rare to find a pearl in nature (to find one, it may be necessary to kill and open thousands of oyster shells). For this reason, natural pearls are extremely rare and hence these are valued as precious gems. They have variable colours of white, rosy, blue and black. They take the shape of the nucleus, and though a few rare and highly valued ones are regularly shapedspherical, ellipsoidal, etc., more common are the irregularly shaped pearls. These have been highly prized since prehistoric times. As per known records, it was first taken from the river water mussels in China some 4,000 years ago (2000 BC). By the 5th/6th centuries BC, pearls became known and were regularly produced from

the seas off the coasts of India, Sri Lanka and Persia (Iran). The finest pearls are found in the Persian Gulf off the island of Bahrain, in the Gulf of Mannar, in the Red Sea, in the sea off the west and north coasts of Australia, in the Micronesian and Polynesian seas and off the Venezuelan coast. The *Hope Pearl* is the largest natural pearl found so far. It is 5 cm in length, 10 cm in circumference at the middle and it weighs 1800 grains (1 *pearl grain* is equal to 50 mg). It is followed by *Shah Sofi's Pearl* weighing 513 grains, *La Regente* (346 grains), *La Pellegrina* (111.5 grins).

3. *Cultured pearl*: Cultured pearls are also formed naturally, the only difference is that the irritant is inserted into the oyster artificially, and the shape of the irritant and hence that of the pearl can be manipulated by design. Thus it is possible to produce a perfectly spherical pearl by inserting a perfectly spherical irritant. Experiments to stimulate growth of pearl in shellfish were started in Japan in the late 19th century by Kokichi Mikimotu (regarded as the father of cultured pearls), and the first spherical cultured pearl was produced in 1921 by inserting a small bead of *mother-of-pearl* from an American freshwater mussel into an oyster shell by carefully opening it without killing the oyster and leaving it in its natural habitat. The mother-of-pearl served as the nucleus for pearly material to grow around. Since then Japan has remained the main centre of cultured pearl production. This way, it takes 3-6 years depending on the size desired, to produce a pearl. Although it can be produced whenever wanted, the laborious process and the time factor make them costly and ,hence, precious.

Pearls need no cutting or polishing, but all pearls have to undergo elaborate and time-consuming processing before they can be considered as gems and fit for jewelry. Mechanized processing is ruled out because pearls are fragile and the entire operation is labour-intensive. After taking out, the pearls are first sorted according to colour. The natural pink, cream and grey coloured ones are set aside while those with muddy colours are processed. The processing consisting in washing and then heating in pressure cooker for 48 hours, soaked for 4 days in bottles filled with hydrogen peroxide (H_2O_2), ether and water while all the time exposing them to sunlight or very strong light. After this processing, the pearls become bright, smooth and whitish with pearly sheen ready for classification according to size and shape (*drop pearl*, *rice pearl*, etc.). finally they are drilled, strung and made into jewelry.

Pearl powder was used during mythological and historical times in cosmetic skin care. They were rubbed on legs to bring shine on the skin. According to gemmotherapists, pearl, when worn on body, has beneficial effect on piles. They are also believed to be good in urinary and liver troubles, in memory loss and for cooling the body.

Substitutes of pearls called *semi-cultured pearls* (also called *artificial pearls*) are also traded in the market. They are machine-made from mother-of-pearl, glass, plastic, etc. They are produced on a mass scale, and, hence, are inexpensive (about 1/50th of the price of natural/cultured pearls).

CORAL

Coral (called “Munga” in India) is another organic gem and is made up of $CaCO_3$ (calcite) and $MgCO_3$. Like pearl, it is also an inorganic material formed organically, by secretion of calcareous materials by corals which live in colonies in warm seas. Its hardness is 2.5-4.0 on Mohs scale, specific gravity 2.5 and refractive index 1.60. It shows a variety of colours red, orange, blue, black and white. All corals were originally white, and they got their colours from algae that lived within the protective shell of the corals. The white and red gem corals are very popular amongst gemmotherapists according to whom it is beneficial, when worn on body, to a number of diseases like hyperacidity, anaemia, gout, bronchitis, constipation, gall stone, epilepsy, etc.

AMBER

Amber (called “Kohrua” in India) is not an inorganic material at all, and it is a kind of plant fossil or fossilized resin having composition $C_{40}H_{64}O_4$. Its hardness is 2.5 on Mohs scale, specific gravity 1.07 and refractive index 1.54. It is yellow coloured, sometimes light to dark shades of red.

The recorded history of amber mining dates back to 1st century AD in Upper Myanmar. The tribal people of that region used earrings made by cutting amber pieces. Pockets of amber occur within dark blue carbonaceous shale beds of Eocene age.

Chapter 25

GRAPHITE

Graphite (also called plumbago or black lead because during the earlier times, it was confused to be a black variety of the grey lead sulphide mineral galena) is a material of the future. It has a wide range of applications starting from objects of everyday use to those belonging to high-tech areas, and for most of the uses it has no substitute. The name graphite owes its origin to Greek word "graphein" meaning "to write", because traditionally, the main use of graphite was in pencils and even now, common people are most familiar with this use (graphite pencils are popularly called lead pencils, but actually they do not contain any lead). It is made up of a single element carbon or C (derived from the Latin word "carbo" meaning charcoal with which people became familiar long before coal). Carbon has five allotropic varieties of which graphite is one and it is the softest one. The other four varieties are diamond (the hardest one), amorphous carbon or lampblack (the chemical element forming inorganic and organic compounds), white carbon and fullerene. Graphite, like diamond, is crystalline albeit their forms are different. But in nature, it is not found as a mineral made up of hundred percent elemental carbon, and it contains impurities—mainly silica.

Graphite commonly occurs in schistose rock and also, in some places, as a constituent of basalt and nepheline syenite. It is believed to have formed due to thermal metamorphosis under low pressure, of sediments containing carbonaceous matter by reaction of carbon compounds with either hydrothermal solutions or magmatic fluids, and also due to crystallization of magmatic carbon in reducing environment (cf., diamond is formed under high pressure).

Graphite may occur as large masses, veins and scales. Although it may occur in all the three types of rock, igneous, sedimentary and metamorphic, highly metamorphosed rocks like gneiss and schist host the most productive deposits. Mining is confined to the weathered zones of such rocks. The other host rocks of minor importance include quartzite, granite, pegmatite and carbonaceous shale. A rare type of isometric graphite crystals have been found associated with some meteoritic iron, and that has been named *cliftonite*. A steel-making waste known as *kish* is a rich source of high-quality graphite, and a technology for its recovery was developed by the erstwhile US Bureau of Mines in the late 1980s.

Graphite is a widely occurring mineral. The important producer countries are China, Sri Lanka, Madagascar, Brazil, Germany, Kenya, South Korea, Mexico, Norway and Russia. However, the quality of graphite varies widely from country to country. In India, graphite is mined from the states of Orissa, Jharkhand, Andhra Pradesh, Rajasthan and Tamil Nadu.

TYPES OF GRAPHITE

Graphite crystals fall in two forms. The hexagonal form is called the *alpha type* and the rhombohedral form called *beta type* (cf., octahedral/tetrahedral form of diamond). The alpha type is the most dominant, and natural graphite is made up of 70% alpha and 30% beta types. The hexagonal crystals of natural graphite have a unique layered structure consisting of six carbon atoms arranged in widely spaced (0.34 nanometre apart) parallel sheets (referred to as basal panes) grouped together in the form of crystallites. Thus the structure comprises a planar network of hexagons, and for this reason this type of graphite is also referred to in some literature as *planar graphite*.

However, in mining and consuming industry circles, graphite is classified based primarily on degree of crystallization, and then on the basis of form and size of the grains and geological mode of occurrence. The classification system is as follows:

1. Amorphous (in reality micro-crystalline or crypto-crystalline)
2. Crystalline
3. Flake
4. Powder
5. Vein
    (a) Lumps
    (b) Chips
    (c) Dust

In some literature, only three types of graphite find mentions amorphous, flake and vein.

The so-called amorphous graphite reveals, under a microscope, sub-microscopic sized crystals. It is actually metamorphosed coal. It has earthy lustre and is relatively low-carbonthe carbon content being on an average about 60 percent. It is mainly produced in Mexico, China and South Korea.

Crystalline graphite is medium to high carbon. The graphite crystal is made up of sheets of carbon molecules. Within a sheet, the molecules are closely bonded, but between sheets the bond is weak. Consequently, the sheets can slide over one another.. contrary to the earthy lustre of amorphous graphite, all crystalline types of graphite show metallic lustre. In the crystalline flake variety, the individual flakes vary in sizes from 150 micron (or 100 BSS mesh) to 710 micron. However of equal importance is what is called the *aspect ratios* of the flakes, i.e., the relationship of flake length to width. This ratio in a good flake should generally be greater than 20:1. China and Madagascar are the major countries producing flake type of graphite. The powdery graphite is nothing but crystals of size smaller than 150 micron (100 BSS mesh).

The vein types of graphite are produced mainly in Sri Lanka. Its sub-classification into lumps, chips and dust signifies the form in which it is produced from mines and sold in the market.

HISTORY

Discovery of natural graphite dates back to 1564. One day in that year, people of Borrowdale Village, UK accidentally found a black lumpy substance that came to the surface along with an uprooted tree. Their attempt to burn it failed, but they discovered that their hands were all soiled. They called it *wad*, and started using long pieces cut out of it for marking their animals. Thus began the first use of graphite namely, pencil. Gradually the pieces spread to other parts of UK and to Germany, France, etc. The close association of this substance with writing led to the name graphite (Greek "graphein" means "to write"). For a long time UK remained the main source of lumpy graphite. Later on, techniques for making pencil using graphite dust were developed. Evidence of primitive mining in Sri Lanka, however, dates back to 1820s, but actually it might be going on even before that.

In India, graphite occurrences were for the first time discovered in 1840 in the surface laterite deposits overlying crystalline rocks in what is now Kerala and the adjacent areas of Tamil Nadu, and the first official record of graphite mining was for the year 1901. The average annual production during the 10-year period, 1901-1911 was about 3600 tons. During that period, a few small mines came into being in the eastern part of Andhra Pradesh, but their total production was insignificant. By the year 1912, graphite mining in India ceased. Following World War I (1914-1918), sporadic mining activity started in 1919 in Orissa and Rajasthan, and later on in Karnataka, Andhra Pradesh, Madhya Pradesh and Bihar. It was only from 1934 that the production became regular. The average annual production during 1934-1938 was about 500 tons, during 1939-1943 it was about 900 tons, and by 1950 it increased to 1,611 tons. Since then, after a period of ups and downs, the production picked up a regular pattern in 1967 (7902 tons). Thereafter, the production was 11,723 tons in 1970, rising to 54,960 tons in 1980, to 59,140 tons in 1990 and to 120,322 tons in the year ending March, 2006. The grade of graphite mined in India is generally low at 12-13% fixed carbon or FC (fixed means non-volatile, i.e., the carbon left after all the carbon in the form of volatile compounds like hydro-carbons are burnt off) which needs cleaning, washing and (in some mines) beneficiation. Both amorphous and flaky types are mined.

BENEFICIATION

Natural graphite as mined contains impurities like silica, alumina, and oxides of iron, calcium and magnesium. Graphite containing at least 40% FC is regarded as economically usable. However, run-of-mine graphite may contain as low as even 10% FC, which may still become commercially usable after beneficiation. To beneficiate, graphite is first crushed and ground. The ground graphite is subjected to various combinations of different processes like air classification, tabling, jigging, froth flotation, electrostatic separation and magnetic separation. Of these, the most common process adopted is flotation. The commonly used reagents are kerosene or light diesel oil (LDO) as collector, pine oil as frother, sodium silicate as depressor of silica and sodium hydroxide as pH regulator. Generally, several rounds of both grinding and flotation operations have to be repeated to get commercial grade concentrate fractions. After de-watering and drying, different grades are sold for different uses. In India, the feed grade is generally around 13-16% FC and concentrates of up to 93%

FC grade flakes (+210 micron size, may vary up to 1.8 mm) are produced, while the tailings contain around 3-4% FC. However, in some other countries, further up-gradation employing chemical processing is done to achieve +99% purity.

CRITERIA OF USE

Although graphite is non-metallic mineral, in certain respect it behaves like a metal and possesses some characteristics that are normally seen in metals. It is a black coloured mineral with earthy to metallic lustre depending on the type. But the unique characteristics that make it indispensable in many uses including high-tech ones, are as follows:

1. *Chemical composition and characteristics:* It is a rich source of carbon. Chemically it is somewhat inert and it reacts with only oxygen and with some alkali metals and metal halides to form lamellar compounds. It has high resistance to acids and to corrosion.
2. *Physico-mechanical properties:* It is one of the softest substances (hardness less than 2 in Mohs scale) and yet it has high compressive, tensile and shearing strengths. Its elastic modulus is low. It has low *spring-back*, i.e., it is not very resilient, retaining fairly well a shape formed under pressure even after the pressure is withdrawn. It is fairly light having specific gravity varying from 2.09 to 2.23 depending on the degree of porosity and contents of impurities. A very unusual characteristic of graphite is that its strength increases with increase in temperature. Compared to at room temperature, its compressive strength increases by 20% at 1600^0C and tensile strength increases by 50-100% at 2500^0C.
3. *Surface properties:* It soils hand and smears any metallic surface with which it is in contact, on mere touch, even without much rubbing. This is due to the unique layered structure consisting of weakly bonded basal panes which separate out easily as minute flakes and it is these flakes that stick to the surface as smears. Its surface is highly unctuous with slippery feel. It is so slippery that even liquids tend to slip away on its surface giving it the characteristic of high non-wettability.
4. *Co-efficient of friction:* Graphite has a very low co-efficient of friction. This is due to the lamellar or sheet-like arrangement of the molecules in the crystals. Within a sheet the molecules are closely bonded, but between sheets the bond is weak. This allows the sheets to slide over one another without the molecules falling apart.
5. *Thermal properties:* It is one of the most infusible materials known. Its fusion temperature is 3650^0C and it vaporizes at 4500^0C. But, like metal, graphite is also a good conductor of heat and the conductivity becomes high if the graphite is in the form of flakes, because they provide larger surface areas exposed to the heat. Conductivity is also high in manufactured graphite fibers and nano-tubes (discussed later in this chapter). Besides, it has strong resistance to thermal shocks due to the combination of high thermal conductivity and low elastic modulus. In the presence of oxygen, pure graphite burns at between 620^0C and 720^0C at a slow rate with no smoke (because it is almost pure carbon).

6. *Electrical properties:* In this respect also, graphite behaves somewhat like a metal. It can conduct electricity. However, depending on the orientation of the sheets or planes of graphite crystal with reference to the direction of flow of current, there are two different ways in which electricity is conducted. Conductivity perpendicular to the plane is low, but the conductivity increases with increase in heat (this is unlike metals). In this case, in a sense, it acts as a semiconductor with thermal excitement causing increase in the flow of current (semiconductors contain only a small number of loosely bonded electrons at room temperature, and hence their conductivity is very poor of the order of 100,000 times less than that of conductor metals). On the other hand, when electricity is passed through graphite parallel to the plane, the conductivity is 6,000 times higher and it decreases with an increase in temperature (like metals). The electrical conductivity is due to the lamellar or sheet-like arrangement of the molecules in the crystals. Within a sheet the molecules are closely bonded, but between sheets the bond is weak. When electric current is passed and the electrons re-excited, those on the surface of the sheets move and carry electric current. The conductivity increases further if the graphite is manufactured to fibers or nano-tubes (discussed later in this chapter).
7. *Response to radioactivity:* Radioactivity is the spontaneous disintegration of certain heavy elements accompanied by the emission of high energy radiation, which consists of three kinds of ray alpha particles, beta particles and gamma rays. Graphite can absorb radioactivity. However, it does neither absorb nor adsorb neutrons although it can reflect and slow the down.
8. *Alloyability:* Graphite is one of the few nonmetals capable of going into solid solution in some metals.

USES AND SPECIFICATIONS

The diversity of products based on graphite is practically endless and still newer and newer innovative products are being developed, the process technologies of many of which are proprietary. The unique combination of the properties make graphite indispensable in a number of industrial applications. since there may be wide variations in fixed carbon content (40-100%), size (5 micron to 1.8 mm) and shape, it is obvious that there can be any number of permutations and combinations of these parameters to give rise to as many number of specifications. In industries, some 500-600 grades are specified and the range of industrial applications of graphite has been widening moving from traditional to highly sophisticated ones. However, certain specifications may not always be fulfilled by natural graphite, and in applications requiring such grades (e.g., electrode, braid, nuclear moderator etc.), specially manufactured graphite may have to be used. The important uses of natural graphite are as follows:

1. Pencil
2. Refractories
    (a) Graphite brick
    (b) Mag-carb

    (c) Alumina carb
    (d) Zirconia-graphite
3. Crucible
    (a) Clay-bonded crucible
    (b) Silicon carbide crucible
4. Foundry facing
5. Isostatic graphite mould
6. Brake lining
7. Bearings
8. Porous bronze
9. Batteries
    (a) Dry cell
    (b) Alkaline cell
10. Carbon brushes for electric motors
11. Lubricants
12. Graphitized grease
13. Sintered graphite products
14. Paint
15. Expanded or exfoliated or flexible graphite
16. Colloidal graphite
17. Graphite adhesives
18. Phosphoric acid fuel cell
19. Graphene

These uses along with their specifications are discussed as follows:

1. Pencil: This is the first use of graphite dating back to 1564 in Borrowdale, UK. Commonly graphite pencil is called lead pencil, which is a complete misnomer because it does not contain any lead. This term owes its origin to Roman period when there was no graphite. During those times, people used to write on pieces of bamboo by first engraving lines with lead and then filling the lines with colour with the help of brushes called *pencillus*. During the initial years of usage in and around Borrowdale, small stick-like pieces were cut from graphite lumps, covered with thread and used for writing. In 1565, Konrad Gesner started the innovative practice of inserting thin pieces of graphite into wood. But such lumpy graphite was not found in certain other countries like Germany, France, etc., and the practice of mixing graphite powder and clay with a binding substance like gum or sulphur began. During early 19th century, France under Napoleon was at war with England and supply of good grade graphite from the latter was cut off. Then at the instance of Napoleon, the technique of pencil-making was refined by Nicholas Jacque Conte. He mixed graphite powder and clay, moulded it in the shape of thin long pieces and then burnt them in a kiln at a temperature of about 1000^0C. Later, Joseph Hardsmuth found that by adjusting the proportion of clay, the writing could be made hard or soft. This technique is still used today for manufacturing pencils. Graphite constitutes 50-60% of the mixture.

Specifications: Black smear on the hands when touched is an indicator of the degree of softness and the FC content of the graphite, and these three characteristics are the main criteria for this application. The blackness of the streak is regulated by the content of clay in the mixture. But softness should also be within optimum limits. Extremely soft graphite will tend to crumble on burning, and the quality of writing will not be good. On the other hand, too hard graphite will make writing difficult. Since the amorphous graphite is very soft, producing smear easily, it is not preferable, and the crystalline natural flaky type is used.

Since graphite burns resulting in ash formation at a temperature lower than the pencil kiln temperature, high ash in the raw graphite is not desirable. Low ash automatically means high FC. For high-quality pencils, the industry specifies less than 2% ash and more than 98% FC, which may be progressively relaxed with lowering of quality of the products. Further, the ash should not fuse at the kiln temperature (1100^0C) in which case pencils will all stick to one another in a fused mass of ash inside the kiln.

The non-graphitic carbon, on burning, volatilizes off and is measured as the loss on ignition or LOI. When the pencil mould is burnt, this loss will distort the shape, and hence, should be minimum.

Solubility in both water and petroleum is specified to be low, because otherwise, the pencil, when accidentally in contact with these, will become damaged.

Homogeneity of the mixture of graphite and clay is important for a coherent mould. This requires that the graphite should be fine enough in size and should be free from grit. The industry specifies a maximum of 50 micron size.

The Bureau of Indian Standards (BIS) recommended in 1982 specifications of graphite for use in pencil-making. According to this, the different parameters are: *30% (max) blackness of smear; 3% (max) LOI (i.e., non-graphitic carbon content); 0.50% (max) petroleum-soluble matter; 1.25% (max) water-soluble matter; 10% (max) ash (but for high-quality pencil, less than 5%).*

2. Refractories: Refractory materials are defined as those resistant to heat and having a melting temperature of not less than 1580^0 C. The function of refractory lining on a furnace wall is not only to withstand high temperature, but also to withstand temperature fluctuation, and to resist penetration, abrasion, and erosion by hot gases and molten materials in the furnace, and over and above, it should not chemically react with those materials. Life of refractory lining has increasingly been becoming a critical parameter in the productivity of a furnace and economics of a plant, because each time the lining fails and needs replacement, the furnace has to be shut down. Graphite Refractories have been in use since more than 200 years ago, but intensive R and D work resulting in some innovative advancements in the technology has started much later, only 40-50 years ago. The current trend is to combine the beneficial properties of graphite with those of other refractory materials. So far as graphite is concerned, the most important criteria are its high fusion point, thermal shock resistance, thermal conductivity at high temperature, increase strength at high temperature and chemical inertness. There are four types of Refractories using graphite as follows:

(a) *Graphite bricks*: During earlier times, graphite refractory bricks used to be made using a mix of graphite and plastic fireclay, mainly for use in areas of much heat and corrosion. These are no longer popular. Both amorphous and flaky graphite were used, the latter for higher quality bricks. In case of the former, 70-80% FC and 600 micron to 20 mm size were specified, while for the latter, 90-98% FC and 180-75 micron size.

(b) *Mag-carb bricks*: These bricks have now largely replaced mag-chrome bricks. As the name suggests, they contain magnesia and graphite. It was first manufactured in USA in 1960s and its popularity picked up with advancements in steel technology such as basic oxygen converter, water-cooled electric arc furnace (EAF) and steel-refining ladle.

The higher the graphite content, the higher will be the number of casts (i.e., the number of heat cycles after which the brick will need replacement) and the longer the life of bricks. However, too high a graphite content at the cost of magnesite may reduce the refractoriness as graphite is not very refractory (it conducts heat). In basic oxygen converters, the proportion of graphite used generally vary up to 20% (brick life 700-750 casts); in water-cooled EAF, from 15-20% (brick life 500 casts) to 20-25% (brick life 1000 casts) and in ladles, it is around 10% (brick life 50 casts).

Since the number of heat cycles is more, thermal shock resistance, particularly combined with increased strength at high temperature, becomes an important criterion, and since the water-cooled technology involves transfer of heat from the walls of the furnace to the cooling system, heat conductivity, particularly under enhanced heat conditions, becomes important. The graphite-induced heat conductivity of the bricks now allows the furnaces to be fired at higher temperatures in the range of around 2000^{o}C.

With regard to specifications of graphite, the industry prefers fine-sized flakes (150-710 micron) that will evenly distribute itself in the magnesite matrix. Chemically, the graphite should contain low ash (less than 10%) and 87-90% FC, while silica, alumina and iron are considered particularly deleterious. The ash will fuse at 1100^{0}C, i.e., much below the furnace temperature, but since the quantity of graphite used is relatively less and consequently the total quantity of ash generated is also less, up to 10% is tolerated. Silica, alumina and iron react with magnesia and form low-melting compounds.

(c) *Alumina carb or graphitized alumina bricks*: These combine the high refractoriness of alumina with the high fusion point, thermal shock resistance, thermal conductivity at high temperature, increased strength at high temperature, non-wettability and chemical inertness of graphite. Its popularity has started increasing in the 1970s with the advent of the continuous casting technology. In this technology, molten metal directly and continuously flows from the ladle to a water-cooled mould and the function of graphitized alumina is essentially to control the flow. All the criteria important for graphite for use in mag-carb brick, are relevant in this case also. In addition, non-wettability is important so as to smoothen the flow of molten metal. However too high thermal conductivity of the bricks will tend to somewhat cool the molten metal before reaching the mould, and as a result, its viscosity will increase creating impediment to flow. Hence, the proportion of graphite in the brick needs to be carefully determined. Generally, the bricks contain 8-30% graphite.

Graphitized alumina bricks are made by either applying isostatic pressure (i.e., applying pressure from one side to the material confined on all other sides in a mould) to a mixture of alumina, graphite flakes and a binder or by vacuum extrusion (i.e., squeezing the solid heated mixture to flow under an applied pressure through a die-opening and causing it to deform continuously into a shape of predetermined dimensions). However, in the first process the flakes become flattened and oriented perpendicular to the direction of the pressure. Inside the ladle, these flakes provide a larger surface area exposed to the heat resulting in higher thermal conductivity, quicker cooling of the molten metal to a viscous mass, slowing down of its flow and decrease in productivity. Relatively smaller sized flakes are therefore preferable in this case. This problem does not arise in the case of the bricks produced by vacuum extrusion, and coarse flakes can be used. For some applications (e.g., monoblock stoppers) andalusite-graphite bricks can be used.

The broad parameters specified by the industries include 85% (min) FC and 150-500 micron size. Unlike in the case of mag-carb bricks, silica, alumina and iron are not objectionable because there is no magnesia to react with them to form low-melting compounds. On the other hand 10-20% silica is desirable in the whole mixture. Silica, on reaction with nitrogen and carbon, form whiskers of silicon nitride (Si_3N_4) and silicon carbide (SiC) respectively. These whiskers reinforce the bonding of the mixture of graphite and alumina.

(d) *Zirconia-graphite bricks*: These are widely used in billet casting. Zirconia (ZrO2) is a highly refractory and strong material, but it needs first needs to be stabilized by addition of an oxide of magnesium, calcium, scandium or yttrium.

3. Crucible: Compared to furnaces, crucibles are smaller in size. They are advantageous when mixing small quantities of different products requiring different alloys. It is also easier to change a damaged crucible, as opposed to a furnace lining. The main uses of crucibles are for foundry melting of steel, in nonferrous metallurgy (brass, aluminium) and in precious metal metallurgy. The life of crucible is highly sensitive to the type of metal involved. For example, each heat cycle of nonferrous metal melting takes days and each time, the temperature rises from normal to as high as 1500^0C, and the crucible is frequently subjected to rigorous thermal shocks. Prior to World War I (1914-1918), even the best crucibles made in USA based on Sri Lankan graphite flakes used to have life of 28-30 heats. Switching over to Madagascar flakes and improvement in technology during the post-war years extended the life 150-200 heats. There are two types of graphite crucibles namely clay-bonded crucible and silicon carbide crucible. In the early 1950s, consumer preference started shifting from the former towards the latter type.

The thermal conductivity, thermal shock resistance, high fusion temperature, high-temperature strength, non-wettability, chemical inertness and nature of the ash of graphite are the main criteria. High thermal conductivity enables the crucible to absorb the thermal shocks. The conductivity of graphite is more if it is in flake form, because flakes provide larger surface area exposed to heat. What is more important is that in graphite the thermal conductivity increases with increase in temperature. The high fusion temperature and high strength at higher temperature give flexibility to use lower-melting and lower-strength bonding material so as to achieve an average fusion temperature and strength higher than the working requirement. Non-wettability facilitates easy flow when the melt is poured out from the crucible. Chemical inertness enables the crucible to be used for a range of products without entering into the metallurgical reactions.

Composition of ash, more than its percentage, is crucial. Presence of alkalis will lower the melting point and shorten the crucible life. Iron oxide is readily reduced by carbon of the coke oven, and also melts at a relatively lower temperature. Besides, if, in addition, TiO_2 is also present then at the high temperature in furnaces where the refractory products are used, they form low-melting iron-titanate glass causing blisters in the crucible and consequent increase in its porosity. Presence of alumina and silica together is also harmful. Upon fusion, it forms silicates (kyanite, andalusite or sillimanite) with increase in specific gravity (from 2.7 of silica to 3.2-3.7 of the silicates) and then mullite at temperatures 1200-1600^0 C, with disturbance of the eutectics and resultant deformation of texture and weakening of the crucible. Refractoriness is lowered by the presence of fluxes such as lime, magnesia and alkalis which form low-melting brittle glass with silica, and hence these are considered highly deleterious. According to the specifications of 1985 of the Bureau of Indian Standards (BIS), the limits of the deleterious constituents in the ash should be: *Fe_2O_3 1.2% (max); TiO_2 0.5% (max); CaO 0.02% (max); SiO_2 + Al_2O_3 10% (max); alkalis 0.2% (max*).

So far as the size of the flakes is concerned, there should be a mix of medium-to-large sized flakes. The smaller ones get distributed in matrix giving strength to the crucible while larger ones serve to enhance thermal conductivity by providing larger surface area exposed to the heat.

(a) *Clay-bonded crucible*: For making such crucibles, graphite (40-50%), plastic fireclay (20-30%), crucible scrap(25%) and sand (5%) are first mixed, then moulded into the desired shape and size, dried and finally fired in a reducing atmosphere. The graphite for this purpose should contain about 90% FC and flake size should be +150 micron.

(b) *Silicon carbide crucible*: Silicon carbide (SiC) was prepared in laboratory in 1892, and later, commercialized. It is one of the hardest materials known, its hardness being in the region of 9-10 on Mohs scale. For making such crucibles, a mixture of graphite (20-40%), silicon carbide (40-60%) and plastic clay (as bond) is crushed, passed through a magnetic separator to remove iron particles, mixed with suitable proportion of water and the soft mass is left for a month to mature. Then it is moulded into required shapes and sizes, dried in sheds for 15 days, and finally coated with glaze and baked in kilns for 5-6 days. The graphite for this purpose should contain about 80% FC and should be +150 micron in size.

4. Foundry facing: The whole system of mould-making, melting of metals, casting of the melt in mould, solidifying the cast metal to produce an object in the form of the mould, and final dressing and finishing of the object is called foundry. Moulds may be of two types, permanent zinc die and use-and throw kind sand mould (or simply mould). It is the latter type, i.e., moulds, in which graphite finds application for coating the inner surface. It is also used as a parting agent, i.e., coating on the inner surface of the pattern equipments, for easy separation of moulds from them.

A mould for solid cast is made with moist sand bonded by clay or resin or bentonite rammed into the desired pattern by hand or machine, and is suited to casting of metals or alloys which melt at temperatures less than the sand (pure silica melts at 1700^{0}C). The following conditions should be fulfilled in a good mould:

(i) The inner surface of the walls of the mould and outer surface of core should be smooth so as to minimize the need for dressing and finishing of the cast.

(ii) The walls of the mould should be slightly porous and permeable so as to allow the gases released during casting to escape, but not permeable enough to allow metal penetration. The core of the mould, in contrast, should be impermeable so as to prevent metal penetration (the question of gases escaping through the core does not arise as it is inside the mould).

(iii) The sand should not melt and react with the casting metal at the operational temperature of casting.

Graphite has been traditionally used as a refractory coating on the inner surfaces of moulds. Thermal shock resistance, high fusion temperature, high-temperature strength, smooth unctuous surface and chemical inertness are the principal criteria.

High thermal shock resistance, high fusion point and high-temperature strength help to improve the performance of the mould even when temperature of the molten metal is very high. Smooth slippery finish prevents the metals from adhering to the mould, thus allowing the castings to be easily removed on cooling and also reduces subsequent machining and finishing costs. Finely pulverized (53-75 micron or 300-200 BS mesh) amorphous graphite (or even reground scrap or low-grade dust from refining mills) is preferred to flakes because efficient thermal conductivity is not a necessary requirement, and, on the other hand, such fine grains, besides being less expensive, get distributed on the surface leaving enough gaps for the gases to escape. Small amounts of mica and quartz in the graphite are desirable because small quantities of mica are generally added to the coating mix and, of course, silica makes up the main body of the mould. The industries actually use graphite of variable purity containing 40-70% FC, but consider readily fusible sulphides as the most deleterious constituents.

However, according to the specifications recommended in 1984 by the Bureau of Indian Standards (BIS), the parameters should be: *85% (min) FC; 12% (max) ash; 3% (max) volatile matter; and 2.5% (max) non-graphitic carbon*.

5. Isostatic graphite mould: These moulds are used for manufacturing various high-performance tools made of hard metals, ceramics and diamond, by pressure sintering. In the pressure sintering process, the article to be sintered is simultaneously heated to a temperature of above 500^0C and subjected to pressure — generally in an inert atmosphere. Heating is done either by direct passage of current or by induction. The graphite mould serves to facilitate the passage of the electricity and it is also required to be strong enough to withstand the conditions of high pressure, high temperature and thermal shocks. Parts of the mould for this purpose is made by isostatically pressing graphite, i.e., by applying pressure from all directions. This makes the mould very compact and strong. The principal criteria for use of graphite are its electrical and thermal conductivity, thermal shock resistance, smooth and slippery surface, and non-wettability. Very pure and fine grained graphite containing a maximum of 0.2% ash and having 10-20 micron size is required.

6. Brake lining: In automobile brake linings, asbestos monopolized the market for a long time. But due to the world wide campaign against mining and use of chrysotile asbestos on account of its hazardous effect on health, since early 1980s demand for graphite has risen considerably from 1-2% to as high as 15% in some cases. For making these products, graphite particles are impregnated with resin which bonds them. The principal advantages of graphite are its high compressive and tensile strengths and low coefficient of friction which together result in low wear rate. The coefficient of friction becomes further lower as the graphite lining smears the surface of the drum or disk with which it comes in contact. Then the graphite lining rubs against graphite smear and friction is doubly reduced.

With regard to specifications, graphite must be fine (less than 75 micron 200 BS mesh) so that the particles are dispersed on the surface of the drum or disk and wearing is even. But one disadvantage of using very fine sized particles is that their total surface area becomes very large, and the resin bond may not cover each and every particle fully. This may leave some weak spots of loosely bonded particles. Any abrasive substance like silica is the most objectionable. For the maximum efficiency, graphite should be very pure and the FC content specified by industries is 98% or more. However, if silica content is exceptionally low, lower grade graphite containing 90% FC can be tolerated for inferior quality products. Since it is difficult and expensive to beneficiate natural graphite to such pure grade, now-a-days there is a tendency to mix 40% synthetic graphite with 60% beneficiated natural graphite. The disadvantage of fine particle size of beneficiated graphite is also overcome in products based on synthetic graphite (discussed later in this chapter).

7. Bearings: Bearings are important constituents of a machine part, which are designed to transmit load to the shaft rotating concentric to the bearing surface. There are two important types of bearings; the sliding type and the roller/ball bearing type. In the former type, the contact between the shaft and the bearing is a surface contact while in the latter type it is a line/point contact. The sliding bearings are made in cylindrical configuration and are meant for sustaining heavy loads. Bearings are always alloy-based (either solid alloys or bonded to steel backings) as no single material can possess all the properties required for the function. The materials chosen should possess high strength, hardness, low coefficient of friction, high thermal conductivity, corrosion resistance, etc. It is here that graphite has a role to play. Graphite is one of a few nonmetals which can form alloy with certain metals and its high strength, low coefficient of friction, high thermal conductivity and corrosion resistance get added to metals with which it is alloyed. The most common graphite-based alloy used in bearings is:

Name of alloy	Composition	Uses
Graphitic aluminium alloy	Up to 16% graphite with or without coating of Ni/Cu ; Al-Si alloys containing 2-24% Si. Up to 7.5% Ni, 4% (max) Cu and up to 1% Mg employed as base.	Used in self-lubricating bearings and other antifriction applications.

8. Porous bronze: Bronze is an alloy containing copper and tin and it is heavy. In porous bronze, a small amount of 3% graphite is added to bronze containing 87% Cu and 10% Sn. Addition of graphite particles serves to make the bronze lighter. Alloyability and low specific gravity of graphite are the criteria. Porous bronze is useful for making light portable motors such as those used in domestic appliances, starters of automobiles, business machines, etc.

9. Battery: A battery consists of two or more cells grouped together. The principle underlying the working of a cell is that if two different metals are immersed in an electrolyte, then their differential solubility generates a difference in voltage, and one of the metals appears to be positively charged (anode) in relation to the other which appears to be negatively charged (cathode). In this process, the chemical energy of the metals and electrolyte is converted into electrical energy. If in this process, the metals and the electrolyte are consumed irreversibly, then the cell is called *primary or non-rechargeable cell*. On the other hand, if the chemical energy can be restored through reversion of the chemical reaction by electric current, the cell is called *secondary or rechargeable cell*. Primary cells are of two main types dry cell and alkaline cell. The dry cell in its turn, may be either *voltaic cell* or *Leclanche cell*. Out of all these, graphite finds use only in the Leclanche cell and the alkaline cell.

(a) *Leclanche cell*: In the Leclanche cell, carbon rod (anode) is dipped in ammonium chloride solution while the container itself is made up of zinc which serves as the cathode. As zinc dissolves in NH_4Cl producing $ZnCl_2$, a difference in charge between C and Zn is produced causing electric current to flow. This chemical reaction also liberates hydrogen gas which goes towards carbon anode and accumulates around it. This is called *polarization*. The cover of hydrogen film on the anode causes resistance to the flow of current, and consequently decreases the efficiency of the battery. MnO_2 serves as a depolarizer. It is put in a linen bag, and the carbon anode rod is enclosed by it. The hydrogen ion, while passing through this MnO_2, combines with the oxygen and harmless Mn-hydroxide is formed, leaving the anode free from any deposition of hydrogen.

(b) *Alkaline cell*: This is also a primary or non-rechargeable cell. The positive pole (anode) contains zinc, while the negative pole (cathode) contains manganese dioxide. The electrolyte is a strong alkali like potassium hydroxide or sodium hydroxide.

In both types of cells, graphite is added to MnO_2 as a filler to improve the electrical conductivity. In addition, graphite has the advantage of chemical inertness. The only difference is that in the Leclanche cells, the function of MnO_2 being of supporting nature, lower grade graphite (88% FC or above) serves the purpose while in alkaline cells, the function of MnO_2 being pivotal, high grade graphite (not less than 98% FC) is specified by the industry to impart high conductivity. The grain size is less than 75 micron in both cases, but in the alkaline cells, lower the size, the better and more uniform its dispersion in the MnO_2 matrix will be, and the industry often specifies as low as 5 micron size. Further, in the alkaline cells, since higher electrical conductivity is required, the graphite should be free from metallic impurities like copper, cobalt, antimony, arsenic etc. which may cause short circuiting.

10. Carbon brushes: Carbon brush is a component used for collecting current and then distributing it to a rotating electrical motor to drive and keep it in motion. A carefully controlled mixture of graphite powder and a binder (coal tar pitch or synthetic resin) are compressed into homogeneous solid coherent blocks with particles of graphite serving as electrical conductive points exposed on the surface giving it a mesh-like appearance. Current is collected and distributed through these points. High electrical conductivity, low coefficient of friction with low wear rate and high thermal conductivity that prevents it from being overheated due to constant contact with the rotating motor, are the chief criteria for this application of graphite. High spring-back means strong resilience, i.e., easy deformability both when pressure is applied and when it is withdrawn (spring-back is the ability to retain a shape formed under pressure during making of the blocks even after the pressure is withdrawn, or in other words, it is the percentage of increase in volume of a compressed block after release of the pressure). This will make the brush vulnerable to disintegration under the constant shearing stress to which it is subjected to. Therefore, the lower the spring-back of the graphite, the stronger the brush block will be.

The most widely used brushes used are the *electro-graphitic brushes*, which are suitable for conditions of strong current and which have a long life. For making such brushes, pure graphite is resin-bonded and baked at 2400^0C. Ordinary brushes are suitable for use under conditions of somewhat weak current and have shorter life. Another type of brushes called *metal graphite brushes* are made out of a mixture of natural graphite and finely divided metal powder (copper, tin, lead or silver), the latter producing a polishing effect.

For minimum current loss, a high grade graphite is desirable. Minimum FC-content of 95% is specified for ordinary brushes. But for very high-quality electro-graphitic brushes, manufacturers demand graphite of more than 99% purity. It is difficult to beneficiate natural graphite to such high purity and ideally, synthetic graphite (discussed later in this chapter) should fit the bill. But synthetic graphite has the disadvantage of a relatively high spring-back, sometimes as high as 50 percent. Therefore, nowadays, industries use a mix of beneficiated natural and synthetic graphites. The size should be very fine, less than 53 micron (300 BS mesh). Natural graphite with spring-back of 5-12% is available for this application.

11. Lubricants: Graphite powder by itself is used as a lubricant for application in the areas of high temperature and high stress such as steel-rolling and automotive applications and in nylon bearings (used in domestic appliances like mixers, grinders, juicers, etc. where conventional lubricants like oil, grease are not acceptable) required to function under high temperature and pressure conditions. In this application, its only major competitor is molybdenum disulphide (MoS_2). The principal criteria for use of graphite as an industrial lubricant for these applications are its smoothness, softness, low coefficient of friction, chemical inertness and thermal resistance. Besides, the lubricant must not wear the moving parts and so freedom from grit is necessary. It must not dissolve in petroleum (of automobiles) nor should it be washed away by water during cleaning of the parts. Hence low solubility in both oil and water is specified, flakes will have higher efficiency because the contact area will be more.

Further, graphite lubricant is also applied as non-sticking coatings on glass-forming trays, aluminium moulds, etc. here, besides the above characteristics, non-wettability is also an important criterion, because the glass, castings etc. should come out easily and smoothly without sticking the surface and with smooth surface finish.

The industry, in general, specifies a minimum of 96% FC (in special case up to 99%) and size of 53-106 micron (150-300 BS mesh). Some Indian industries accept coarse size up to 700 micron. The Bureau of Indian Standards (BIS) recommended in 1967 a set of specifications. According to that, the parameters should be: *5% (max) ash,; 3% (max) non-graphitic carbon; 0.5% (max) petroleum-soluble matter and 1.25% (max) water-soluble matter*.

12. Graphitized grease: Very fine sized high-purity graphite is added to grease for imparting certain properties like lowered friction, high thermal conductivity at high temperature, high fusion temperature and smoothness. The grade of graphite specified is +99% FC and the maximum size of 38 micron.

Such graphitized grease is used for certain high-stress applications, the most important of which is manufacturing of various seamless tubular products like *seamless steel pipe*. The principle of manufacturing such products consists in piercing of a solid round helically rolling billet by another one of smaller diameter which is revolving in the opposite direction and which is heated to a temperature of 1300^0C. As the larger bar keeps advancing due to helical rolling, the smaller billet keeps piercing it, creating a bore of smaller diameter. Throughout the operation, special devices are employed to maintain the specified dimensions. Graphitized grease is applied as a coating on the smaller billet for enhancing the efficiency of piercing.

Another application of graphitized grease is in *wire drawing*. In this, a metal bar is rolled into a round billet and then forced through a series of die-openings. Each successive hole is of smaller diameter, through which progressively thinner and thinner wire is pulled rapidly. The entire operation is carried out in cold state. High-performance graphitized grease is applied to the die-openings to facilitate drawing and to give smooth finish to the wire.

13. Sintered graphite products: These include objects like cogs or teeth in gears. Sinter is a somewhat porous lumpy mass made by application of just enough heat to fuse the corners of the particles so as to make only the corners to join together. Sintered graphite products are made by mixing 1.5% of powders (5 micron size) of high-purity graphite and 98.5% of steel, and then heating into the required shapes. Absorption of graphite in the steel matrix strengthens the product, and finer the size of the graphite better will be the absorption. As the percentage of graphite in the product is very small, it should be of high purity containing a minimum of 96% FC, but 98-99% is desirable for high-quality products. High tensile and shearing strengths and low rate of wear of graphite are the main criteria.

14. Paint: Graphite is a good conductor of electricity and it is strongly resistant to corrosion. Graphite-based paint is, therefore, ideally suited when a black electrically conductive corrosion resistant coating is required on a metal or a plastic surface. This kind of coating finds application in computers. In certain applications like automotive industries, its power to absorb radioactivity and its light-stability on account of black lustrous surface become important. In sensitive areas with electrical installations involving handling of combustible chemicals, the floors can be coated with graphite paint. The coating eliminates the build-up of static electricity, gives a good resistance to chemicals, particularly with low *flash point* (temperature at which vapours break into flames) and imparts low wear and long durability.

Purity of graphite is not of critical importance, because first, ash will not be produced as no heating is involved, and second, in any case, 20-25% silica has to be added to facilitate distribution of the graphite particles throughout the paint medium (without the silica, the graphite particles will tend to flocculate). Generally, 50-70% FC is acceptable, but for specialized applications, 88% FC is specified. Large flakes are not desirable, because they will have a tendency to peel off when the paint becomes dry. So either amorphous graphite or powdered flaky graphite is specified. For the same reason, flaky minerals like mica is objectionable. Over a period of time, pyrites decomposes on weathering, to form sulphuric acid, and hence is considered deleterious.

15. Expanded or exfoliated or flexible graphite: This is a binderless all-carbon material used for making foils, sheets, seals, gaskets, etc. It is the most resilient gasket material known with a high spring-back of 50%, having very low coefficient of friction giving it self-lubricating properties. Besides, it is a good thermal conductor with high thermal shock resistance, non-wettable by molten glass, ceramics or metals and strongly resistant to creep with negligible ageing effect resulting in practically infinite life. It is impermeable to gases and fluids. It can be easily cut, punched, glued and pressed into dies. It can be used under conditions of temperature ranging from (-) 200- 500^0C in an oxidizing atmosphere and up to 3000^0C in a reducing atmosphere.

It is nowadays widely used as a sealing material in flat gaskets and packing materials. The range of uses covers the entire field from rocket and space technologies to oil refineries, fuel pumps, automobiles and thermal and nuclear power plants, where a very high degree of functional effectiveness is required. This material is emerging as an ideal substitute for asbestos, the mining and use of which have been deceasing due to the worldwide campaign against it on account of its hazardous effect on health. Recent developments include use of flexible graphite as a protective layer on graphite crucibles for making micro-electronic products by vapour deposition techniques, for electromagnetic shielding purposes in defence, for making flame-retardant tubes (mix of flexible graphite and poly-olefinic resin) for protecting electric wires and cables, for making moulded graphite products by extrusion, for making conductive composites (mix of flexible graphite and thermoplastic resins) and for making bearings by vapour depositing zinc on the inner surface of exfoliated graphite ring.

The process of converting natural graphite to exfoliated graphite takes advantage of the gap between its basal planes. Various chemical species can be intercalated inside the gaps and the intercalated molecules cause further increase in the distance between the basal planes on removal of these molecules, i.e., de-intercalation by heating the bond between the planes weakens further causing them to expand. The process for making expandable graphite was first developed in the late 1970s. It consisted in a two-stage treatment of crystalline graphite involving oxidation by chromic acid and then addition of sulphuric acid. This weakened the bonds amongst the sheets in the crystals to allow up to 7 times expansion perpendicular to the basal planes on heating with subsequent decrease in density. The material so obtained is then pressed into dies to obtain foils of desired thickness, shape and thickness, shape and density. However, according to a report of 1996, a process developed by the national Physical Laboratory, India, it has been possible to achieve 200-300 times exfoliation resulting in a highly puffed up material possessing extremely low density.

The primary graphite raw materials specified by the industries are the flake type varying from 85-99% FC content and from 250 micron to 1.8 mm grain size.

16. Colloidal graphite: It is a suspension of fine 99.9% pure graphitic powder of sub-micron size (0.7-0.8 micron) in a liquid (water, alcohol), usually with a small amount of polymeric binder. It is new-generation product of graphite which can be applied as a coating on sensitive instruments to protect them against electromagnetic induction (EMI). Its potentiality for admixture with cement paste for EMI-shield effectiveness of underground vaults housing telecommunication equipments and power transformers is under research. It is manufactured from exfoliated graphite in which the molecular bonding within the crystals have already become considerably weakened.

17. Graphitized adhesive: Adhesive is an organic or inorganic substance capable of bonding together other substances by surface attachment. Graphitized adhesives are used for bonding and sealing applications under conditions of high temperatures up to 3000^0C. Amorphous graphite is the preferred type, because flake grains having a larger area of a smooth slippery surface do not bond well and tend to develop cracks along the boundaries. The principal criteria are strength, high fusion point and chemical inertness. If the operating temperature is less than 300^0C, then the adhesive is made of primary graphite; if it is up to 600^0C, then electro-graphite made by baking resin-bonded pure graphite at 2400^0C is used; and if the temperature is higher, then the electro-graphite is subjected to further specialized treatment. The application areas are steam joints employed in the paper industry, chemical and oil pipeline, aircraft fuel pumps etc.

18. Fuel cell: It is believed that fuel cells will become the norm in many applications within the first quarter of the 21st century – be it for transport or energy supply or in an industrial application. Fuel cell is a device that generates electricity through a non-combustion electrochemical reaction oxidation of hydrogen or CO-gas, the former being more popular because of its environment-friendliness. The principle was first conceived by William Grove in 1839, who hypothesized that if water could split into hydrogen and oxygen by electric current, then the reverse should also be true i.e., combination of hydrogen and oxygen should produce electricity. He experimented and proved his hypothesis true. In 1889, Ludwig Mond and Charles Langer made the first practical model and named it fuel cell. It was further streamlined by W. Ostwald in 1894, and now it is believed that fuel cells will become the norm in many applications within the first quarter of the 21st century, be it for transport or energy supply or in industrial applications.

A fuel cell basically consists in four main components namely, (-) anode (hydrogen), (+) cathode (oxygen), electrolyte and catalyst (usually nano-particles of platinum). The catalyst ionizes the hydrogen atoms into positively charged protons and negatively charged electrons. The electrons go into an external circuit and reach the anode where oxygen is supplied and ionized by the catalyst. Thus an electric current flows through the circuit for utilization. Meanwhile, either the positively charged hydrogen protons pass internally through the electrolyte and reach the anode or the oxygen ions move through the electrolyte and reach the anode. Eventually, all the oxygen and hydrogen ions reunite to form water—either in the cathode or in the anode. Since the fuels hydrogen and oxygen are continuously supplied into the cell, it never goes dead unlike a normal cell. The electrolyte is the key and its function is to selectively allow either oxygen ions or hydrogen protons to pass through—directly or by reacting. Depending on which material is used as electrolyte, there are six types of fuel cells:

(a) Solid oxide fuel cell (SOFC)
(b) Polymer exchange membrane fuel cell (PEMFC)
(c) Alkali fuel cell (AFC)
(d) Phosphoric acid fuel cell (PAFC)
(e) Direct methanol fuel cell (DMFC)
(f) Molten carbonate fuel cell (MCFC)

Graphite finds use in fuel cells in two ways as follows.

(a) Phosphoric acid fuel cell: Operating temperature in this type of cells ranges from 150-2000^{0}C, and these are already in use at utility power plants, hospitals, hotels, schools, office buildings and airport terminals. Graphite is mixed with poly-tetra-fluoro-ethylene and fluorinated ethylene propylene to form a paste which is applied as a caulking material to prevent leakage of the phosphoric acid. The main criteria for using graphite are its high thermal conductivity and inertness to phosphoric acid.
(b) Connecting plate: Output of a single fuel cell, depending on the type, varies from only a few kilowatts to a couple of megawatts or so. For practical usage, therefore, many fuel cells are usually assembled in a stack. Graphite plate is the material used for connecting two fuel cells because of its bipolar nature, i.e., ability to conduct electricity both perpendicular to its lamellae and along them.

19. Graphene: This is a very recent craze amongst material scientists and is under vigorous research during 2007. It is the thinnest material known so far and is derived from natural graphite. The theory consists in making use of the unique layered structure of a hexagonal crystal of natural graphite and the weak bond between these layers. Each such layer consists of six carbon atoms. Within a layer, the atoms are closely bonded, but between layers the bond is weak. It has been possible in the laboratory to separate the individual layers by rubbing natural graphite crystals on a silicon surface, and then arranging them in the form of a one-atom thick single-layer sheet to which the name *graphene* has been given. It shares many of the properties of a nano-tube (discussed later under "manufactured graphite"). In fact, the latter is conceived as a sort of rolled up graphene. As in early 2007, only transistors have been made out of graphene, but its potentialities seem to be immense.

20. Other uses:

- *(a)* *Drilling mud*: As additive to enhance lubricating properties.
- *(b)* *Explosives*: As coatings on the grains with a view to controlling the burning rate, reducing the smoke (graphite burns slowly without smoke), and reducing the chance of accidental ignition due to intergranular friction (graphite has low coefficient of friction).
- *(c)* *Magnetic tape*: As a coating on the 8-track tape for reducing friction.
- *(d)* *Laser material*: Due to high thermal conductivity, graphite has been tried with some success in lasers with operating current less than 20 amperes. However, graphite suffers from the problem of sputtering accompanied by dust formation.
- *(e)* *Recarburization of steel*: Generally synthetic graphite is widely used (see Manufactured Graphite below), but in some countries where high-grade natural graphite is readily available, the same is utilized.

MANUFACTURED GRAPHITE

In many applications, very high-purity graphite is required which is very expensive, if not impossible, to produce by beneficiating natural graphite. Such graphite is manufactured. There are five forms of manufactured graphite:

1. Synthetic graphite
2. Pyrolytic graphite
3. Graphite fiber
4. Fullerene and carbon nano-tube
5. White carbon

Most of these have special industrial applications. These are as follows:

1. Synthetic graphite: Pure graphite was accidentally made by Edward G. Acheson when he was conducting some experiments by heating silicon carbide or carborandum (SiC) to 4150^0C. At this high temperature, silicon vaporized off and he found that the structure of the residual pure carbon was like that of graphite. He patented it in 1896 and its commercial production started in the following year. Later on, it was found out that certain other organic materials, when heated to 2500-3200^0C, also left a carbon residue which underwent complete transformation. Petrocoke and small imperfect crystals of graphite were amongst such materials, and since 1918, these have formed the basic materials for producing synthetic graphite of 99.0-99.5% purity. Petrocoke is a solid byproduct of thermal cracking of petroleum (in cracking of petroleum, molecules are broken down under high temperature into smaller units, and a new type of hydrocarbon namely, olefin is produced). It is mainly composed of carbon and has a lower ash content than coal coke.

For manufacturing synthetic graphite, petrocoke or anthracite or natural amorphous graphite (60% FC) is calcined, mixed with coal tar pitch, heated to 1650^0C and formed by extrusion or moulded to *green shapes*, which are baked at 750-1400^0C. The baked shapes are laid in the form of a bed, covered with an insulating layer of SiC, coke and sand, and then heated to 2600-3000^0C by passing electric current through it. For making ultra-pure graphite containing less than 20 ppm ash, the electrical heating is done at a temperature of 2500^0C with simultaneous bathing in a purifying gas.

In the applications of natural graphite discussed above, where high-purity graphite is required, synthetic graphite is preferred as in the case of high-quality products of electro-graphitic carbon brushes, automobile brake linings and castings. But there are some applications where only ultra-pure synthetic graphite (and not beneficiated natural graphite) can be used. The applications of synthetic graphite are:

(a) *Electrode*: Graphite rods (as a substitute of petroleum coke electrodes) can be used as anodes in electric arc furnaces (EAF) for electrolytic production of carbon steel, chlorine, chlorates, magnesium, sodium etc., in *gouging rods* and in *arc lamps*.

Gouging rods are copper-coated graphite electrodes used for giving smooth finishes in iron and steel castings with the help of electric arc (referred to in industry circles as arc-clearing or *gouging*, trimming and washing).

Arc lamps employ the principle of arc discharge. Arc discharge takes place when a strong electric current is passing through two electrodes in contact with each other and then they are moved a little apart. Such a strong resistance develops at the gap that the tips of the electrodes are heated to 4000^0C and they begin to glow and emit electrons ionizing the intervening air. Through the latter, current flows and the bombardment of electrons causes the positive electrode to become white-hot producing white light. When the electrodes are again moved and brought in contact, the light is switched off. In arc lamps, special control mechanism comprising springs is provided to effect this movement of the electrodes. Such arc lamps were earlier widely used in cinema projectors.

The same principle of arc discharge is employed in EAF. Here, the intense heat of the arc is utilized for melting metals.

(b) *Moderator in nuclear reactors*: A nuclear reactor houses the fuel elements which in its turn is a sort of container of matrix within which the fuel is placed. The function of a reactor is primarily (i) to contain the dangerous radioactive emissions, and (ii) to prevent loss of the heat generated within it. Reactors may be of two types: (i) thermal reactors which use thermal or slow neutrons (0.025 electron volt or eV energy), and (ii) fast or fast breeder reactor, which use fast or high energy neutrons (1 MeV – 100 KeV) and in which more fissionable material is produced than consumed. It is in the thermal reactors that moderators are used for controlling the speed of the neutrons. The moderator should only bring down the energy of the incident neutrons, and should not absorb them. Graphite makes a good material for moderator by virtue of its ability to reflect and slow down neutrons.

(c) *Recarburization of iron and steel*: Steel is essentially a refined alloy of iron and carbon with carbon content lower than in pig iron – generally varying from 0.01-1.7%, but it may go up to 2 percent. Total absence of carbon would make it very soft and unusable for most of the purposes. Steel-making is, therefore, nothing but the removal, by combustion, of the carbon contained in the iron and then raising the carbon level by adding it in just the requisite amount. As a result, the metal becomes more resilient, more flexible, stronger and better workable than iron. This addition of fresh carbon is particularly necessary if the steel is produced in EAF where a scrap, which is low in carbon, constitutes a significant portion of the raw material mix. In iron foundry also, carbon is added to make special customized products. This addition of carbon is called *recarburization* (cf., decarburization is the process of removal of carbon by heating in an atmosphere in which the concentration of decarburizing gases exceeds a certain value).

For recarburizing steel, a readily soluble recarburizer with at least 99% carbon is specified, because the whole technology of iron and steel manufacturing is about removal of deleterious constituents present in the raw materials, and hence, no fresh impurity can be allowed to get into the product through the recarburizer. The most versatile recarburizer is micronized synthetic graphite because of its high purity and fast solution rate. It is generally sourced to the scrap generated during manufacturing of its high-purity products like electrode.

In foundry for casting special iron products, synthetic graphite of size less than 75 micron and containing 2% (max) volatile matter and 3% (max) ash is specified.

2. Pyrolytic graphite: It is a highly ordered crystalline graphite in the form of 6 mm thick plates, made by pyrolyzing organic gases at 1400-2000^{0}C. It possesses a high degree of anisotropy with high thermal conductivity (comparable to copper) in the direction parallel to the thickness perpendicular to the thickness it is 1/200th of that. It finds application in rocket nose cones. After annealing, it develops high reflectivity and becomes suitable for use in monochromators for X-ray and thermal neutrons.

3. Graphite fiber: Graphite and carbon fibers are made by carbonizing or charring an organic polymer yarn (e.g., rayon, poly-acrylo-nitrite or PAN, pitch). The dividing line between graphite fiber and carbon fiber is very thin. Some has suggested that since these fibers do not possess the three-dimensional order characteristic of graphite crystallites, they should be called carbon fibers only. But according to others, if the carbonization temperature is 2500^{0}C or above, it should be called graphite fiber and if below this temperature, then it should be called carbon fiber. Generally, the former definition has found wider acceptance. However, both graphite and carbon fibers are flexible, light weight, chemically inert, good conductor of both electricity and heat, and very strong with modulus up to 80 million psi or 552 gigapascals. The degree of orientation of the micro-crystals parallel to the fiber axis is crucial for high tensile strength. Tensile strength of an average fiber is 500000 psi and can be as high as over one million psi. The uses of graphite fibers are as follows:

(a) *Sealing braid*: Low-modulus (less than 20 million psi or 138 gigapascals) pure carbon/graphite fibers impregnated with lubricants and graphite particles, can be woven in the form of ropes, cloths, mats, felts etc., which can be wound like a braid around shafts, valves and joints of high-temperature equipments. Such braids are suitable for use as gaskets for packing and sealing super-hot steam, oil, solvents, acids and alkalis in high-temperature heating equipments; as thermal insulators of high-temperature vacuum furnaces; as vehicle heat shields; as sealing rings around rocket nozzles, etc. These braids are resistant to corrosion by strong acids and alkalis; can function at 1750^0C and above; are effective thermal insulators; and have low friction.

(b) *Structural applications*: High-performance (modulus +25 million psi or 172 gigapascals) are used as a reinforcing component in structural composites, sporting goods (e.g., golf club shaft, tennis racket, fishing rod, sail boat structure etc.). mainly epoxy and also polyamides serve as the matrix. These are suited for use under conditions of $173\text{-}343^0$C temperature range.

(c) *Graphite fiber-strengthened glass matrix materials*: These were investigated as early as in 1972. But problems with oxidation during fabrication led to abandoning the experiments, and instead, SiC was preferred as the source of carbon.

4. Fullerene and carbon nano-tube: Fullerene is one of the allotropic varieties of carbon discovered in 1985 as a byproduct of molecular beam experiments. The first fullerene isolated was in the form of hollow geodesic spheres and was named after Richard Buckminister Fuller, the architect who popularized geodesic dome structures. Later on, ellipsoidal and tubular or cylindrical forms were also identified. Fullerene can be manufactured by passing strong electric current between two closely spaced graphite electrodes in an inert atmosphere. A plasma arc containing carbon ions results. On cooling, a sooty residue is left from which fullerene is isolated. The cylindrical fullerene forms the basis of what is nowadays called nano-tube.

"Nano" means one-billionth of a unit and *nanotechnology* means the technology dealing with materials of one-billionth of a metre size. This field of technology started after the invention of *Scanning Tunnelling Microscope* in 1981, which can detect individual atoms, and the name nanotechnology was coined by K. Erce Dexter in 1986. A breakthrough in the research in the field of nanotechnology was achieved in early 2004, when some scientists of USA and Australia reported the creation of industry-ready sheets of a new material made from *carbon nano-tubes*. These carbon nano-tubes were made by laser vaporization of graphite.

Carbon nano-tube is very flexible and is the hardest, stiffest and strongest material known so far, being harder than diamond, and its tensile strength is 62.5 gigapascals (30 times that of steel); it is also transparent and extremely light-weight (a one metre wide sheet made of one kilometre long carbon nano-tubes will weigh only 30 kg). Further, due to the tubular structure, the bonding force acts inward on the atoms on its external surface, and it is difficult to displace them. As a result, the nano-tubes are chemically very weakly reactive and are stable. Best conductors of heat and electricity, being able to carry 1000-times more electric current than copper wire.

Intensive research and development are underway and carbon nano-tubes and the sheets made thereof are believed to be the material of the future. In 2005, paper-thin sheets having solar cell capabilities and having great potentiality in the manufacture of racing cars have been developed. Efforts are on to reduce the cost of making such sheets. *Carbon nano-tube* *composite (CNTC)* ribbons are already being produced in USA and Japan on industrial scale. They have opened up a whole new vistas of applications including construction and high-performance aircraft. The carbon nano-tubes can also be spun into fibers that are 4-times tougher than spider silk, the toughest natural filament known. These also form the main plank in the researches that are currently going on for making *space elevators* and *solar sails*. CNTC ribbons are conceptualized by space scientists to be one of the quickest and the most cost-effective future modes of transporting men and materials into space. Solar sails are conceptualized to be super-light sheets that can allow the pressure of the sun's light to propel spacecrafts though space. In India, a national nanotechnology programme has been drawn up under which research is being carried out in several institutes.

Like nano-tubes, nano-balls are now under investigation. These are said to have the ability to attract reactive oxygen called *free radicals* which cause damage to human body system. By mopping up electrons of the free radicals, the nano-balls may render them ineffective and thus they may have potentiality for application in pharmaceuticals.

5. White carbon: White carbon is the transparent allotropic variety of carbon discovered in 1969. When graphite was sublimated under low pressure, this substance is formed as transparent crystals on the edges of the planes of the graphite crystals. It has the ability to split a single beam of light into two beams. However, no commercial application of white carbon is known to have been reported.

Chapter 26

GYPSUM

Gypsum is hydrous calcium sulphate having chemical composition $CaSO_4.2H_2O$ (cf., composition of anhydrite is $CaSO_4$). It has five varieties, namely:

1. Alabaster: The massive fine grained granular compact type; the name is related to a place in ancient Egypt called Alabaston, where this mineral used to be quarried for sculpturing (it is not known for certain whether the name of the place was after the name of the mineral or the other way around).
2. Selenite: The transparent and crystalline type, name originating from the Greek word "selen" meaning moon (cf., name of the metalloid selenium from the Greek word "selas" meaning light).
3. Satinspar: The fibrous type with silky lustre; the name coming from the silky fabric called satin (it is believed that this fabric used to be exported from the ancient Chinese city named "Zaitun" present Tsinkiang from which the name satin was derived).
4. Gypsite (also called gypseous clay): The porous earthy impure gypsum mixed with sand and clay.
5. Rock gypsum: Medium to coarse grained gypsum forming extensive thick sedimentary beds.

Out of these, the first two, rock gypsum and alabaster, are of the most significant from an economic point of view and are most widely mined and used. Usually, people do not differentiate between these two and refer to them by the generalized term gypsum. But all the types are chemically alike and exhibit the same properties.

Gypsum is a very common mineral found in nature (very frequently, in association with anhydrite). Most of the gypsum deposits originated due to evaporation of salt-rich waters seawater or lake brine or spring water or underground saline water rising to the surface by capillary force. Some deposits also originated due to hydration of anhydrite ($CaSO_4$) and a few vein deposits, due to action of sulphuric acid (coming along with volcanic eruptions or forming by oxidation of sulphide minerals) on limestone.

HISTORY

Alabaster has a long history of usage dating back to what is referred to as *Painted Pottery Civilization* which preceded the *Copper Age* in 4000 BC. The ancient civilizations of Mohenjodaro and Haraapa of the Indus valley, Nile Valley, China, Mesopotamia and Persia all belong to this. During this time, evidences of vessels carved out of alabaster by the Egyptians and the Assyrians have been found. The Egyptians used gypsum as plaster in Pyramids. Later, the Greeks used to convert gypsum to plaster for building by "burning" (calcining) it. The name gypsum is believed to have originated from this practice of burning. The Greek words "epseo" means burning or cooking and "ge" means earth ("gepseos" originally meant chalk). However, scope of its usage other than for building-related purposes was recognized not long ago. It was first used as a soil conditioner in USA in 1808. In undivided India (India and Pakistan), efficacy of ground gypsum as a conditioner for the soil in certain areas of the Punjab-Sind area was first recognized by A. B. Wynne in 1875, but it was actually tried for the first time only in around 1925 in certain fields of southern Bihar.

Records of its organized mining in undivided India and production statistics are available since around 1915. It was initially confined to the Punjab-Sind-Rajasthan region. From a meager 19,160 tons in 1915 it increased to 41,000 tons in 1925, to 53,300 tons in 1935 and to 89,000 tons in 1945. After, independence in 1947, growth of its production in India is as below.

Year	Production
1950	210,000 tons
1960	997,000 tons
1969	1,391,000 tons
1970	926,000 tons
1980	0.87 million tons
1990	1.66 million tons
Year ending March 2001	2.67 million tons
Year ending March 2006	3.14 million tons

Presently, gypsum is widely mined in many countries of which the leading producers are USA, Spain, Iran, Canada, China, Mexico and Thailand which accounted for about 66% of the total world production of 97.1 million tons in 2001. In India, Rajasthan, Gujarat and Jammu and Kashmir are the main producing states.

CRITERIA OF USE

1. *Physical properties*: It is soft, its hardness being only 2 on Mohs scale (it may even be less for impure gypsite). It has moderate specific gravity of 2.2-2.4, but the bulk density of its fine powder is higher. Crystalline varieties exhibit subvitreous to pearly shining lustre while the massive rock gypsum and alabaster have a dull earthy appearance.

2. *Chemical characteristics:* Pure gypsum is saturated with water and has 32.6% CaO, 46.5% SO_3 and 20.9% H_2O. Chemically, gypsum is acidic because of the SO_3 radical. It reacts with HCl acid, and it dissolves in excess water (400-500 times). It has low oil absorption (less than 5%).
3. *Calcination behaviour:* When partially calcined at 150-180^{0}C under steam pressure, gypsum loses three fourths of its water to become calcium hemihydrate ($CaSO_4.1/2\ H_2O$ or $2CaSO_4.\ H_2O$) which is a loosely bonded granular compound crumbling easily to powders, but when mixed with water it returns to and sets as gypsum. As calcination temperature rises, it starts losing its remaining water, losing all of it and fusing at 950^{0}C to becomes *anhydrite* (or dead-burnt gypsum) which is a harder, heavier and compact substance unable to set in water, and having hardness 3.5 on Mohs scale and specific gravity 3.0.
4. *Colour and optical properties:* Pure gypsum is white, but it may also be red, yellow, etc. depending on presence of impurities. Its refractive index varies from 1.52-1.53 (cf., linseed oil 1.48, ordinary glass 1.53, titanium dioxide 2.40, diamond 2.42).
5. *Forms:* Its availability in nature in the form of massive blocks (alabaster), in silky fibrous form (satinspar) and crystalline form (selenite) is taken advantage of in certain uses.

USES AND SPECIFICATIONS

Gypsum is used both in calcined form and raw form. The former is invariably mixed with water to make it plastic. The principal industrial applications of gypsum are:

1. Gypsum plaster and products made of it

(a) Plaster of Paris or surgical plaster
(b) Mould plaster for pottery
(c) Casting of artifacts

2. Construction works

(a) Building plaster and stucco
(b) Boards
(c) Partition blocks
(d) Concrete aggregate
(e) Acoustic tiles
(f) Scagliola (or imitation marble)
(g) Temporary buildings

3 Cement
4 Fertilizer
5 Soil conditioning
6 Paint
7 Fly-ash brick

8 Sculpture
9 Textile
10 Pharmaceuticals
11 Adhesive

These uses are discussed in details as follows.

1. Gypsum plaster and its applications: When partially calcined at 150-180^{0}C, gypsum loses three-fourths of its water to become calcium hemihydrate ($CaSO_4.1/2\ H_2O$ or $2CaSO_4.H_2O$) which is a loosely bonded granular compound crumbling easily to powders which flow smoothly almost like water. Now, if water is added to these powders, they become a plastic mass. This plastic mass is called *plaster*. By varying the temperature of calcination, different grades of plaster can be obtained. Gypsum plaster has some unique properties such as:

(a) When mixed with excess water, it partially dissolves precipitating gypsum crystals.
(b) Due to this precipitation of crystals of gypsum, it quickly sets (20-40 minutes) to a hard mass.
(c) It expands slightly during setting.
(d) After setting, it does not dissolve in water easily.
(e) Due to presence of water in excess of the water of crystallization, the set mass is porous making room for the excess water molecules to occupy.
(f) When the excess water is dried, the porous mass becomes very light.
(g) Air occupying the pores imparts resistance to heat; in addition, the water of crystallization prevents plaster of Paris from catching fire. This makes it a heat insulator and fire resistant.

Following are the applications using purely gypsum plaster (save some minor additions of other ingredients sometimes).

(a) *Plaster of Paris or Surgical plaster*: Plaster of Paris is nothing but the high grade variety of gypsum plaster used in surgery. During the 16th century, Turkish doctors used to cover broken bones with gypsum. A new type of bandage called 'Plaster of Paris bandage' was for the first time made in 1852 by rubbing cotton bandage with gypsum mined from Montmartre deposit near Paris from which the name was derived. Such plasters find application in dentistry and orthopaedics. The plasticity, quick-setting, slight expansion on setting and lightness of the set plaster are the main criteria. In dentistry, it is used for taking casting for denture purpose (on setting, the plaster expands to fit tightly into the dental cavity and the impression becomes sharp and dimensionally accurate) while in case of orthopaedic application, plaster is applied over fractured bones to keep them in position till they heal. Sometimes it may become necessary to accelerate the setting time and also to increase the strength by adding other ingredients. For making surgical plaster, gypsum is ground very fine and then calcined to transform all the grains to calcium hemihydrate. Otherwise, poor and incomplete transformation will require more water for dissolution, and crystallization may also be imperfect with the result that the set plaster will have excessively porous and weak. With regard to specifications, the Bureau of Indian

Standards (BIS) has stipulated in 1973 the parameters as: *96% (min)* $CaSO_4.2H_2O$*, 1% (max) each of free water and* CO_2*, 0.7% (max) insolubles including* SiO_2*, 0.1% (max)* Fe_2O_3 *+* Al_2O_3*, 0.5% (max) MgO and 0.01% (max) NaCl*. Free water and carbonates (expressed in terms of CO_2) are objectionable because they will consume a part of the heat for expulsion of the steam and CO_2, raising the cost of calcination. Grains of free silica (quartz) and alumina increase grinding cost on account of its hardness. Moreover, the insoluble grains are carried to the plaster of Paris affecting its plasticity and homogeneity. Fe_2O_3 has undesirable colouring effect. MgO is highly hygroscopic absorbing as much as 120% of its volume of water. Its presence in the plaster of Paris will make the set plaster prone to cracks. For the same reasons, NaCl which is also hygroscopic will tend to make the plaster crumble.

(b) *Mould plaster for pottery:* Moulds made of gypsum plaster are used for casting of potteries. In this case, the main criteria are plasticity, quick-setting and porosity. A porous plaster is advantageous because when some plastic clay is poured into a mould made out of plaster of Paris, the moisture from the clay evaporates slowly into the pores of the plaster without exposing the clay to quick drying resulting in cracks. Here, the constituents free water, CO_2, SiO_2, Fe_2O_3, Al_2O_3, MgO and NaCl are considered deleterious for the same reasons as in case of surgical plaster, but only the degree of purity required is less as higher degree of porosity and consequent weakness are permissible. The Bureau of Indian Standards (BIS) has stipulated in 1973 the parameters as: *85% (min)* $CaSO_4.2H_2O$*, 1% (max) free water, 3% (max)* CO_2*, 6% (max) insolubles including* SiO_2*, 1% (max)* Fe_2O_3 *+* Al_2O_3*,1.5 % (max) MgO and 0.1% (max) NaCl.*

(c) Casting of artefacts: Statues and various decorative objects are made by casting gypsum plaster in moulds made of other materials. The property of slight expansion on setting enables the plaster to take accurate shape with the surface finish of high order. Purity of gypsum depends on the type, colour, etc. required for the product.

2. Construction material: In building construction, although gypsum plaster forms the main plank, generally it is mixed or reinforced with other materials. A high degree of purity of the gypsum is not essential, instead a somewhat lower cost is desirable. But the criteria of plasticity, an optimum combination of strength and porosity, and heat- and fire- resistance must be satisfied. Higher porosity means more trapped air and higher heat insulation, but at the same time it also means reduced strength. So there should be both lower and higher limits of porosity. Porosity is the result of escape of steam from free water and CO_2 from carbonates ,i.e., loss on ignition (LOI). Industries specify LOI as 4-9 per cent. Both NaCl and MgO are hygroscopic and on exposure, they absorb water and increase in volume resulting in crumbling of the plaster. For optimum strength of the plaster, industries specify a maximum limit of 0.1% for these two constituents taken together. Following are the important products.

(a) *Building plaste :* This may be of four types:

i. *Stucco*: White plaster made from high-grade gypsum is used for finishing coat on interiors surfaces of walls and roofs to give them beautiful smooth appearances. However, for application on exteriors of buildings that are exposed to dampness or abrasion, a mixture of ordinary portland cement and gypsum plaster.

ii. *Retarded hemihydrate gypsum plaster*: In this type of plaster, gypsum is first partially calcined at 150-180^{0}C to its hemihydrate form ($CaSO_4$.1/2 H_2O, which is the starting material for making plaster) and ground. But instead of mixing it with water alone, it is mixed with sand, expanded perlite or vermiculite, some retarder and water, and then—generally applied on gypsum-based boards. The role of retarder is to delay the setting and give enough time for working with it after mixing. The common retarder materials include cattle hair, hoofs and horns after processing them with lime and caustic soda.

iii. *Keene's plaster*: Keene's plaster was invented in England in late 19th century. For making this plaster, gypsum with some seeds of aluminium sulphate [$Al_2(SO_4)_3$] or alum (hydrated double sulphates of aluminium with potassium, sodium or ammonium) added to it, is calcined by heating it repeatedly at above 170^{0}C. this results in an anhydrous material called *Keene's plaster* (also called *Keene's cement*), which is a very hard mass consisting of intertwined needles of crystals and which is characterized by slow setting. After mixing with water, it is used where a very high degree of smooth and uniform finish is required. The gypsum used in this process is specified to contain at least 80% $CaSO_4.2H_2O$.

iv. *Anhydrous gypsum plaster*: This a low grade version of Keene's plaster requiring lower grade gypsum.

In all these uses, NaCl is considered the most deleterious because, due to its hygroscopic nature, it will absorb moisture and will cause the plaster to crumble and come off the walls. The industries specify a maximum limit of 0.03 percent.

(b) *Boards*: Gypsum boards, panels and laths are light-weight, fire-resistant and heat-insulating sheets with smooth surface and pleasing appearance, and also, they can be erected speedily. They can be fixed by nails or adhesives, can be painted and are best-suited for internal lining of walls, as interior partitions and as false ceilings. Plaster and paper are the basic raw materials for making these. But, depending on the method of using the paper, there may be two types:

i. *Gypsum plaster board*: In this, a paper sheet is used as the surface of a sheet made of gypsum plaster. The plaster is spread on a paper and pressed. The former fills up the pores of the paper and sets, the two forming a firm bond with each other. Only one side that is exposed is surfaced with paper. The paper imparts a smooth appearance as well as strength and flexibility to the board.

ii. *Gypsum fiber board (GFB)*: In this, paper sheets are inserted between layers of gypsum plaster instead of on one surface. Pores on both surfaces of the paper get filled up with plaster. After the latter sets, a sheet is formed that has greater strength and flexibility than a plaster board besides possessing all the properties of the latter.

(c) *Partition blocks:* Gypsum partition blocks are not strong enough to bear load like bricks, wood and the like, but they are fire-resistant, heat-insulating, pleasing in appearance and resistant to pest. They are, therefore, best suited as interior partitions, as protective lining of columns and in other similar applications where there will be no load.

(d) *Gypsum concrete:* In such concrete, an aggregate comprising partly calcined hemihydrate, wood chips and water. The liquid mixture is poured on conventional concrete slabs. After setting, it provides the slab protection against heat without, at the same time, increasing the load.

(e) *Acoustic tiles*: These find application as lining on the inside walls and roofs of auditoria to prevent echo of sound. Gypsum-based acoustic tiles are made by mixing plaster and saw dust in the ratio 65:35, shaping them in the form of tiles and allowing them to set. Saw dust provides zigzag interconnected paths for the air to pass through, thus slowing down the propagation of sound waves and imparting acoustic insulation to the tiles. In addition, the properties of heat-insulation, fire-resistance and light weight are retained.

(f) *Scagliola (imitation marble)*: Scagliola is a gypsum-based imitation marble. The name *scagliola* has come from the Italian word “scaglia” meaning chips. It is used for cladding columns, walls and other architectural elements in a manner that mimics fixing of natural marble (with patches and veins of different colours). Although, this marble possesses 250 kg/cm^2 strength, it is not strong enough for use in flooring. But its advantage over natural marble lies in its ability to be made with ornate designs (this is possible by simply making moulds with required designs). There is evidence of its use in ancient Rome, but it has become very popular in Europe since the 17th century and in USA only since the end of the 19th century. It is made in two ways:

i. Ground gypsum is mixed with some animal glue and desired pigments, pressed into shape of rectangular tile in a mould and polished after drying.

ii. In USA, instead of ground gypsum, very hard Keene’s plaster (see under ‘plaster’ above) is used. This is called *American scagliola*.

In addition, the properties like heat-insulation, fire-resistance and light weight, the refractive index of gypsum also is an important criterion.

(g) *Temporary building*: Plaster is used for construction of temporary building which can be dismantled and shifted conveniently (e.g., film sets). The gypsum used for this purpose is popularly known as *staff*. Light weight and low cost are the chief considerations.

(h) *Glass-reinforced gypsum (GRG)*: It was developed by the Central Glass and Ceramic Research Institute (CGCRI), India in 1988 as a low-cost substitute of wood in buildings. It was claimed to be strong, fire-proof, termite-resistant and amenable to sawing, drilling and milling. He process consists in even dispersion of glass fiber in a matrix of gypsum plaster.

3. Ordinary portland cement (OPC): OPC is essentially a powdered aggregate containing tri-calcium alumino-silicate [$(3CaO.SiO_2).(3CaO.Al_2O_3)$], gypsum [$CaSO_4.2H_2O$] and iron oxide ($Fe_2O_3$). It contains 60-70% CaO, 20-25% SiO_2, 5-10% Al_2O_3, 4-6% gypsum and 1-2% Fe_2O_3. The material is burnt in a kiln at 1400-1500^0 C to obtain the product tri-calcium alumino-silicate in the form of glassy balls called “*clinker*” which is cooled, mixed with gypsum and ground to ultra-fine size (300-350 nanometre or 40000 mesh). When mixed with water, these compounds react with water, and the cement becomes a mixture of hydrated calcium silicate [$2CaSiO_3.5H_2O$], hydrated tetra-calcium aluminate [$4CaO.Al_2O_3.12H_2O$] and slaked lime [$Ca(OH)_2$]. All these compounds crystallize in the form of interlacing needles which gives rise to a strongly bonded cement. On exposure to air, the slaked lime gives off water and tends to absorb CO_2 to quickly become $CaCO_3$, and thus the cement becomes hardened.

The role of gypsum is to slow down the absorption of CO_2 through a complex mechanism. It reacts with tri-calcium aluminate and water to first form calcium sulpho-aluminate hydrate (called "*ettringite*"). This ettringite is deposited as layers on the particles of tri-calcium aluminate and prevents rapid hydration of the CaO. Gradually, as the reaction continues, hydrated tetra-calcium sulpho-aluminate or simply, mono-sulpho-aluminate is formed which is a stable hydrate, and which allows hydration of CaO. But this slowing down allows sufficient time to use the cement mix for plastering, etc. Finally, when the cement dries up, it becomes a mixture of mono-calcium alumino-silicate and $CaCO_3$, which sets to a strongly bonded solid homogeneous mass.

The deleterious constituents in gypsum are MgO, NaCl, phosphorus and moisture. Both MgO and NaCl being hygroscopic, absorb water with accompanying volume change. MgO absorbs 120% of its volume of water and forms brucite or $Mg(OH)_2$. When the cement is exposed and becomes dry, this absorbed water is given off and the cement becomes prone to cracking and crumbling. Presence of phosphorus beyond 1% prolongs the setting time by several days. Moisture is also not desirable because it unnecessarily impedes free flow during grinding operation.

The Bureau of Indian Standards (BIS) has stipulated in 1973 the parameters as: *70-85%* $CaSO_4.2H_2O$*, 3 % (max) MgO and 0.5% (max) NaCl*. In addition, industries generally specify the maximum limit of 2% for moisture.

4. Fertilizer: Gypsum is used for making ammonium sulphate [$(NH)_2SO_4$] which in its turn is used for making water-soluble ammonium phosphate sulphate or APS fertilizer, the basic composition of which is 60% ammonium sulphate and 40% ammonium phosphate. This mixture contains 20% P_2O_5 and 16% N and practically whole of the phosphate is water soluble. For making ammonium sulphate, the process consists in reacting ammonium carbonate with gypsum. The ammonium sulphate solution is then added to phosphoric acid and finally, the mixture is ammoniated.

In this usage, the SO_3 radical of gypsum is the key. So a very high grade gypsum should be the ideal. But that will make the product costly. Therefore, a balance has to be struck between purity and cost. Some industries use anhydrite if it is cheaply available.

With regard to the deleterious constituents, SiO_2 is objectionable beyond a limit because it increases the grinding cost. Fe_2O_3 and Al_2O_3 are considered undesirable because both have affinity for SO_4 and will interfere with the reactions besides consuming a part of the gypsum. In addition, unreacted Fe_2O_3 will have a colouring effect on the fertilizer product and may face consumer resistance. MgO is objectionable because of its affinity to CO_3-radical. Besides, the unreacted MgO, being highly hygroscopic (MgO absorbs 120% of its volume of water), will hold up a lot of moisture of the soil to which the fertilizer is applied. NaCl has also affinity for CO_3, and both Na_2CO_3 and the unreacted NaCl are highly injurious to plants.

The Bureau of Indian Standards (BIS) has stipulated in 1973 the parameters as: *85% (min)* $CaSO_4.2H_2O$*, 6% (max) insolubles including* SiO_2*, 1.5% (max)* $Fe_2O_3 + Al_2O_3$*, 1 % (max) MgO and 0.003% (max) NaCl.*

5 Soil conditioning: Finely, but not uniformly, ground low-quality gypsite or gypseous clay is applied directly to soil under the name *land plaster* for serving the following purposes:

- (a) By virtue of its acidic nature, it neutralizes the adverse effect on plants, of soda or *black alkali* (Na_2CO_3) which is either originally present in the soil or is introduced through the irrigation water.
- (b) Both soda and overdose of ammonia-rich fertilizers tend to deflocculate and disintegrate and disperse the fluffy aggregates of soil thereby making the soil pervious. Consequently, the soil is not able to hold its water. Gypsum helps restoration of imperviability of the soil.
- (c) Gypsum keeps the soil moist by virtue of its water of crystallization.
- (d) It provides calcium to the soil.
- (e) It has the ability to fix ammonia which has an affinity for the SO_4 radical, and thus help the soil retain its nitrogen-content.
- (f) Gypsum has the ability to decompose the double silicates of magnesium and potassium thereby liberating potassium which is a plant nutrient. However, this utility will be of relevance only if the soil contains potassium.

Application of gypsum helps growth of oil seed crop. In this application cost is the most important factor, and so, generally, locally available low-grade gypsum is used. But Na_2O, being highly injurious to soil [see (i) and (ii) above], is considered deleterious. A variable size of the particles (unlike uniformly fine-sized) will ensure porosity. The Bureau of Indian Standards (BIS) has stipulated in 1971 the parameters as: *50% (min)* $CaSO_4.2H_2O$*, 1% (max) NaCl and size 50% between 2 and 150 microns and 50% above 150 micron*.

6. Paint: Paint comprises a pigment (the colouring substance), extender (a white neutral substance to reduce viscosity), suspending agent (a colloidal substance to keep the pigment in suspension in the medium) and a medium like oil (linseed oil) or water. Finely powdered high-grade white gypsum known as *mineral white* or *terra alba* is used in paint in two ways as follows:

- (a) Its suspension in oil is used an undercoat to cover porous surfaces for subsequent application of distemper. Bulk density of its particles enables them to settle down and get firmly locked up in the pores providing a smooth base.
- (b) It is used as an extender in oil paint.
- (c) It is sometimes used to neutralize the colouring effects of some coloured substances like chrome, iron oxide, etc.

In these applications of gypsum, its neutral white colour coupled with refractive index (1.52) that is very near to that of linseed oil (1.48) does not affect the gloss of the oil paint coating. Besides, its low oil absorption (less than 5%) helps it to remain in suspension in the oil, but for this, gypsum has also to be in very fine size.

The most harmful constituent is lead because of its strong affinity for oxygen. It quickly oxidizes to form Pb_3O_4 which is itself a red pigment. Lead has also affinity albeit weak, for SO_4 radical. The Bureau of Indian Standards (BIS) has stipulated in 1950 the parameters as: *75% (min)* $CaSO_4.2H_2O$*, 0.5% (max) Pb and less than 240 mesh (63 micron) size.*

7. Fly-ash brick: For making fly ash bricks, a new technology called "Fal-G" using fly ash, lime and gypsum is being popularized. In this technology, the raw materials are ground and water is added to obtain a semi-dry mass. The mass so obtained is shaped into bricks by machine moulding and then the pressed bricks are subjected to specific curing cycle in sun or in air and steam, to gain the required strength.

8. Sculpture: Massive blocks of alabaster are used for sculpting statues and decorative artefacts. Pleasing colour, pearly lustre, smooth appearance, light weight and softness are the principal criteria.

9. Textile: Here, gypsum powder is applied to cotton textiles for giving a glossy appearance and increasing the density. It is generally mixed with china clay or talc to reduce cost. SiO_2, Al_2O_3 and calcite are considered deleterious. Because of their hardness, SiO_2 and Al_2O_3 will increase the grinding cost. As regards calcite, the sharp edges of its grains may damage the textile product. Industries generally specify 82% $CaSO_4.2H_2O$ and a maximum limit of 4% for calcite and, in special cases, even 1 per cent.

10. Pharmaceuticals: Earlier, high grade gypsum (+99% $CaSO_4.2H_2O$) used to be considered as a calcium-supplement. But, later it was found that intestinal absorption of calcium from gypsum was very limited and this practice has been dispensed with. Now, it is used as a diluent in tablets and capsules for reducing the concentration of their active ingredients.

11. Adhesive: Adhesive is an organic or inorganic substance capable of bonding together other substances by surface attachment. Gypsum is suited to use in adhesives based on polyvinyl acetate (PVA) which are used in dry conditions. Gypsum is not suitable for use in wet conditions because of its low water-resistance.

11. Other uses:-

(a) *Source of sulphuric acid*: The SO_3-content is the criterion.
(b) *Paper*: Gypsum powder is used as a filler on account of its lustre, colour and high bulk density.
(c) *Rubber*: It is added as a bulking agent due to its high bulk density.
(d) *Rubber stamp*: Moulds made of plaster is used for casting rubber stamps.
(e) *Insecticide*: The high bulk density of gypsum powder makes the chemical settle on the plants.
(f) *Coal mining*: Here the role of ground gypsum is to cover coal dust particles and minimize coal dust explosion by virtue of its heat-insulation and fire-resistance.
(g) *Flux*: It can be used as flux in nickel metallurgy.
(h) *Ornament*: Satin spar, by virtue of its beautiful fibrous structure and silky lustre, is used.
(i) *Microscope*: Crystalline gypsum has been used as gypsum plates.
(j) *Beet sugar*: Micronized gypsum has been used for processing of beet sugar.
(k) *Foundry*: Plaster, by virtue of its porous smooth surface is used as a foundry-facing material, the pores allowing the gases to slowly get into them (sudden escape may result in vesicle on the surface of the cast).
(l) *Cosmetics*: Powdered gypsum is used as a filler.
(m) *Pharmaceuticals*: Gypsum finds application as an ingredient of some Ayurvedic medicine.

(n) *Chalk pencil*: By virtue of its softness and white colour, gypsum powder can be made into chalk pencil for writing on blackboards.

WASTE UTILIZATION

During certain uses of gypsum, wastes are generated that can be utilized. Two economically significant examples are as follows.

1. While making ammonium sulphate for APS fertilizer by reacting ammonium carbonate with gypsum, $CaCO_3$ is produced as a waste. This can be used for cement manufacturing.
2. The plaster used for making moulds for pottery is recoverable and is regularly recycled in India.

SUBSTITUTION

In certain industrial processes, $CaSO_4.2H_2O$ is recovered as byproducts, and these are called byproduct gypsum. Such byproduct gypsum is, in certain conditions, more economical to use as substitute for natural gypsum. Following are the different types of byproduct gypsum:

1. Phosphogypsum
2. Marine gypsum
3. Flue gas gypsum or scrubber gypsum or desulpho-gypsum
4. Fluoro-gypsum
5. Boro-gypsum
6. High sulphur coal

Besides, in certain uses another natural mineral, namely, anhydrite and some synthetic material, are better substitutes of gypsum. These substitutes are discussed as follows.

1. Phosphogypsum: The dirty-coloured waste slurry produced in the wet process of manufacture of phosphoric acid (H_3PO_4) from phosphorite or apatite, contains gypsum as can be seen from the chemical equations

$$Ca_3(PO_4)_2 + 3H_2SO_4 + 6H_2O \rightarrow 2H_3PO_4 + 3(CaSO_4.2H_2O)$$
(Phosphorite)

$$3Ca_3(PO_4)_2.CaF_2+10H_2SO_4+20H_2O \rightarrow 6H_3PO_4+2HF+10(CaSO_4.2H_2O)$$
(Apatite)

The mixture in the form of slurry is filtered so as to remove the solid gypsum. Generally, for every ton of P_2O_5-content in the phosphoric acid produced, 4.5-5.0 tons of phosphogypsum is generated. Phosphogypsum produced in India contains 75-97% $CaSO_4.2H_2O$, 0.25-1.10% NaCl, 0.3-0.7% F and 0.12-1.10% P_2O_5.

Until 1977, it used to be discharged as waste in India. But, discharging huge quantities of solid waste material involves cost. Consequently, since 1977, the use of gypsum for making ammonium sulphate fertilizer has been dispensed with in India and it has been replaced by this phosphogypsum. Its suitability has also been found in cement industry and for soil-conditioning.

A common problem is, however, the content of the radioactive element radium, which is a common impurity in many phosphorite deposits and which is carried forward to the products. This problem makes phosphogypsum particularly unacceptable for making construction materials. The latter specifies less than 25 picocurie (a “curie” is a unit of radioactivity equal to the amount of a radioactive isotope that decays at the rate of 37 billion disintegrations per second) of radioactivity in the phosphogypsum.

The high content of phosphorus as such makes it unsuitable for use in cement as its presence delays the setting time (beyond 1% P prolongs the setting time by several days). Other ingredients which are considered deleterious, are fluorine and NaCl, both of which are injurious to plants. Besides NaCl being hygroscopic, tends to absorb moisture and cause cracks in the cement after its application. However, all these three constituents can be washed without much difficulty, because both phosphorus and fluorine are present in the form of soluble acids (phosphoric and hydrofluoric acids) and NaCl is as such soluble in water. Though, moisture impedes free flow of the material during grinding, it can be driven off by heating.

2. Marine gypsum: It is a byproduct obtained during production of common salt (NaCl) by fractional evaporation of seawater in saltpans. Total salts dissolved in seawater is 3.7 percent. This saline matter contains on an average 3.6% $CaSO_4$ (c.f., 77.76% NaCl and 2.47% KCl). The recovery of $CaSO_4$ is generally of the order of 70-80% and this is a renewable inexhaustible source of gypsum (one cubic mile of seawater contains about 5.94 million tons). Marine gypsum is in the form of selenite crystals.

Density of sea water varies from $2.5\text{-}3.5^0$ $Be^/$ (equivalent to specific gravity 1.0175-1.0247 at 15^0C). On progressive evaporation stage by stage in a series of condensers or reservoirs, the density increases. In the first stage density reaches 10^0 $Be^/$ (equivalent to specific gravity 1.0741at 15^0C) and volume becomes 37% of the original, when FeO and $CaCO_3$ separates out. It is in the stage where density reaches 25^0 $Be^/$ (equivalent to specific gravity 1.2083 at 15^0C), that gypsum separates out (cf., NaCl separates at density 25.5^0 $Be^/$-30^0 $Be^/$ or equivalent specific gravity 1.2134-1.2609 at 15^0C). Lumps of gypsum floating on the surface of the residual dense brine are collected, washed for removal of any adhering clay, NaCl and organic matter and dried by spreading on mats. It is practically free from moisture as it is produced under hot and dry conditions, and is, therefore, well-suited to cement.

3. Flue gas gypsum (or scrubber gypsum or desulpho-gypsum): Its technical name is *flue gas desulphurization (FGD) gypsum*. FGD gypsum is based on SO_2-gas recovered from sulphur-bearing waste flue gas given off by coal-fired power plants. This was first developed in Germany and in Scandinavian countries under pressure to protect flora and fauna from the adverse effects of acid rain caused by sulphurous gas emissions. Later on, it became popular in USA, Austria and Japan. The process involved in as follows.

First, SO_2 is removed from flue gas by spraying a mist of ultra-fine limestone slurry as a result of which an aqueous sludge of calcium sulphite is produced. Then, by passing air though this sludge, it is oxidized forming very fine-sized gypsum. By using high purity limestone containing more than 95% $CaCO_3$ and less than 2% MgO, it has been possible to recover as high as 95% of the SO_2-gas, and good quality gypsum free from moisture and radium has been produced.

Its main disadvantage is that it often contains NaCl in the range 0.13-2.48% and is too fine. These make it unsuitable for use in plaster-based products, where more than 0.03% NaCl is not tolerated, and where evenly distributed size is specified (uniformly fine sized particles cause shrinkage of the plaster). Higher content of NaCl causes gypsum boards and tiles made out of such plaster to crumble and come off the walls because, due to its hygroscopic nature, it absorbs moisture. Although, by applying special technologies it has been possible to reduce NaCl-content from 2% to 0.001% in Germany, the fine size still discourages its use in plaster. Hence, it is mainly used in cement manufacturing. It serves the additional purpose of reducing environmental pollution.

4. Fluoro-gypsum: Hydrofluoric acid (HF) is manufactured by reacting dilute sulphuric acid with fluorite (also called fluorspar, CaF_2) at 300-800^{0}C. In the process, gypsum is produced as a byproduct. The reaction is

$$CaF_2 + H_2SO_4 + H_2O \rightarrow 2HF + CaSO_4.2H_2O$$

This byproduct gypsum is called *fluoro-gypsum*. Its quality depends on the impurities present in the fluorite, but some Indian plant are producing high grade fluoro-gypsum, which is reported to contain 95-98% $CaSO_4.2H_2O$, 1.5-2.0% CaF_2, 0.5-1.0% H_2SO_4, 0.1% P_2O_5 and 0.2% SiO_2. It is used in fertilizer and cement industries.

5. Boro-gypsum: For making boric acid (H_3BO_3), the calcium borate colemanite ($2CaO.3B_2O_3.5H_2O$) is reacted with sulphuric acid. Gypsum is produced as byproduct. The reaction is

$$2CaO.3B_2O_3.5H_2O + 2H_2SO_4 + 4H_2O \rightarrow 6H_3BO_3 + 2CaSO_4.2H_2O$$

This byproduct gypsum is called *boro-gypsum*. Its quality depends on the impurities present in the borate minerals. Boro-gypsum produced in an Indian plant is reported to contain 78.3% $CaSO_4.2H_2O$, 4.8% $MgSO_4$, 4.5% H_3BO_3 and 9.3% SiO_2. It can be and is used in cement.

6. High sulphur coal: When an evenly distributed flow of air or gas is passed at low velocity through a bed of fine particles of sand, the particles remain still. As the air velocity is increased slowly, the particles are first lifted, and then gradually a stage is reached when the entire mass of the particles is churned in a suspended state. It then appears to behave like a fluid in turbulent motion or a boiling liquid. When fuel is added to this bubbling bed, it gets distributed uniformly and if the bed is hot enough, combustion can be sustained. This is, in essence, the principle underlying *fluidized bed combustion (FBC) system.*

In a FBC system, high-ash washery rejects are treated. The system consists of a bed made up of an inert substance like sand or ash. Coal is crushed to 10 mm size. A mixture of hot flue gas and air is blown through the system. The velocity of the gas is maintained at an optimum level. Too high a velocity will carry away the particles and too low a velocity will not fluidize the bed. This technique was originally developed in U.K. in the late 1960's, and now it is being used in UK, US, China, etc. In India its use is limited, and 10-15 MW power plants based on this technique are in operation.

It has been claimed that high-sulphur coal can be used in FBC systems. In such cases, limestone or dolomite is added to the bed in order to fix up the sulphur by way of formation of calcium sulphate which is recovered as a by-product. This however, increases the overall cost of the process.

7. Anhydrite: Anhydrite ($CaSO_4$) is preferred to gypsum in uses where SO_3-content is the key, such as for making ammonium sulphate [$(NH)_2SO_4$] component of the ammonium phosphate sulphate and sulphuric acid. Anhydrite is closely related to gypsum, and in nature, they very frequently encountered together. Theoretically, anhydrite contains 58.8% SO_3 (c.f., 46.5% SO_3 in gypsum). It is harder than gypsum 3-3.5 on Mohs scale and heavier) specific gravity 2.90-2.99. But these are of no relevance and only the higher SO_3-content is what counts.

8. Fiber glass: Since the 1970s, fiber glass tape has become very popular in USA and some countries as a substitute for plaster of Paris in orthopaedics. Fiber glass is more flexible, lighter, stronger and more durable than plaster of Paris, and patients can bathe and swim while wearing fiber glass cast.

9. Precipitated calcium carbonate: Pure $CaCO_3$ prepared by chemical processes (see chapter on limestone, ‘lime manufacturing and products) is preferred to gypsum as diluent in pharmaceuticals.

Chapter 27

KYANITE-SILLIMANITE-ANDALUSITE

The name kyanite is derived from a Greek word meaning blue, sillimanite was named after an American chemist Benjamin Silliman and andalusite after a place called Andalusia. These trio of allotropic forms are identical in chemical composition and similar in many other properties. Chemically all are aluminium silicates ($Al_2O_3.SiO_2$) containing 63.2% Al_2O_3 and 36.8% SiO_2. The most striking difference amongst them is in the crystal form kyanite has bladed crystals; sillimanite, columnar to fibrous crystals; and andalusite, prismatic crystals. These are due to their modes of formation. All of them are metamorphic minerals, but while kyanite is formed by dynamo-thermal metamorphism accompanied by magmatic emanations, sillimanite was the result of simple high-temperature metamorphism and andalusite formed due to metamorphism accompanied by pneumatolytic action of igneous intrusives. Amongst the three, sillimanite is the most stable mineral.

So far as the production of kyanite in India is concerned, from 16,220 tons in 1947, it reached a peak of 120,923 tons in 1970. Thereafter maintaining a fluctuating but, by and large, declining trend and in the year ending March, 2007, it stood at a mere 7,341 tons. With regard to sillimanite its production was only 240 tons in 1947 and in the year ending March, 2007 it was 32,278 tons mostly granular sillimanite recovered as concentrate from beach sand deposits. There is no andalusite production in India currently. It registered production for a brief period from 1976 to 1987 and its maximum production was 2,759 tons during 1983.

USES

1. Mullite refractories: These minerals are used in high-alumina refractory applications. Refractory materials are defined as those resistant to heat and having a melting temperature of not less than 1580^0 C. The function of refractory lining on a furnace wall is not only to withstand high temperature, but also to withstand temperature fluctuation, and to resist penetration, abrasion, and erosion by hot gases and molten materials in the furnace, and over and above, it should not chemically react with those materials. Life of refractory lining has increasingly been becoming a critical parameter in the productivity of a furnace and economics of a plant, because each time the lining fails and needs replacement, the furnace has to be shut down.

Kyanite, sillimanite and andalusite are made into refractory bricks for lining electric arc furnaces for melting nonferrous metals and alloys, glass-melting furnaces, gold-refining furnaces, etc., and also for use in saggars in ceramics. However, none of these three minerals are meant for performing as such in industries, and they eventually get converted to a glassy mixture of *mullite* and silica under conditions of high temperature.

Mullite is also an aluminium silicate, but with higher percentage of alumina compared to the three minerals. Its composition is $3Al_2O_3.2SiO_2$ containing 71.8% Al_2O_3 and 28.2% SiO_2. The part of the silica released from the minerals is in a stable glassy form (cristobalite) and remains intimately mixed with the mullite to form a stable glassy composite material. Mullite was identified as argillaceous inclusions within Tertiary lavas in a place called Mull in Scotland, and hence its name. Mullite is stable up to 1810^0C, is resistant to chemical attacks by many gases, silicates, oxides, etc. and is also resistant to thermal shocks, decrepitation and abrasion.

Commercial deposits of mullite are not found in nature and the comparative values of kyanite, sillimanite and andalusite are pinned around their convertibility to mullite. In fact, these are called “mullite-forming minerals”. Kyanite is transformed to mullite at 1350^0C; sillimanite, at above 1650^0C and andalusite at 1400^0C. Technically, they can be used interchangeably, but their actual use depends on availability at an economical price, physical form and also behaviour under heat.

Although kyanite changes to mullite at a lower temperature, its change is associated with some problems. When heated to between 1200^0C and 1300^0C (i.e., before mullite formation), it expands in volume by about 20% accompanied by shattering. This sudden expansion and shattering of the refractory linings made of kyanite when exposed to high furnace temperatures render them useless. It is therefore a common practice in industry to pre-calcine kyanite before making refractories out of it. The shattering in the precalcination stage, however, is taken advantage of in its later crushing for refractory-making. Compared to this, the expansion of sillimanite is insignificant, only 4 percent.

Sillimanite changes to mullite at a higher temperature. But, it is of particular advantage if naturally available in the form of large-sized lumps as was the case with Sonapahar deposit in Khasi Hills district of Meghalaya in India (the deposit is now exhausted). There, it occurred in the form of large boulders weighing several tons as surface float deposits. These boulders used to be sawn into suitably sized blocks (18 inches X 12 inches X 8 inches) for direct use as refractory lining.

More commonly, however, these minerals have to be crushed and then used as ramming cement or as refractory bricks after bonding with some binder like sodium hexametaphosphate, clay, polyvinyl alcohol etc.

In India, kyanite and sillimanite are used by the refractory industries. For both of them, the Indian industries specify the grades as containing 54% (min) Al_2O_3 and 1.5% (max) Fe_2O_3. For kyanite, the Bureau of Indian Standards (BIS) has stipulated in 1995 the additional parameter of $K_2O + Na_2O$ as 1.0% (max). Fe_2O_3 melts at a relatively lower temperature and alkalis form low-melting brittle glass with silica. Hence these are considered highly deleterious. In order to identify kyanite or sillimanite, the minimum cut-off is taken as 40% Al_2O_3 in India. Andalusite is neither produced nor used in India. But elsewhere, industries specify 53% (min) Al_2O_3 and 1.0% (max) Fe_2O_3.

2. Composite refractories: A mixture of pre-calcined kyanite and sillimanite have also been used with good results. For some applications (e.g., monoblock stoppers) andalusite-graphite bricks can be used. Kyanite and sillimanite are also added to fireclay to improve the performance of firebricks.

3. Glass: Small quantities of uncalcined kyanite have occasionally been used as an additive in glass-making mixture as a source of alumina.

4. Gem: Hardness of kyanite, andalusite and sillimanite is 5-7.25, 6-7 and 7.5, respectively, on Mohs scale (cf., quartz 7); their refractive indices are 1.72, 1.66 and 1.7, respectively, (cf., glass 1.53 and diamond 2.42) with pearly to vitreous and even sub-adamantine lustre; and they occur in attractive crystalline forms and they show pleasing colours kyanite is blue at the centre with white margins, sillimanite shows olive green colour and andalusite shows rose-red, flesh red, olive green and white colours. The hardness, colours and optical properties make some specimens of all these minerals qualify as semiprecious stones.

SUBSTITUTION

Synthetic mullite products equal or superior to mullite have been developed. It is made by fusing in an electric arc furnace pure alumina and siliceous material. Alternatively, a mixture of aluminous material like bauxite, alumina, kaolin, kyanite concentrates, etc. and some silica mineral like flint can be sintered in a rotary kiln at temperatures exceeding 1750^0C. However, synthetic mullite is costlier than mullite based on kyanite/sillimanite/andalusite where indigenous sources of these minerals are available.

Chapter 28

LATERITE

Laterite literally means *brick-stone* having its name derived from the Latin word for brick "latter". The term was first coined by Buchanon in 1807 when he identified a sample of this mineral from Angadipuram, Kerala in India where it was used by local people as bricks for construction of houses. The name was given by him not because it resembled brick but because bricks were made from it. Laterite deposits developed by intensive and long lasting weathering of the underlying parent rock in hot and wet tropical areas and is now seen as thick covers enriched in iron and aluminium oxides, overlying the parent rocks and themselves overlain by lateritic soils. The percolating rain water caused dissolution of primary rock minerals and a decrease in a easily soluble elements like sodium, potassium, calcium, magnesium, etc. This gave rise to a residual concentration of more insoluble compounds, predominantly iron and aluminium oxides. Their formation was favoured by a slight relief which prevented erosion of the surface cover. Laterites occurring in non-tropical areas were products of former geological epochs.

The process of laterite formation is called *lateritization*. If the process is extended, bauxite which is an aluminium-rich laterite variety can form from various parent rocks due to very intensive drainage leading to a very strong leaching of silica and equivalent enrichment of aluminium hydroxides (gibbsite). Lateritization of ultramafic igneous rocks (serpentinite, dunite, or peridotite containing about 0.2 – 0.3% nickel) often results in a considerable nickel concentration.

DEFINITION

The main constituents of laterites are Al_2O_3, Fe_2O_3 and SiO_2, in the form of the minerals kaolinite, goethite, hematite, gibbsite and quartz. Gibbsite ($Al_2O_3.3H_2O$) formed in the course of weathering, and quartz has remained as a relatively stable relic mineral from the parent rock. But the definition of laterite has been and still is an enigma.

In geosciences only those weathering products are defined as laterite, which are geochemically - mineralogically most strongly altered. They are distinguished from less altered saprolite which has often a similar appearance and is also very widespread in tropical areas.

A.W.R. Joachim and S. Kandiah suggested in 1941 a definition based on the ratio $[(SiO_2)/(Al_2O_3+Fe_2O_3)]$. According to him, if this ratio is less than 1.33, then it is laterite; if it is 1.33-2.00, then it is lateritic soil; and if more than 2.00, then it is non-lateritic soil (cf., in ordinary portland cement, this ratio varies from 2.0-2.8). But a universally acceptable definition is still elusive.

For the purpose of export, the Government of India, in 1988, has defined laterite as a mineral containing not more than 40% alumina (above 40% Al_2O_3 will mean bauxite into which laterite often transits).

HISTORY

Most of the Khmer temples at Angkor, Kampuchea are built with laterite and have survived for over 1000 years. Laterite stone which has been plenty available in Malabar region of Kerala and Karnataka states of India and also in Orissa of India, has been the traditional building material for centuries. Temples, forts (e.g., Fort St. Angelo at Kannur, Kerala) and old houses built of non-plastered laterite bricks found in some parts of the northern region of Kerala still give off a weatherworn natural appearance. There, in local parlance, laterite is known as "Chenkallu." It is quarried for bricks throughout Kannur and Kasaragod in this state to meet the local demand.

In India laterite is produced mainly for use in building construction locally and in cement industries across the country. Its production, which stood at 64,285 tons in 1947, has, by the end of the year ending March 2007, risen to 93,1297 tons.

CRITERIA OF USE

1. Colour: Laterite has a pleasing natural red-brown colour which is due to the presence of iron oxides goethite and hematite.

2. Porosity: It is high, varying from 8-30 percent, believed to be due to leaching action of percolating water during formation of laterites.

3. Swelling: Laterite does not swell on absorption of water (due to absence of illite and montmorillonite).

4. Physico-mechanical property: Laterite stone is soft and can be sliced easily when fresh, but becomes indurated on exposure to air. Therefore, it is most economical to cut the soft blocks of laterite into shapes of suitably sized bricks soon after quarrying and leave them exposed to air for hardening. This way it is quite an inexpensive building material in the areas where it is locally available. The compressive strength of fresh laterite is low, being only 150-400 kg/m^2. The reason why it hardens on exposure is not clearly understood. It may be due to formation of glassy matter and filling up of the pores through slow reactions amongst the oxides of aluminium, iron and silicon and the alkalis over a period of time, because that is the process observed when laterite is heated.

5. Chemical composition: Chemically laterite is rich in alumina and silica (which are also the main ingredients of ordinary clay), besides iron oxide. These chemicals enable it to support some tropical plant growth.

USES

Historically, in India, the highly porous thick beds of laterite have served as aquifers for ground water supply. But laterite is mined for its relatively low cost, softness when fresh (which facilitates quarrying, cutting and shaping), hardening after exposure, pleasing natural colours and chemical composition. These properties make laterites suitable for the following uses.

1. Building construction: It is traditionally been very popular in areas where it is available locally. In such areas, even now it is used as a substitute of clay bricks which require precious top soil for making and energy (coal) for burning. Laterite bricks are generally made in bigger sizes than conventional bricks (e.g., a common size is 6"x9"x12" compared to conventional brick of 2.5"x4"x9"). Nowadays, mechanised stone-cutting makes the quarrying processes and cutting and shaping faster, easier and less costly with greater dimensional accuracy than hand-cutting. Moreover, unlike conventional bricks, laterite bricks do not need cement and sand binder for construction. This factor coupled with the larger sizes of laterite bricks enables workers to construct structures faster. The one disadvantage is that the laterite bricks are heavier than conventional bricks which makes their handling difficult.

2. Road and dam construction: Hardened laterite varieties can be applied for the construction of simple roads (called *laterite pistes*) and earth dams. Experiments have been conducted in India (Indian Institute of Technology and Bhabha Atomic Research Centre, Mumbai) in the early 1980s for hardening laterites by heating them. It was observed that at 1000-1100^{0}C, goethite transforms into hematite, and at 1300-1400^{0}C, the latter into magnetite with decrease in porosity. However, for ordinary purposes, heating at 800^{0}C for 8 hours (without any significant decrease in porosity) was found to be good enough. But the processes will involve increase in costs.

3. Aquariums: Nowadays a bed of lateritic gravel is put in aquariums where it favours the growth of tropical plants.

4 Cement manufacture: Cement is essentially a complex combination of lime, alumina, silica and ferric oxide in precise ratios. In order to balance the contents of alumina, silica and ferric oxide, one of the materials commonly preferred by cement manufacturers for addition is laterite which contain all these three compounds. There is no standard specification for the laterite for this purpose, and it depends on the composition of the other raw materials of the cement (e.g., an Indian cement manufacturer is reported to use laterite containing 21% SiO_2, 19% Al_2O_3, 38% Fe_2O_3, 2% CaO, 5% MgO and 18% LOI).

5. Source of aluminium metal: Possibility of extracting aluminium metal from aluminous laterite containing as low as 35% Al_2O_3 have been explored. The processes being tried include (i) carbothermic process, (ii) Toth process, and (iii) Kuwahara process. In carbothermic process, the alumina of the laterite is reduced with carbon. The aluminium carbide produced is separated from clay, decomposed at 2100^{0}C at below atmospheric pressure, and is reduced to aluminium. The Toth process developed in USA, consists in calcination of the laterite, feeding the fine grained calcined laterite to a fluidized bed reactor, and then chlorination, yielding aluminium chloride which is reduced to aluminium by manganese. In the Kuwahara process developed in Japan, the laterite is mixed with coal, finely ground, briquetted, and then heated in a coking furnace to 600-900^{0}C in an inert gas. These ‘coke briquettes’ are heated in a furnace by electric arc to 2000^{0}C, yielding an alloy containing 60% Al and 40% Fe, Si and Ti. By spraying molten lead in the furnace at 1200^0C, the Fe, Si and Ti are separated and an aluminium-lead alloy is produced, which is then liquefied in a pot. The heavy lead settles at the bottom and aluminium floating at the top is recovered. This somewhat impure aluminium containing about 1% lead is purified by fractional vacuum distillation.

Chapter 29

LIMESTONE GROUP OF MINERALS

Limestone refers to a group of sedimentary rocks composed of two igneous minerals, namely, calcite and aragonite, both calcium carbonate ($CaCO_3$), but of different crystal structures, and is different from marble (also $CaCO_3$) inasmuch as the latter is a recrystallized metamorphic rock. Although limestone is a rock, it is considered, by the established convention , both in law and in industry, as a mineral, particularly in India.

The processes of formation of limestone deposits can be classified as:

1. Inorganic

(a) Precipitation from sea water (fine grained lithographic and oolitic or milliolitic limestone comprising micro-sized rounded fossils of milliolite).
(b) Precipitation from lake water (marl)
(c) Precipitation from spring or river water (calc-sinter alias tufa alias travertine)
(d) Precipitation from ground water (stalactite and stalagmite)
(e) Precipitation by evaporation of near-surface subsoil water and capillary action (kankar)

2. Organic

(a) Deposition by marine animals (lime shell)
(b) Deposition by bacteria (chalk)

Inorganic limestone is formed by chemical precipitation. Granular alias oolitic limestone comprising fine concretionary grains and lithographic limestone of fine grained homogeneous compact texture are the most widespread and the most extensively exploited limestone. Marl and marlite or marlstone are high silica variety of limestone. Calc-sinter alias tufa alias travertine are not very significant in India, but there are large deposits in USA. Stalactites and stalagmites are regarded as showpieces of nature and are of economic importance in the sense they attract tourists. Kankar of concretionary from (1.25-10 cm diameter) occurs as encrustations on the ground in some dry places and their deposits are not widespread. In the formation of organic limestones, there is involvement of some types of marine organism and bacteria which absorb calcium carbonate from the surrounding water and then secrete the same as shells and tests. After those organisms and bacteria die, the shells and tests are deposited in different forms like mounds (Biohermal deposit), thick fine-grained beds (Biostromal deposits) and thin very fine-grained bands (pelagic deposits). The common organic limestone deposits of economic interest are chalk (containing remains of the microscopic organism foraminifera), shelly limestone alias lime shell alias "c*oquina*" (containing large fragments of shells) nummulitic limestone, etc.

In nature, limestone is never found in perfectly pure state (56% CaO, 44% CO_2), and it usually occurs mixed with clay and other impurities due to the very manner in which it is formed i.e., deposition in basins where other materials could be present. The common impurities may include silica, iron oxide, alumina, magnesium carbonate, carbonaceous matter, sulphur, phosphorus and alkalis. Due to the widespread occurrence of massive easily mineable beds of limestone, it is a relatively inexpensive natural source of calcium oxide (CaO).

HISTORY

The oldest usage of lime was for building and liming of soil. In India, although building activities started long back and huge temple structures were constructed during the ancient period, lime was not a popular mortar for bonding blocks of rock or bricks, at least till the 3rd century BC. The famous Nalanda University (Bihar) and many temples were built using a mixture of materials like rice husk, jaggery, etc. as mortar. But, lime was definitely known to the Romans a couple of centuries before Christ, as evident from the ruins of some undersea constructions made of a kind of "*hydraulic cement*"—a mixture of lime, water and volcanic tuff excavated from Pozzuoli in present Italy (from which the name "*pozzolana*" is derived). The main use of limestone continued to be as a source of lime, the application of which diversified beyond construction to many other industries. The backbone of today's construction industry – portland cement was invented in 1824 by Aspdin of Leeds, England. Later, it started being manufactured using chalk and mud from Thames river.

In India, apart from limestone, kankar was widely exploited due to its occurrence as easily accessible surface encrustations. Later on, lime shell - abundantly available in some coastal areas - joined the duo. But the earliest portland cement plant established in 1875 near Kolkata was based on chalk obtained free as ballast in incoming empty cargo ships and mud from the Ganges, and the second plant in 1904 at Chennai used lime shell as the principal raw material. By 1950 a total of at least 48 cement plants were established. According to unofficial estimations, the annual production of limestone and kankar in India was about three million tons in 1925 reaching about 6.75 million tons by 1946. However, the published official statistics show the production in 1947 as 3.42 million tons. Since then the growth of mining of the trio of minerals, namely limestone, kankar and lime shell, is as follows.

Year	Production (million tons)
1950	4.94
1960	12.94
1970	24.36
1980	29.32
1990	67.40
Year ending March 2001	127.65
Year ending March 2006	170.38

The production of the year ending 2001 includes a little of that of chalk also (109 tons). However, chalk is mainly produced as a minor mineral and statistics are not available for most of it.

As far as cement is concerned, its production in 1920 was 92000 tons rising to about 565,000 tons in 1930 and reaching the over two million tons mark in 1950. The production was10.6 million tons in 1965, and in the year ending March, 2002 it was about 107 million tons.

CRITERIA OF USE

1. Chemical:

(a) *Composition and reactivity*: Limestone, lime shell, kankar, chalk, etc. (all $CaCO_3$), on being calcined in a kiln to a temperature of $800\text{-}1000^0$ C, releases its CO_2 and what remains are lumps of CaO or "*quicklime*" or (simply) lime (lime is the general term, and if it is obtained quickly by calcination in a kiln in particular, it is called quicklime). Lime produced from a very pure source mineral is called "*fat lime*". Lime being highly reactive, this process is reversible and, when exposed to atmosphere, this lime can again absorb CO_2 of the air and become $CaCO_3$. If instead of air it is treated with water, lime quickly absorbs and reacts with about one-third of its weight in water with generation of considerable heat, and the product is a white amorphous powder called "*slaked lime*" [$Ca(OH)_2$]. But the bonding between lime and water is not strong and, on exposure to dry air, slaked lime can again give off the water. If diluted with excess water (concentration of calcium ions 70-90 grams per litre water), slaked lime becomes a white colloidal solution called "*milk of lime*". If this milk of lime is re-carbonated, then the product is called "*precipitated calcium carbonate*" which is a pure chemical.

(b) *Chemical bonding*: The highly reactive CaO readily reacts with SiO_2 and Al_2O_3 to form strongly bonded compounds.

(c) *Solubility*: $CaCO_3$ and CaO are insoluble in sugarcane juice.

(d) *Disinfection*: Lime can kill germs and pests.

2. Physical:

(a) *Hardness*: Unlike crystalline calcite (hardness 3 in Mohs scale), limestone, lime shell ,etc. being all sedimentary rocks, the question of crystals and cleavages do not arise, and they are fine-to coarse-grained compact homogeneous materials. Consequently, they are hard enough to be crushed into lumps and the grains are bonded enough so as not to generate much fines. Moreover, when the lumps are heated, they do not sputter or decrepitate.

(b) *Colour*: Pure limestone, lime kankar and lime shell are white, but in nature, they assume various colours from reddish to black depending on the impurities present. However, chalk is found in nature in the purest form, and is white. Both quick lime and slaked lime are white.

(c) *Melting point*: Lime fuses at 2000^0 C.

(d) *Bulk density*: Bulk density of slaked lime is very low (half of quick lime). This means small particle size and high speed of dispersion of slaked lime.

(e) *Adhesive property*: Adhesive is an organic or inorganic substance capable of bonding together other substances by surface attachment. Powders of limestone, chalk etc. have good adhesive property.

USES AND SPECIFICATIONS

For all the products of limestone and the related minerals, lime is the base, and hence, those minerals are first converted to lime by calcination. This conversion may be done either independently or as a part and parcel of the main process for manufacturing the final product (e.g., cement, iron, etc.). In the latter case, the mineral, rather than the intermediate product lime, is regarded as the raw material feed. The important uses of these minerals and lime are:

A. Limestone and related minerals

1. Cements (ordinary portland cement, belitic cement, hydraulic or natural cement, high-alumina cement , white cement and pozzolanic cement)
2. Iron
3. Steel
4. Glass
5. Nitro-lime fertilizer
6. Sodium chemicals
7. Sea-water magnesia
8. Glazing of ceramic bodies
9. Rubber
10. Manufacture of lime and its products

B. Lime and its products

1. Sand-lime brick
2. Paper
3. Sugar
4. Leather
5. Calcium carbide
6. Bleaching powder
7. Textile

8. Water and sewage treatment
9. Soil reclamation
10. Soil and asphalt stabilization
11. Sealant
12. Mineral wool

These and some minor uses are elaborated as follows.

A. Uses based on limestone and related minerals

1. Cement: The key to the definition of cements is the *lime saturation factor*, i.e., [$CaO/(2.8\ SiO_2 + 1.18\ Al_2O_3 + 0.65\ Fe_2O_3)$] or (if MgO is present appreciably), *lime standard* [$(CaO + 0.75\ MgO)/(2.8\ SiO_2 + 1.18\ Al_2O_3 + 0.65\ Fe_2O_3)$] as follows:

(a) Ordinary portland cement or OPC.- 0.90 and above saturation factor
(b) Belitic cement. 0.82-0.90 saturation factor
(c) Hydraulic material for mortar - Below 0.82 saturation factor
(d) Special types of cements for special purposes (hydraulic cement high-alumina cement and pozzolanic cement).

(a) Ordinary portland cement (OPC)

(1) *Composition and properties*: It was first made in 1824 by Aspdin. The name ‘portland’ owes its origin to its resemblance to a natural stone called “*portland* stone” occurring near Portland in UK. Essentially, it is powdered aggregate containing tri-calcium alumino-silicate [$(3CaO.SiO_2).(3CaO.Al_2O_3)$], gypsum [$CaSO_4.2H_2O$] and iron oxide ($Fe_2O_3$). It contains 60-70% CaO, 20-25% SiO_2, 5-10% Al_2O_3, 4-6% gypsum and 1-2% Fe_2O_3. When mixed with water, these compounds react with water, and the cement becomes a mixture of hydrated calcium silicate [$2CaSiO_3.5H_2O$], hydrated tetra-calcium aluminate [$4CaO.Al_2O_3.12H_2O$] and slaked lime [$Ca(OH)_2$]. All these compounds crystallize in the form of interlacing needles which gives rise to a strongly bonded cement. On exposure to air, the slaked lime gives off water and tends to absorb CO_2 to quickly become $CaCO_3$, and thus the cement becomes hardened. But the gypsum slows down the absorption of CO_2 through a complex mechanism. It reacts with tri-calcium aluminate and water to first form calcium sulpho-aluminate hydrate (called “ettringite”). This ettringite is deposited as layers on the particles of tri-calcium aluminate and prevents rapid hydration of the CaO. Gradually, as the reaction continues, hydrated tetra-calcium sulpho-aluminate or simply, mono-sulpho-aluminate is formed which is a stable hydrate and which allows hydration of CaO. But this slowing down allows sufficient time to use the cement mix for plastering etc. Finally, when the cement dries up, it becomes a mixture of mono-calcium alumino-silicate and $CaCO_3$, which sets to a strongly bonded solid homogeneous mass.

(2) *Manufacturing* process: For manufacturing tri-calcium alumino-silicate, two processes may be employed depending on the type of kiln used – large slowly rotating rotary kiln or small fixed vertical kiln. The feed consists mainly of limestone or some other calcium carbonate mineral, argillaceous material like clay, laterite etc. (source of alumina and silica) and coal. Some iron oxide should be present in the form of either laterite or

separately added hematite, to provide oxygen to the coal for initial ignition as the affinity of oxygen to coal is stronger than that to iron (the reduced iron eventually remains in the cement and adds to its strength).

i. Rotary kiln process: In the case of the rotary kiln process, all these raw materials are mixed in exactly the right proportion, ground to 60 micron (200 mesh) size, mixed with water, thoroughly mixed in cyclones and then charged into the kiln to form a slurry and fed into the kiln (wet process) or directly fed into the kiln (dry process). The feed (slurry or dry material as the case may be) is fed from the top, and pressurized air introduced from the bottom passes up through the feed. In the wet process a part of the capacity of the kiln is taken up by water and some heat is lost in driving off the water while the dry process does not suffer from these disadvantages. But, on the other hand, the passage of the air and exposure of the materials to the oxygen and their reactions are faster in case of wet process than in case of dry process. The wet process is employed when the calcareous material is wet due to beneficiation by froth flotation or is of lime shell variety mined from sea shores.
ii. Vertical kiln process: In the case of the vertical kiln process, the ground feed material is first pelletized and then the pellets are charged into the kiln from the top and air is blown from the bottom. The pellets form a bed of sufficient permeability so as to facilitate passage of air up (the furnace would choke if fine material is used).

In the kiln, the material is burnt at 1400-1500^{0}C to obtain the product tri-calcium alumino-silicate in the form of glassy balls called "*clinker*" which is cooled, mixed with gypsum and ground to ultra-fine size (300-350 nanometre or 40000 mesh).

(3) *Grades*: Depending on the quality of the raw materials and the processing parameters, the hardened mortar of portland cement may possess varying compressive strengths (measured in Newton/mm^2 or N/mm^2, at the end of 28th day as per international standard). When the minimum compressive strength of the mortar is 53 N/mm^2, the grade of cement is '53', when the minimum strength is 43 N/mm^2, the grade is'43', and when it is 33 N/mm^2, the grade is '33'.

(4) *Specifications*: This is a product made from multiple raw materials, and specification of limestone or (for that matter) any single commodity is meaningless. The most important parameters for the raw material mix are:

i. *Silica modulus,* i.e., [$SiO_2/(Al_2O_3 + Fe_2O_3)$] should be 2.0-2.8.
ii. *Iron modulus,* i.e., [Al_2O_3/Fe_2O_3] should be 1.3-1.8.
iii. *Lime saturation factor,* i.e., [$CaO/(2.8\ SiO_2 + 1.18\ Al_2O_3 + 0.65\ Fe_2O_3)$] or (if MgO is present appreciably), "*Lime standard*" [$(CaO + 0.75\ MgO)/(2.8\ SiO_2 + 1.18\ Al_2O_3 + 0.65\ Fe_2O_3)$] should be 0.90-0.97.

These parameters are pre-set according to the strength and quality of the end product cement desired. Cement being a low-priced commodity, individual materials have to be accepted as available locally, and deficit or excess of any of the main constituents (lime, alumina, silica and iron oxide) in the basic materials is balanced by addition of a suitable material like laterite (for iron oxide and alumina), bauxite (for alumina), hematite (for iron oxide, alumina and silica), clay (for alumina and silica), higher grade limestone (for lime), low-ash coal (for lowering silica), etc. Indian limestone is invariably low in both alumina and iron (1-2% of each), and addition of materials containing these constituents is a general practice in Indian cement plants.

The technology (rotary kiln or vertical kiln) is very important for silica. In case of rotary kilns, the raw materials are charged in a loose mixture. About 75% of the ash (mainly silica) of the coal is blown off, and only the remaining 25% enter into the clinker. So, for a given ash-content of coal, this technology can accommodate limestone with a relatively higher silica content. On the other hand, in vertical kilns, the raw materials are made into pellets and then charged. So, there is no chance of any ash (silica) of the coal to be blown off, and all of it goes into the clinker. For the same given ash content of coal, therefore, this process will require low-silica limestone. However, the form in which silica is present, has a bearing on the economics of cement manufacturing. While silica in the form of silicate as present in clays is desirable, that in free form is not, because free silica is hard and it adds to the grinding cost. Limestone containing up to 12-16% total silica (including silicates and free silica) is accepted by Indian cement industries which employ rotary kiln process, considering the quality of coal available to them.

So far as lime is concerned, limestone or any other related mineral can be used. The Indian industries generally use limestone because of its widespread and abundant availability in the country. The coastal plants also use lime shell, but its mining has been restricted by Coastal Zone Regulation Act. Limestone being the only source of lime in the entire charge, its content of CaO is important, but at the same time it depends on the availability of the right grade at the right price. Moreover, too high CaO means lower silica, alumina and iron, and addition of more clay or laterite to the charge. But use of ultra-fine grained sticky clay, laterite etc beyond limits creates problems like jamming of mixing cyclone (in wet rotary kiln process), formation of layers on the wall of the kiln etc. Hence, very high CaO-content in the feed is not desirable. The Indian industries prefer an average grade of 44-45% CaO. But lower grades are often blended with higher grades in order to maintain consistency, and as low as 38% CaO grade limestone is known to have been used for blending.

There are certain deleterious constituents however, which, if present in cement, are very harmful to its performance. These, therefore, are highly undesirable in any of the raw materials including limestone. These are sulphates and sulphides, MgO, P, Mn_2O_3 and soda (Na_2O_3).

Unlike gypsum which is added to the cooled down clinker and which does not chemically react with the latter, the sulphates and sulphides that are present in the limestone, enter into chemical reactions under the high temperature inside the kiln and form calcium sulpho-aluminate. This calcium sulpho-aluminate is highly expansive.

So far as MgO is concerned it is frequently found associated with limestone in nature. MgO slakes at a rate slower than CaO. Partly dry MgO gets carried into the applied cement, and when it slakes to $Mg(OH)_2$, it expands in volume by up to 120% resulting in cracks. Indian industries prefer a maximum of 2.5% MgO in the limestone, but due to constraints of availability, they are sometimes forced to accept up to 3.5%, but the quality of cement has to be compromised.

Phosphorus tends to slow down the setting time excessively (1% P_2O_5 increases the setting time to several days) and is undesirable. Mn_2O_3 carried into the cement, tends to oxidize and crumble the cemented structure. Soda ($Na_2C\ O_3$) will react with silica at the clinkering temperature (1400^0 C) to form sodium silicate (Na_2SiO_3). Thus it will deprive the lime of a part of silica. Moreover, sodium silicate being soluble in water remains in the applied mortar plaster, and later, on drying, forms crystals and weakens the plaster.

(b) Belitic cement

Belite is the mineralogical name for di-calcium silicate or Ca_2SiO_4, and *belitic cement* is a material which reacts with water to produce a hydrated calcium silicate according to the reaction:

$$2Ca_2SiO_4 + 4H_2O \rightarrow 3CaO.2SiO_2.3H_2O + Ca(OH)_2$$

This hydrate grows as a mass of interlocking needles that provides strength. Belitic cement is characterized by late strength. Belitic clinker can be manufactured from calcareous marl containing 20-26% CaO. Its lime saturation factor i.e., [$CaO/(2.8\ SiO_2 + 1.18\ Al_2O_3 + 0.65\ Fe_2O_3)$] is 0.82-0.90. But even lower grade marl having saturation factor 0.77-0.79 can be made into belitic clinker after sweetening with limestone.

(c) White cement

The process is the same as for ordinary Portland cement described above, but the raw material feed is different. In case of white cement, the raw material mix consists mainly of high grade low-alumina limestone and pure white silica sand. White cement is made of 65% CaO, 24% SiO_2 and only 5.9% Al_2O_3 which form an aggregate generally consisting of 46% di-calcium silicate, 33% tri-calcium silicate and only14% tri-calcium aluminate. A little of pure gypsum is of course added to slow down the rate of setting.

Specifications: Ideally, both limestone and silica should be pure and white in colour. In practice, high grade limestone containing 48% (min) CaO, and 1% (max) each of Al_2O_3 and Fe_2O_3 is used. Alumina is objectionable because it has no role and if present, it will be at the cost of CaO. Iron oxide has colouring effect and is not tolerated. To sum up, the silica modulus i.e., $SiO_2/(Al_2O_3 + Fe_2O_3)$ should be very high.

(d) Hydraulic or natural cement

The term hydraulic here means that the lime has the ability to set hard under water, and the term ‘natural’ refers to use of only naturally occurring substances without any burning or processing. This is actually not cement, but a hydraulic material suitable for mortar preparation. This material was known in the ancient times in Rome, in India, in London etc. and used for building underwater dams. Limestone containing sufficient argillaceous or siliceous matter (e.g., kankar, marl). When such a material is made into a mortar by mixing with water and applied to a surface, the lime reacts with the silica to form calcium hydro-silicate which has strong bonding property. Since the water is retained under water, the bond persists under water. In a modern version of this natural cement called “*masonry cement*” or “*portland cement base*”, additional limestone and some plastic material are mixed with portland cement and then ground together. The plastic material absorbs and retains water and also strengthens the bond.

(e) High-alumina cement

The principal constituent of high-alumina cement is mono-calcium aluminate (cf., tri-calcium silicate in case of portland cement). Consequently, its Al_2O_3 content is very high (of the order of 50-60% compared to around 5-10% in the portland cement), while CaO and SiO_2 contents are low (of the order of around 30-40% and 5-10% respectively compared to 60-70% and 20-25% respectively in the portland cement). On mixing with water, the mono-calcium aluminate of high-alumina cement transforms into di-calcium aluminate with liberation of gelatinous alumina. Its properties include quick setting (2-4 hours), high strength achieved in 24 hours, and ability to withstand high temperatures up to 1200^0 C. There are two types of high-alumina cement, namely: (i) high iron (also called *ciment fondu)* and (ii) low iron.

i. High iron cement: After setting, the high iron type rapidly becomes hard and resistant to corrosion by chemical attack. It is manufactured by melting a mixture of limestone, high-iron bauxite, and coke in a vertical kiln in which the rising volatile gases preheat the feed before its melting. The melt is then cast into ingots, solidified and ground. The iron contributes to hardening properties. Its rapid-hardening properties, resistance to sea water and ground water containing sulphates in solution, and impermeability make it suitable for use in the construction of reservoirs and foundations in marshy conditions, of piers and harbour works, of drainage and sewerage pipes, of internal linings of water tunnels, of power station flue gas chimneys etc.
ii. Low iron cement: For manufacturing the low-iron type, chalk or limestone fines and low-iron bauxite fines are mixed and melted in an electric arc furnace. It is more refractory than the high-iron type, but not as hard as the latter.

Both these types are used, along with a suitable aggregate of refractory grog, as refractory cement or refractory mortar for applying on refractory linings, and also as castable refractories.

(f) Pozzolanic cement

It is also called "*oil well cement*" due to its extensive use in oil wells – both on-shore and off-shore. Calcium hydroxide reacts with industrial waste micro-silica having good pozzolanic properties, in presence of water to form calcium aluminium hydrate compounds (C-S-H) which is a compact substance with low porosity and having cement-like properties at room temperature. Further, due to the acidic nature of pozzolan, the C-S-H produced from it is resistant to corrosion by sulphates and it is also resistant to water leakage and spalling due to low porosity. Taking advantage of these characteristics, ordinary portland cement is mixed with microsilica to produce what is called "*portland cement-pozzolan*" for use underwater in oil wells as well as offshore oil wells.

2. Iron manufacturing:- Limestone is used in manufacture of pig iron through the blast furnace route to serve two purposes :

i. It acts as a flux and lowers the temperature of melting the charge thus reducing the quantity of coke required;

ii. It combines with SiO_2 and Al_2O_3 of the iron ore to form a complex compound calcium aluminium silicate which comes out as slag.

Here, limestone is used (and not lime), because in any case the limestone gets calcined within the blast furnace, and separately calcining it is neither economical nor necessary.

Iron can also be made in the form of sponge iron or hot briquetted iron (HBI) by direct reduction (DR) process. In a typical Indian coal-based process, a mix of iron ore, coal and limestone (or dolomite, as flux) is fed into the rotary kiln and heated at a temperature of about 1100^0 C.

Specifications:

(1) Pig iron: The strength of limestone is of importance so that it can withstand the stress of falling from the top of tall blast furnaces during charging. Crumbling will lead to generation of dusts that will tend to obstruct the passage of air. It should therefore be in the form of compact lumps. The Bureau of Indian Standards (BIS) recommended in 1982 a size range of 26-60 mm. But in actual practice, different plants in India, larger lumps of 75-125 mm size are also used.

Silica and alumina are objectionable mainly for the following three reasons:

(a) The purpose of adding limestone is to remove these impurities present in the iron ore. Their presence in the limestone will only add to the impurities in the charge, and some lime will be consumed for reacting with its own impurities necessitating addition of more limestone which, in its turn, will increase the volume of slag.

(b) Limestone gets calcined at the temperature of the blast furnace to form a porous mass of lime. These pores provide larger surface areas for its reactions within the furnace. If, however, silica and alumina are present in it, they will immediately combine with the lime to form calcium aluminium silicate which will shut the pores, thus decreasing further reactivity of the lime.

(c) Of the two, alumina is more objectionable, because it has a high melting point and it requires more heat to melt and become fluid. Imperfect melting of the alumina results in higher viscosity of the slag. If the charge, however, is high-phosphorus and high-sulphur due to introduction of these elements through iron ore and coal, then a relatively larger slag volume is desirable for removal of these elements. Large slag volume requires higher SiO_2/A_2O_3 ratio and some manufacturers add quartzite and bauxite, while others prefer high-silica limestone with minimum addition of quartzite.

The BIS recommended in 1982 a maximum limit of 10% for combined silica and alumina out of which alumina should not exceed 2.5 percent.

Magnesia (MgO) does not contribute to the slag formation. So its presence in the limestone at the cost of CaO is undesirable. The BIS recommended in 1982 a maximum limit of 9%, but some of the Indian industries prefer as low as 2 percent.

If phosphorus is carried into the final product, i.e. steel, it reduces ductility and makes the steel brittle under shocks. Sulphur, when carried to the steel, produces cracks at the edges at the time of rolling of the steel. Both these elements are highly objectionable in limestone (or for that matter in the entire charge), because they are the most difficult deleterious elements to remove through slag, and they tend to segregate towards the border zone between the slag and iron. By increasing the slag volume and basicity of the slag, they can, at best, be partly removed, but invariably a part goes into the iron. So limestone must not add to their percentage in the charge.

The alkali load has an adverse effect on the reactions within the blast furnace. The alkalis (Na_2O and K_2O) combine with silica to form light fusible silicates which float toward the molten slag, and the availability of silica decreases, affecting the formation of an effective slag. Indian industries specify up to 0.4% alkalis (Na_2O and K_2O) in the limestone.

Ideally, the higher the content of lime in the limestone, the better the performance will be and the economics of the furnace. But large volumes of limestone are required in blast furnace – approximately 1.4 tons per ton of pig iron. So, generally plants in India cannot afford to use high-lime limestone, and prefer to accord more importance to local availability. Apart from this economic reason, there is also technical reason for using low-lime limestone. When the blast furnace charge contains high phosphorus and high sulphur, as explained in an earlier paragraph, high slag volume requiring high SiO_2/Al_2O_3 ratio is desirable, and in some plants quartzite and bauxite are added, while in others high-silica limestone with minimum addition of quartzite is preferred. Low silica means higher lime while high silica means lower lime, and so, while in the former case high-lime limestone is used, in the latter case low-lime limestone is used. Summing up, in India, limestone containing 42 % CaO is considered acceptable although one or two plants use up to 50% CaO grade.

(2) Sponge iron manufacturing**:** Here, iron ore is reduced in solid state, and there is no slag formation nor there is any possibility of the impurities of limestone to go into the iron. Role of limestone is to reduce the melting temperature of the charge, and its grade is of not much importance, except that higher grade will reduce the frequency of kiln shut-down for cleaning purpose.

3. Steel making: In steel melting shop (SMS), role of limestone is mainly to: (i) act as flux for helping the charge in melting, (ii) neutralize acidity of the melt caused by the presence of certain impurities like silica, alumina, etc., (iii) stir the molten charge in open hearth (OH) furnace by what are called "*lime boils*" formed due to escaping CO_2 gas, and (iv) remove phosphorus and sulphur present. Steel is essentially a refined alloy of iron and carbon with carbon content lower than in pig iron – less than two percent. Steel-making, therefore, primarily consists in removal, by combustion, of the carbon contained in the iron. But, there are some deleterious elements including phosphorus and sulphur, which are not totally assimilated by the calcium aluminium silicate slag during pig iron manufacturing, and which has to be removed in the SMS. For making steel, iron, coke and limestone are placed in the hearth and is melted at 1800^0 C by a mixture of gas and air. Phosphorus and sulphur are oxidized, and these oxides react with limestone to form a slag which, being lighter, floats on the molten steel, and is drained off. Then the steel is tapped. Their removal is further facilitated by the alkaline conditions provided by the limestone.

In L-D furnace, pure oxygen instead of air is blown to expedite the reactions and reduce the steel-making time. To improve efficiency further, in some versions of the process, limestone powder is mixed with oxygen and then injected into the furnace.

In the charge for electric arc furnace employed for making steel from sponge iron, limestone is not needed, because: (i) the temperature of the arc is too high to need any fluxing agent, and (ii) the solid sponge iron is about 85% pure metallic iron from which silica, alumina, phosphorus, etc. has already been removed.

Towards the end of operation, quick or hydrated lime, which supplies additional free oxygen ions, is used as a slag-dressing with a view to thickening the slag so that transfer of the oxygen ions out of the bath is prevented. Thus the phosphorus and sulphur trapped in the slag remain in oxide form and the efficiency of their removal is improved. Oxygen activity in the bath tends to be depressed due to presence of carbon and silicon, and so, extra oxygen becomes desirable if the amounts of phosphorus and sulphur are high

Specifications: The added function of lime is to neutralize the acidity of the melt in the furnace in order to facilitate removal of P and S in the slag. For use of limestone in steel-making by open hearth (OH) process, SiO_2, Al_2O_3, P and S besides being objectionable for the same reasons as in case of pig iron, are also so because they tend to add to the acidity. Here the furnace is much smaller than blast furnace, and also, much of the P and S has already been removed there. So high slag volume reduces productivity and is not desirable. On the other hand, high CaO is necessary for effectively neutralizing acidity, and high CaO means commensurately low SiO_2, Al_2O_3 and MgO. The BIS, in 1982, recommended 50% (min.) CaO, 3% (max.) MgO and 4% (max.) acid insoluble (out of which SiO_2 should not exceed 1.8%). Morever, the operating temperature is much higher (1800^0 C) compared to blast furnace (1100^0 C), and this necessitates the limestone to be in the form of dense, massive, preferably fine-grained, compact lumps (35-125 mm size)which are non-fritting on burning.

Soda is a stronger base and should be desirable for increasing the basicity of the bath – necessary for removal of phosphorus and sulphur. But soda also tends to corrode the refractory lining.

In case of L-D process, the reactions in the furnace have to be quick and complete. So very high purity limestone containing up to 53% CaO is preferred by manufacturers, and this leaves very little room for the impurities MgO, SiO_2 and Al_2O_3 – only 3 percent for all together (One Indian industry namely Rashtriya Ispat Nigam, Vishakhapatnam specifies a minimum of 53% CaO and the maximum limits of impurities as MgO 1.5%, Al_2O_3 0.3%, SiO_2 0.6%, P 0.05% and S 0.025%). In the version of L-D process involving high pressure injection of powdered limestone, silica is particularly objectionable because it will increase grinding cost and manufacturers prefer as low as 0.5 per cent. In some advanced countries, lime (containing 98% CaO), instead of limestone, is preferred.

In both OH and LD processes, alkalis (Na_2O and K_2O) are highly objectionable and no more than 0.1% is tolerated. The alkali load has an adverse effect on the reactions within the furnace and also tends to corrode the furnace lining.

4. Glass: The composition of typical common colourless soda-lime glass is sodium calcium silicate. [$18Na_2O.2MgO.8CaO.72SiO_2$]. Essentially, the process of manufacture of glass consists in melting a mixture of 47% silica sand,14% soda (Na_2CO_3), 12% dolomite ($CaCO_3.MgCO_3$), 3.5% limestone ($CaCO_3$), 2.5% carbon (coke) and the balance broken waste glass (called cullet) at $1400\text{-}1500^0$ C. So lime is introduced in the charge in the form of both limestone and dolomite. The function of the lime (along with soda and broken glass) is to act as flux for lowering the melting point of silica from 1580^0 C to 1400^0 C. However, lime has a tendency to form crystals and addition of magnesia helps prevention of this devitrification. The CO_2 of the carbonates of calcium and magnesium are expelled reducing them to CaO and MgO. The low-melting soda and broken glass become liquid first and silica (quartz) being soluble in boiling soda, dissolves in this liquid to form low-melting sodium silicate which then reacts with the CaO and MgO to form glass. The calcium silicate component imparts great chemical stability to the glass and also reduces the latter's thermal expansion.

Specifications: Fe_2O_3 and organic matter are highly objectionable because they have colouring effect on the glass. Even in coloured glass in which iron oxide is added later, its presence in the initial charge hampers control of the colour. Phosphorus and sulphur are also considered deleterious because their gaseous oxides may get trapped in the glass and make it brittle. A little MgO is not objectionable, because it also forms a component of the charge and the final glass product, but limestone should contain as high CaO as the economics of manufacture may permit.

Even for ordinary low-quality glass, the Indian industries use limestone containing 94.5% $CaCO_3$ (53% CaO), 1.5% MgO and 0.20% (max.) Fe_2O_3. For colourless glass, the limestone should be almost pure containing minimum 98.5% $CaCO_3$ (over 55% CaO) and a maximum of 0.04% Fe_2O_3, while in bottle glass Fe_2O_3 up to 0.05% is used. The BIS (1973) recommended somewhat similar specifications: 53.0% CaO, 0.10% Fe_2O_3, 2.5% SiO_2, 54.50% (CaO + MgO)

5. Nitro-lime fertilizer: Limestone is used only as a carrier of ammonium nitrate (NH_4NO_3) fertilizer. The NH_4NO_3, produced in a liquor form, is mixed with limestone which absorbs the liquor to form nitro-limestone granules. These granules are dried, cooled and coated with some coating material to obtain the finished fertilizer.

Specifications: Limestone should be porous so as to act as the absorbent of the ammonium nitrate liquor. Argillaceous matter (containing alumina and reactive silica), Fe_2O_3 and organic matter are undesirable. Argillaceous matter fills up the pores of limestone. Fe_2O_3 reacts with NH_4NO_3. Organic matter, on decomposition, may render the soil acidic.

MgO is totally undesirable. MgO is strongly hygroscopic absorbing 120% of its volume of water. This volume expansion may crumble the granules to powders, and in powder form the fertilizer is not suitable for application to soil, as the natural pores of the soil become choked blocking movement of water to the roots of plants. On the other hand, after application of the nitro-lime granules to the soil, the MgO will increase the water-holding capacity of the soil.

For this purpose, the industries prefer limestone containing 85% (min.) $MgCO_3 + CaCO_3$, 5% (max.) SiO_2 and acid 14% (max.) insolubles. Limestone should be porous so as to act as the absorbent of the ammonium nitrate liquor. Argillaceous matter (containing alumina and reactive silica), Fe_2O_3 and organic matter are undesirable. Argillaceous matter fills up the pores of limestone. Fe_2O_3 reacts with NH_4NO_3. Organic matter, on decomposition, may render the soil acidic.

6. Sodium chemicals: Limestone, as a source of both CaO and CO_2, is the starting material. Both CaO and CO_2 are used for making various sodium-based chemicals. For this purpose, limestone is first calcined at 1000^0 C (see 'manufacture of lime' below), and then a series of three chemicals are manufactured as follows.

(a) *Sodium bi-carbonate ($NaHCO_3$)*: First with the help of CaO, ammonia is distilled. Na_2S is added to precipitate iron as sulphide. Then compressed CO_2 is passed through purified ammoniac brine to obtain this compound. Calcium chloride is recovered from waste liquor for reuse.
(b) *Soda or soda ash(Na_2CO_3)*: It is obtained by calcining $NaHCO_3$.
(c) *Caustic soda (NaOH)*: This is made by causticizing soda ash with milk of lime [$Ca(OH)_2$ with excess water].

Specifications: Since limestone is the starting material, the specifications are for limestone. Unlike other uses of limestone, both CaO and CO_2 are important as both of them take part in the production process. A little $MgCO_3$ is not objectionable in limestone meant for this purpose, as it also contributes CO_2 to the process, but too much of it increases the content of MgO in the product CaO that will slow down the slakability of the latter. MgO absorbs 120% of its weight of water and formation of $Mg(OH)_2$ is much slower than that of $Ca(OH)_2$.

Silica and alumina are objectionable because they tend to combine with CaO forming calcium alumino-silicate. Moreover, if, by chance the kiln temperature goes up beyond 1400^0C, silica will melt forming coatings of thin films of liquid glass around the pieces of limestone that may damage the kiln. Also such melted silica will react with kiln lining forming aluminium tri-silicate layers which slowly grow and obstruct the passage of air. Fe_2O_3 is objectionable as it requires treatment with Na_2S for its removal with increase in cost.

The Indian industries specify limestone with a minimum of 92% total carbonate ($CaCO_3$ + $MgCO_3$) of which $MgCO_3$ should not be more than 3%. The maximum limits of the deleterious constituents are 4% SiO_2 and 3% Al_2O_3 + Fe_2O_3. The BIS, in 1978, has recommended the specifications of limestone intended for manufacturing caustic soda, as containing 53% (min) CaO, 42% (min) CO_2, 1% (max) MgO, 3% (max) SiO_2+Al_2O_3+Fe_2O_3.

***7. Seawater magnesia*:** Sea water contains 0.2 % MgO. For its recovery, the basic process involves the following steps.

i. Limestone calcination and lime slurry (i.e., a suspension of $Ca(OH)_2$ in water) preparation
ii. Sea water and fresh water pumping
iii. Magnesium hydroxide precipitation
iv. Calcination of $Mg(OH)_2$ to MgO
v. Briquetting
vi. Sintering of briquettes

Lumps of limestone of high purity is first calcined (see ‘Manufacture of lime’ below) and slaked with freshwater. More water is added to make a slurry containing no more than 5% solids. Further purification of the slurry is carried out at this stage by removing whatever impurities get into it from limestone and freshwater.

The next step is to rid the seawater of dissolved CO_2, which if carried into the process, will form precipitated $CaCO_3$ (see ‘Manufacture of lime’ below) and eventually contaminate the magnesia product. To eliminate CO_2, the seawater is first made acidic by treating it with sulphuric acid and then de-carbonizing.

In the next step, $Mg(OH)_2$ is precipitated by mixing seawater with $Ca(OH)_2$ and using a seed. Then the $Mg(OH)_2$ cake is dried at 1000^0 C, briquetted by pressure and finally sintered at 2000-2300^0 C.

Specifications: The product magnesia is very costly and is meant for applications requiring almost cent per cent purity, and hence the starting material limestone has to be exceptionally pure unlike that required for manufacture of lime or other lime-based products. The industry specifies a minimum 55% CaO (cf., limestone theoretically contains 56% CaO), and maximum 0.2% SiO_2. The impurities MgO, Fe_2O_3 and Al_2O_3 together should not be more than 0.5 per cent. These impurities are liable to be carried to the MgO briquettes and react at the high sintering temperature of 2000-2300^0 C.

8. Glazing of ceramic bodies: The purpose of glazing is to provide a uniform firmly adhering coating on the surface of the ceramic body concealing defects such as pinholes, bubbles etc. Glaze may be "*raw glaze*" or "*fritted glaze*". Raw glaze consists of insoluble material applied as such (soluble components crystallize in the mixture and cause blemishes on the treated surface), while fritted glaze is heated beforehand to cause chemical change in the components. The glaze is made predominantly of quartz and feldspar. But sometimes, limestone is also added. The ingredients are mixed, finely ground, and mixed with water, and this mixture is the glaze. The fine grinding ensures that the materials do not settle quickly and remain in suspension in the water long enough for them to deposit as a uniform coating on the body. The moulded raw body of the product is dipped into the glaze and then fired to a temperature of about 1400^0 C. Limestone acts as a flux lowering the fusion temperature. After firing, it becomes lime and combines with the silica of quartz and the alumina of feldspar to form calcium alumino-silicate which is a hard glassy substance (cf. blast furnace slag) making the glazed surface hard and impervious. Colours and decorative designing, if required, are painted after glazing and before firing.

Specifications: Since limestone is used in powder form, free silica which is harder than limestone, is not desirable. Fe_2O_3 has undesirable colouring effect on white or coloured ceramic bodies, but for ordinary potteries it can be tolerated to some extent. MgO is undesirable because it increases the fusion temperature of the glaze. MgO which is in the form $MgCO_3$, requires higher temperature for calcination (1600-1800^0C compared to 1000^0C in case of $CaCO_3$) and fusion of MgO takes place at 2000-2300^0C.

Sulphates, which are soluble in water, are also deleterious. They remain in solution in the glaze coating. When the glaze is fired, the water is evaporated and the sulphates are first brought to surface by capillary action and the deposited on the surface as scum.

The Indian industries specify limestone containing 96-97% $CaCO_3$, and maximum 2% SiO_2 and 0.3% Fe_2O_3.

9. Rubber: Powders of chalk or lime shell and precipitated calcium carbonate (see 'Manufacture of lime" below) are used as non-black fillers. Adhesive properties of limestone powder are made use of. Adhesive is an organic or inorganic substance capable of bonding together other substances by surface attachment. Ground limestone is useful where off-white colour is permissible. In rubber, it serves to increase hardness, while precipitated calcium carbonate increases resilience, elongation and tensile strength and tear resistance.

Specifications: Whiteness and softness are the two most crucial criteria. Chalk and lime shell of high purity are preferred to other variations of limestone.

10. Manufacture of lime and its products: Lime (quick lime), slaked lime and precipitated calcium carbonate are starting materials in many important usages.

(1) Process of manufacturing lime: Lime is manufactured by calcining limestone (or other related minerals) at 1000^0 C in lime kilns lined internally with refractories. For calcination, there are two processes – intermittent or batch process and continuous process. In the former, the kiln is loaded with a batch of alternate layers of coal and limestone and heated. After unloading the batch of calcined lime, another batch is loaded. The lime produced by this process is impure, being contaminated with coal ash. To obviate this problem a kiln with grated bottom zone is employed. Limestone is stacked in the kiln, coal is burnt outside the bottom area and hot air is introduced through the grates and blown up through the limestone to drive off CO_2. In this process, the limestone of the bottom zone near the fire is calcined first and is removed continuously through an opening at the lower portion, and simultaneously, fresh limestone is charged through the top. The control of the temperature is very important, because if it reaches about 1100^0 C, the calcium oxide reacts with the silica and alumina of the limestone to form calcium alumino-silicate.

(2) Products of lime: The product is sold as such as quick lime, or is converted to slaked lime or milk of lime or to precipitated calcium carbonate and sold. For making slaked lime, the lime is crushed to 10 mm size. On adding water, hydration takes place with a hissing sound releasing heat. About 80% of the weight of lime is required. The product $Ca(OH)_2$ is ground to 100 mesh (+100 microns) size, and sold.

Slaked lime can be diluted with excess water to reduce the calcium concentration to 70-90 grams per litre to obtain milk of lime.

To make *precipitated calcium carbonate (PCC)*, there are three commonly employed processes as follows.

(a) *Lime carbonate process*: Lime kiln off-gases contain a suspension of 30-40% calcium ions in CO_2. These gases are washed with excess water to form a mixture of milk of lime and CO_2, and pumped into what are called ‘lime suspension in-carbonation towers’. When the mixture is sprayed in the tower, reaction between the CO_2 and the $Ca(OH)_2$ takes place converting the latter into a suspension of $CaCO_3$ particles in water. It is filtered and dried to get the final product.

(b) *Calcium chloride process*: When $CaCl_2$ liquor obtained as byproduct from some other industry (ammonia soda process) is treated with soda [Na_2CO_3] or ammonium carbonate [$(NH_4)_2CO_3$] solution , $CaCO_3$ is precipitated.

(c) *Causticization process*: Precipitated $CaCO_3$ is produced as a byproduct of the lime-soda process of manufacturing (causticization) caustic soda. In this process, calcium hydroxide is reacted with soda as:

$$Ca(OH)_2 + Na_2CO_3 \rightarrow 2NaOH + CaCO_3$$

PCC is in the form of ultra-fine particles and is pure white in colour.

It can be seen that all the processes depend on byproduct recovery of one or more of the process materials, and, in fact, the economy of the making precipitated calcium carbonate depends largely on this factor.

(3) Specifications: In the calcination process, the hot air must be able to pass through the bed of limestone minerals. For this, there should be enough porosity and permeability in the

bed. As limestone is fine grained and compact, it has to be in the form of lumpy pieces. Since the intended product is lime, as high a lime-content as is available is desirable. All other constituents should, therefore, be as low as possible. The BIS in 1982, has recommended 52% (min) CaO, 2% (max) each of MgO and acid insolubles (including silica, alumina). The latter is particularly risky, because at about 1100^0C, there will be formation of calcium alumino-silicate. MgO which is in the form $MgCO_3$, requires higher temperature for calcination (1600-1800^0 C compared to 1000^0 C in case of $CaCO_3$).

B. Lime-based uses

1. Sand-lime brick: Also called "*calcium silicate* bricks", these are used particularly where clay bricks are scarce or where consistently high-strength bricks are required. Sand-lime bricks are compact with water absorption less than 7.15% by weight after 24 hours. Here, calcium hydroxide or slaked lime [$Ca(OH)_2$], instead of cement, is mixed with sand and water to form a paste which is then pressed into solid, perforated or hollow bricks and hardened under high-pressure steam whereby calcium hydroxide and silica combine to yield calcium hydrosilicate, and strongly bonded bricks become ready. These are ordinarily off-white in colour, but pigments can be added to make coloured bricks. Since lime is the base for manufacturing these bricks, higher the lime content in the limestone or any other related mineral, the better.

2. Paper: The limestone is used in the form of lime in the different processes as follows.

(a) Soda process: In this process, caustic soda (NaOH) is used to digest the wood and other fibers. After digestion impure waste caustic soda is recovered from the wash and treated with slaked lime which causticizes it for re-use. Lime coagulates the suspended impurities in the waste caustic soda and serves to precipitate them.

(b) Sulphite process: By passing SO_2 gas, slaked lime is converted to $CaHSO_3$ which is acidic in nature. The $CaHSO_3$ dissolves all the constituents of wood chips except cellulose.

(c) Steam process: Lime is used to digest and cook the rags.

Calcium carbonate ($CaCO_3$) is used as a filler in certain magazine and book papers to increase whiteness. But this $CaCO_3$ is not natural limestone, but a precipitated $CaCO_3$ (a pure chemical obtained by re-carbonating milk of lime).

Specifications: Free silica and grit are objectionable because their grindability is poor and they are not soluble. They may affect the smoothness of the finished paper.

Argillaceous matter (containing silicates and aluminates) remain in colloidal suspension in water and in the soda process slows down the purification of the waste caustic soda. Moreover, argillaceous matter fills up the pores in the calcined lime and slows down the process of its hydration. Hence argillaceous matter is undesirable in the soda process.

In the sulphite process, MgO is desirable, because $MgHSO_3$ is also formed along with $CaHSO_3$. The former is more reactive, more soluble and more stable than the latter, and consequently it increases the efficiency of the process. In other processes, however, it is undesirable because it slakes at a slower rate than lime and affects the efficiency.

Iron oxide is a colouring substance, and is carried to the final pulp affecting the whiteness of the product.

3. Sugar: In sugar manufacturing, role of lime is for refining cane juice. Lime in the form milk of lime, i.e., over-saturated $Ca(OH)_2$, is poured into the boiling cane juice, and SO_2 or CO_2 is blown through it. The water of the $Ca(OH)_2$ goes off and the SO_2/CO_2, the phosphates and organic acid combine with CaO to form $CaCO_3$, $CaSO_4$, calcium phosphates and some organic compounds. When the juice is cooled, all these compounds settle down trapping with them all the impurities in suspension in the juice. The clear juice is decanted out.

In another process called "*Steffen process*", sugar is precipitated and the impurities remain in solution. In this case, lime forms insoluble salts with sugar which are later decomposed by CO_2 and sugar crystals are separated out.

Specifications: $MgCO_3$, argillaceous matter (showing as SiO_2 and Al_2O_3 in the analysis) and Fe_2O_3 are the most objectionable constituents. $MgCO_3$ is soluble in cane juice, and as the juice boils and becomes concentrated, it is deposited as scales on the vessel. Argillaceous matter forms colloidal suspension in the juice and separates out as gelatinous matter coating the sugar crystals, retarding their growth and obstructing filtration. Fe_2O_3 has colouring effect on the sugar. Some of the sugar mills do not purchase lime, but has their in-plant facilities for making lime from limestone. For them, the BIS in 1978, has recommended limestone containing 50% (min) CaO, 1% (max) MgO, 2% (max) SiO_2 and 1.5% (max) Al_2O_3 and Fe_2O_3 together.

4. Leather: In leather industry slaked lime is used to loosen the hairs of the skin so that they can be removed easily. Lime water softens the epidermal cells and dissolves the mucous layer, thereby loosening the hairs.

Specifications: Since lime is slaked for this use, MgO and argillaceous matter are considered deleterious as they tend to slow down the slaking. Fe_2O_3 is also objectionable because it may stain white leather.

5. Calcium carbide: The main use of calcium carbide (CaC_2) is to generate acetylene gas (C_2H_2) for use in gas welding, carbide lamp, etc., to prepare calcium cyanamide [$Ca(CN)_2$] weed killers and for de-sulphurization of iron and steel. Acetylene is generated instantaneously as soon as the carbide is immersed in water.

$$CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2$$

For manufacturing calcium carbide, lime and coke (or charcoal) are heated in presence of air to a temperature of 2000^0 C in an electric furnace. The CaO reacts with carbon to produce calcium carbide (CaC_2). The molten product is cooled and solidified.

Specifications: Within the bed of lime-coke/charcoal mix in the furnace there must be sufficient air pockets for accumulation of heat to enable the reactions to take place effectively. This requires that the lime should be in the form of lumps, and also that the lumps should be strong enough not to crumble into powders during charging.

CaO-content in the lime should be as high as possible. The Indian industries specify a minimum of 92% CaO. Argillaceous matter (showing as alumina and reactive silica), free silica, alkalis, MgO, iron oxide, phosphorus, arsenic and sulphur are considered deleterious.

Higher argillaceous matter means less strength of the lime lumps. If both free silica and alkalis are present, then the alkalis (Na_2O and K_2O) combine with silica to form fusible silicates that get incorporated in the calcium carbide. Further when both free silica and MgO are present, they may dissociate in the furnace into silicon and magnesium which get incorporated in the calcium carbide. When such carbide is treated with water, these elements cause very rapid evolution of acetylene gas in the form of dense brown carbonaceous dust that tends to clog the gas jet. MgO will also tend to increase the melting temperature of the bath (MgO fuses at $2000\text{-}2300^0$ C). Fe_2O_3, if present in the charge, it will be reduced to metallic iron by the carbon at the furnace temperature and go into the carbide product besides using up part of the available carbon. The Indian industries specify maximum limits of these constituents as 2% total SiO_2, 1% Al_2O_3, 1.75% MgO and 0.5% Fe_2O_3.

Phosphorus, when carried into calcium carbide leads to contamination of acetylene gas causing explosion. Arsenic also causes explosion. Sulphur if carried to the carbide, affects the purity of the acetylene gas and produces SO_2 gas. This SO_2 gas in the carbide lamp will not only give out offensive smell but also be injurious to health. It may even get into the welded metal during gas welding.

For the lime, the Indian industries specify a minimum of 92% CaO, and the maximum limits of the deleterious constituents as 2% total SiO_2, 1% Al_2O_3, 1.75% MgO and 0.5% Fe_2O_3. The BIS has not recommended any specification for the lime, but, in 1978, it has recommended the specifications of limestone intended for manufacturing calcium carbide, as containing 54% (min) CaO, 0.8% (max) MgO, 1% (max) SiO_2 and 0.25% (max) Fe_2O_3, 0.5% (max) Al_2O_3+Fe_2O_3, 0.01% (max) P and 0.1% (max) S.

6. Bleaching powder: Bleaching powder [CaO(OCl)Cl], as the name suggests, is white coloured powder. It is used for whitening stains, purifying drinking water and also as a deodorant. In purification it is useful both in killing bacteria by the chlorine and in coagulating suspended impurities and settling down. For making it, chlorine gas is passed through slaked lime [$Ca(OH)_2$].

Specifications: Most objectionable constituents are Fe_2O_3 and Mn_2O_3, both of which have colouring effect. SiO_2 affects smoothness of the fine powder. When bleaching powder is applied to water for its purification, argillaceous matter (Al_2O_3 and SiO_2), being in colloidal suspension impedes settling of bleaching powder and (along with it) of the suspended impurities. Hence both Al_2O_3 and SiO_2 are undesirable. MgO has strong affinity for chlorine and forms deliquescent chloride making the bleaching powder pasty. Otherwise also, MgO is hygroscopic, and it absorbs 120% of its volume of water making the bleaching powder also hygroscopic and affecting its shelf life.

For the lime, the Indian industries specify a minimum of 95% CaO, and the maximum limits of the deleterious constituents as 2% total SiO_2, 2% MgO and 0.3% Fe_2O_3. The BIS has not recommended any specification for the lime, but, in 1978, it has recommended the specifications of limestone intended for manufacturing bleaching powder, as containing 54% (min) CaO, 2% (max) MgO, 0.75% (max) SiO_2 and 0.15% (max) Fe_2O_3, 0.06% (max) Mn_2O_3.

7. Textile: Slaked lime [$Ca(OH)_2$] is used for: (i) boiling, bleaching, softening and smoothening of the vegetable fibers (somewhat similar to the steam process of paper manufacturing, see also 'paper' above), and (ii) lining the inside wall of the vessel in order to prevent the vegetable fibers from getting contaminated and damaged by any iron powder.

Specifications: MgO is objectionable because it slows down the slakability of lime (MgO absorbs 120% of its weight of water and formation of $Mg(OH)_2$ is much slower than that of $Ca(OH)_2$). Free silica is considered deleterious because its sharp edges may cut the fibers. SiO_2 and Al_2O_3 in the form of clay is remains in colloidal suspension in the water and get into the vegetable matter. Fe_2O_3 has colouring effect and hence not desirable.

The Indian industries specify lime containing a minimum of 91% CaO and maximum of 6% MgO, 5% SiO_2 and 4% Fe_2O_3+Al_2O_3.

8. Water and sewage treatment:- In these applications, lime and slaked lime are generally used. Nowadays, lime powders generated as wastes from iron and steel industries are also being used.

When water is dissolved bicarbonates of calcium and magnesium, it is called "*hard water*". Excess lime added to this water converts the soluble bicarbonates to insoluble carbonates which settle at the bottom. Thus the hard water becomes "*soft water*". Besides, lime added to water increases its pH and a high pH level is more conducive to the action of chlorine which kills 99% of bacteria and viruses in 3-10 hours (cf., action of bleaching powder added alone).

In the case of sewage containing $FeSO_4$ and phosphorus, added slaked lime reacts with $FeSO_4$ to form a sludge rich in phosphorus, which can be used as a fertilizer.

Lime added to water and sewage with suspended impurities slakes to a colloidal suspension of $Ca(OH)_2$ which coagulates the suspended impurities and helps to settle them.

9. Soil reclamation: Applying lime to soil for this purpose is one of the oldest practices in agriculture. Its function is fivefold:

(a) If the soil is clayey, then lime makes it friable and porous by absorbing excess water;
(b) If the soil is loose sandy, then lime makes it compact by chemically bonding with water and sand, and enables the soil to hold moisture during dry season;
(c) Lime accelerates decomposition of organic and inorganic substances releasing plant nutrients;
(d) It controls pest and plant disease;
(e) It neutralizes acidity.

10. Soil and asphalt stabilization: Addition of lime to soil reduces its moisture and makes it strong, well bonded, compact and resistant to shrinkage/expansion with variation of water content. Addition of 1-2% of slaked lime to asphalt prevents its later cracking due to contraction on cooling, because the small particles of slaked lime, by virtue of their high dispersion, fills up the gaps.

11. Sealant: Sealants are organic substances soft enough to pour or extrude and capable of subsequent hardening to form a permanent bond with the sealed object. In certain high-tech sealants, neither limestone nor lime, but one of the products manufactured from lime, namely, precipitated calcium carbonate or PCC, is used as an additive by virtue of its ultra-fine particle size and water-resistance. PCC powders can efficiently and uniformly disperse in the matrix. Generally, PCC is treated with stearate, moisture-cured silicone or moisture-cured polyurethane to form a rubber-like substance which can elongate without breaking and resist slump or heavy fall without cracking. A sealant thus made is gunned or pored into place and cured through the action of atmospheric moisture. After curing, the sealant becomes tough and weather-resistant that is capable of repeated stretching and flexing.

With regard to specifications of the PCC, it must contain very low moisture not exceeding o.2%, because otherwise it will begin to cure before its application.

12. Mineral wool: *Mineral wool* is a general term meaning fibers made from inorganic substances that may include minerals, rocks and metal oxides — synthetic or natural. Both lime and the lime-rich iron and steel furnace slags (35-55% CaO) can be made into a fibrous netlike substance by blasting steam or air through the molten lime or molten slag and cooling. Alternatively, the molten mass is subjected to high-speed spinning on wheels. Both are types of mineral wool because they contain metal oxide — CaO. In the former case the product is called *lime wool* while in the latter case it is called *slag wool*. The wool is a mass of fine interwined fibers the diameters of which can be as low as 6-10 nanometres. Sometimes, a resinous binder (e.g., phenol formaldehyde) is added to strengthen the wool and oil may also be added during processing to prevent dust formation. These wools can be used for heat and sound insulation, for filtering, in brake pads, in gaskets and in fireproofing systems. Because these wools can retain water, they are nowadays used in hydroponics (growing plants on only water and without soil).

C. Miscellaneous uses:

(a) Fillers: Limestone or chalk powder is used as an adhesive where off-white colour is permissible, as in insecticide (as a carrier) and in putty (due to high oil absorption).
(b) Calcium metal: It is an emerging alloy metal. It is isolated by electrolysis of molten $CaCl_2$. The currently important uses are in alloys, nuclear reactor, lead-calcium battery, vacuum tubes and vanadium metal recovery; it is also a micronutrient.
(c) Limelight illumination: Hard, lumpy quick lime; when heated to a high temperature, it glows with brilliant white incandescence.
(d) Lime painting : Rock paintings using, inter alia, lime-based white colour discovered in Mirzaput district, Uttar Pradesh, India and believed to be 8,000 years old, suggest how old this use of lime is. Now, also, it is a popular substance for white washing of walls.
(e) Chewing with betel leaves: Very common in some countries including India.
(f) Abrasives: Limestone powder used for polishing delicate surfaces.
(g) Road material: Hard and compact limestone pebbles are used as a base below tar – particularly if locally available, on account of good bonding of limestone with tar.
(h) Food preservation: Lime can repel pests.
(i) Medicine
(j) Desulphurization of waste flue gas: Hot sulphur trioxide trapped by limestone dust which is converted partly to CaO by the heat and the CaO combines with SO_3 (technology developed in Finland).
(k) Writing chalk

(l) Calcium silicate: It is made by the reaction between calcium chloride and sodium silicate in solution, and the filtering, drying and grinding the precipitate. It is used as a filler in rubber whenever hardness, stiffness, abrasion resistance and tear resistance are required. It can also be used as an additive to salt with a view to reducing the latter's stickiness and making it free-flowing (see also the chapter on rock salt).

SUBSTITUTION

The largest consumption of limestone is in the manufacture of ordinary portland cement (OPC), and efforts are being continuously made to substitute part of the limestone by other cheap materials – generally wastes from other industries having pozzolanic properties. True "*pozzolana*" is a fine, sandy volcanic ash and "*pozzolan*" is an acidic alumino-siliceous material (also see the chapter on pozzolanic clay). It reacts with calcium hydroxide in the presence of water to form calcium silico-aluminium hydrate compounds (C-S-H) which is a compact substance with low porosity and having cement-like properties at room temperature. Further, due to the acidic nature of pozzolan, the C-S-H produced from it is resistant to corrosion by sulphates and it is also resistant to water leakage and spalling due to low porosity.

A. Additive to clinker: The materials with pozzolanic property, commonly used as an additive to clinker and indirectly substituting limestone, are as follows.

1. Fly ash: Fly ash can be used as either partial or complete replacement of limestone clinker and such cement is called *pozzolana Portland cement*. Fly ash can be mixed with clinker and then ground. Certain percentage of ash in cement does not alter the properties and suitability of the latter. As per the status in India as in 2004, the usage of fly ash is to the extent of 15-35% of the total raw materials. Fly ash-based roller compacted concrete (RCC), experiments on the technology for which had first started in the world in 1970s, has now gained worldwide acceptance as an alternative to conventional concrete in dams. In India, recently, in the beginning of 2006, the first dam based on this technology, has been constructed in Ghatghar Hydroelectric Project in Maharashtra.
2. Slag cement: Different slags are processed to yield granulated slag, the major use of which in India is in cement making. The granulation has to be done before the slag cools down to a solid mass, because the cold solid slag is very hard and its granulation will be cost-prohibitive. Typical compositions of Indian slags and Portland cements are:

Ingredient	EAF slag (%)	Steel slag (%)	BF slag (%)	Portland cement
CaO	35-40	45-55	35-45	60-65
SiO_2	22-25	15-18	30-40	20-22
Al_2O_3	7-8	2-3	10-15	3-6
Fe_2O_3	3-6	10-20	1-2	2-5
MgO	10-12	5-12	4-10	--

The advantages of mixing slag with the clinker are that it reduces the emission of CO_2, SO_2 and NO_x, and also consumption of power, fuel and labour in mining, crushing and clinkerization. In India, slag can constitute up to 55% of the raw material mix for cement.

3. Paddy Husk: Mixing of 5-10% burnt paddy husk ash clinker has become a common practice.
4. Crushed brick: This is an old practice in some parts of India, where it is called "*surkhi*".

B. Additive to raw mix: Locally available (hence, cheap also) calcareous shale has been tried in Tummalapenta cement plant in Andhra Pradesh, India as an additive to the raw mix itself, partially substituting limestone, laterite and iron ore in one stroke. To correct the deficiencies of silica, alumina and iron oxide, addition of laterite and hematite to the raw mix is a standard practice in cement plants. But this can be done up to a limit, beyond which problems of jamming are encountered in pre-heater cyclones. A locally available calcareous shale having typical composition of 28% CaO, 25% SiO_2, 8% Al_2O_3 and a little Fe_2O_3 has been found to be an answer to this problem. This calcareous shale, being rich in CaO, can substitute a part of limestone also.

Chapter 30

MAGNESITE

Magnesite is the carbonate of magnesium, $MgCO_3$, theoretically containing 47.6% MgO and 52.4% CO_2. In nature, magnesite often transgresses into siderite ($FeCO_3$), and an intermediate mineral called *breunnerite* or *brown spar* containing up to 30% $FeCO_3$ is generally included in commercial magnesite. Breunnerite is mined in Austria, but $FeCO_3$ is a common impurity in many other magnesite deposits. Magnesite occurs in nature as secondary deposits formed due to: (i) alteration of serpentines and dunites, (ii) replacement of dolomite beds by magnesium-bearing solution associated with intrusive rocks, and (iii) vein fillings. In the first type, the magnesite is crypto-crystalline, in the second type it is coarse crystalline and layered (*spathic*), and in the third type it occurs as crystals. In India, the famous deposits belong to the first and second types. The deposits of Chalk Hills of Salem area, Tamil Nadu and of Dodhkanya of Karnataka are alteration products of dunite occurring as networks of veins while those of Almora-Pithoragarh area, Uttarakhand were formed by replacement of dolomite.

HISTORY

The origins of the names magnesite, magnesia and magnesium can be traced to a region in Greece called Magnesia. There was abundance of some white alkaline earth materials, some soft black materials and some magnetic stones. The alchemists of the mediaeval period called the white material *magnesia alba* or *white magnesia*; the soft black material, *magnesia nigra* or *black magnesia* and the magnetic stones, *magnesia lapis* or ‘stones from Magnesia’ (incidentally, the term ‘magnet’ is also after Magnesia where these magnetic materials came from). The black magnesia was later identified to be pyrolusite or MnO_2 and the magnetic stone as magnetite or lodestone, but right since the days of the mediaeval alchemists until the middle of 18th century the identity of the magnesia alba could not be ascertained.

In 1707, M.B. Valentine prepared a white-coloured salt similar to the magnesia alba by calcining the residue left after evaporation of mother liquor that was obtained as a byproduct during preparation of potassium nitrate (KNO_3). But he confused it as lime (CaO). In 1729, Hoffman reacted both magnesia alba and lime separately with sulphuric acid (H_2SO_4) and obtained two types of salts — magnesia alba yielded a bitter salt soluble in water while lime yielded a tasteless salt insoluble in water. But still, he could not come to a conclusion regarding the chemical composition of magnesia alba. It was in 1754 that Joseph Black for the first time definitively described its chemical composition. He calcined magnesia alba and obtained CO_2 gas and a residue of a metallic oxide which he called magnesia (it was referred to it by some as '*Black's magnesia*' which is not to be confused with '*black magnesia*', the archaic term for pyrolusite). He concluded that magnesia alba was in fact a metal carbonate. But the metal magnesium was still unknown.

Subsequently, in 1795, J.C. Delametherie used 'magnesite' as an omnibus name for a series of salts, namely, carbonate, nitrate, sulphate and chloride of the same metal prepared in the laboratory. During the same year, for the first time, a natural occurrence of the same carbonate was discovered in Moravia (then in Austria, but now in Czech Republic). In 1803, C.F. Ludwig called it *talcum carbonatum*. It was in 1808 that D.L.G. Karsten restricted the term magnesite to this natural carbonate. Incidentally, the magnesia alba has by now been confirmed to be a hydrated carbonate of magnesium having a general composition $[xMgCO_3.yMg(OH)_2.zH_2O]$.

Around the same time in 1808, Humphrey Davie, taking cue from '*magnenium*' which was the then prevalent name for what we now call manganese, proposed the name '*magnium*' for the metal in magnesia. But later on the term 'magnesium' was adopted in conformity with the already current terms 'magnesia' and magnesite'.

After the discovery of magnesite in Moravia, other occurrences were discovered in Austria, Greece and Canada. At about the same time, i.e., in the beginning of the 19th century, the Chalk Hills deposits of Salem area in Tamil Nadu, India were discovered. But commercial mining of magnesite began first in Austria, Greece and Canada during the second half of the 19th century. The first discovery of a magnesite deposit in USA was made in 1886 in California where mining started in 1900. Although magnesite deposits of Chalk Hills were discovered in the beginning of the 19th century, it remained forgotten for nearly a hundred years and mining started only in 1902.

Until the outbreak of World WarI (1914-1918), Austria was the leading producer and supplier of magnesite in the world with contributions (albeit insignificant) coming from Greece, USA and India. Calcining technology was first introduced in USA after World War I. Presently, China is the leading country followed by Turkey, Russia, Slovakia, Austria, Australia, South Korea, Spain and Greece which account for over 94% of the total production. The world production which stood at 2.1 million tons in 1937 has increased tenfold to 20.5 million tons in 2001.

Insofar as the growth of magnesite mining industry in India is concerned, it was started in 1902 in Chalk Hills by a company Magnesite Syndicate set up by Henry Turner who is regarded as the founder of basic refractory industry in India. This was followed by opening of the mines in Dodhkanya area in 1921. Later on, several other mines started being operated by other companies in Salem area. The third mining area of Almora-Pithoragarh area was developed much later in the 1970s. The annual productions in India since the start of mining have been as under:

Year	Production
1902-1934	22,000 tons (annual average)
1934-1938	20,200 tons (annual average)
1938-1944	43,600 tons (annual average)
1944-1948	43,700 tons (annual average)
1950	54,000 tons
1960	156,000 tons
1970	354,000 tons
1980	380,000 tons
1990	545,000 tons
Year ending March 2006	351,500 tons

During the initial years after mining commenced in Chalk Hills, wood-fired kilns were used for calcining magnesite (after the run-of-mine is hand-sorted and washed) mainly for export of the product to UK. Later on, another company, Marine Burn House, took over the operations and started dead-burning facilities to manufacture basic refractory bricks for catering to the demands of the nascent steel industry in India. In 1976, this company was taken over by the Government of India and renamed as Burn Standard Co. Ltd., and the operations have been modernized. Meanwhile, several other companies have set up dead-burning facilities in this area.

CRITERIA OF USE

1. Magnesite comprises 47.6% MgO, which is chemically basic.
2. Its specific gravity, depending on the impurities, varies from 2.95-3.20.
3. Magnesite has hardness of 3.0-4.5 on Mohs scale.
4. Magnesite starts losing its CO_2 at 700^0C and, depending on the temperature of calcination, some CO_2 remains in the product. Most of the CO_2 is driven off by heating it at 1560^0C temperature, but the residual product still contains 2-3% CO_2. Due to escape of CO_2 up to 1000^0C it remains porous with the pores cumulatively exposing a large surface area for reactions. Hence, low-calcined magnesite up to this temperature is very reactive and also capable of absorbing both CO_2 and moisture from air. Due to this high reactivity, this low-calcined magnesia is called *caustic magnesia*.
5. The caustic magnesia starts partially fusing at 1560^0C, a process called sintering, and in the range $1700\text{-}1760^0$C, commercial magnesia is converted to periclase (the crystallized form of magnesia) and a dense inert and stable product known as *dead-burnt magnesite (DBM)* or *refractory magnesia* is formed. As a result of dead-burning, the specific gravity increases from less than 3.2 to 3.9. If, however, the magnesia is pure, sintering may take place at higher temperatures up to 2300^0C, as there is no fluxing effect of the impurities.
6. When heated to $2500\text{-}3000^0$C in an electric furnace, the dead-burnt magnesia becomes completely fused and recrystallized, and this white coloured *fused magnesia*

is capable of withstanding very high temperatures and is resistant to very strong bases.

7. Bulk density of fine-sized powder of caustic magnesia is about 2.2 and it is called *light magnesia*.
8. Calcined MgO is a good catalyst.

INTERMEDIATE PRODUCTS

Raw magnesite is used directly for making some of the end products like chemicals and synthetic rubber. In one use, namely fused magnesite refractory, it is used in fused form. But in most of the end-uses, magnesite is used in one of the two main intermediate products namely, caustic magnesia and dead-burnt magnesite or DBM. In all these three intermediate products, magnesite is the raw material, and its specifications are discussed as follows.

1. Caustic magnesia: Caustic Magnesia (low-calcined magnesite) is obtained by calcining raw magnesite in a shaft or rotary kiln between 800-1000^{0}C. However, after manufacturing, the caustic magnesia is generally not subjected to high temperatures during its use.

Caustic magnesia has a number of industrial uses, and consequently, various grades of caustic magnesia with varying porosity (indicated by specific gravity) are manufactured to suit the needs of the consuming industries by varying the temperature of calcination and also the quality of raw magnesite. However, the minimum grade of magnesite specified by the industries is: *40% (min.) MgO, 50% (max.) LOI (includes mainly* CO_2*), 3.5% (max.)* SiO_2*, 0.5% (max.)* Fe_2O_3*, 0.10% (max.)* Al_2O_3*, 3% (max.) CaO and 2.92% specific gravity 2.92.*

At high temperatures, silica reacts with CaO to form beta di-calcium silicate which may undergo rapid inversion to gamma form with considerable expansion resulting in crumbling of the magnesite. If, in addition, alumina is also present, then low-melting calcium alumino-silicate is formed. Hence both silica and alumina are objectionable in both DBM and fused magnesia.

Fe_2O_3 combines with MgO to form magnesium ferrite ($2MgO.Fe_2O_3$) which cements the pores thus lowering the porosity of the caustic magnesia.

Lower the specific gravity in the magnesite is, more it is likely to be porous and more will be porosity and reactivity of the resultant caustic magnesia.

2. DBM: Unlike caustic magnesia, DBM is used only in one class of products namely, refractory. DBM as a refractory is subjected to not only high temperature of over 1550^{0}C, but also repeated heating and cooling (thermal shocks).

Specifications of DBM: Quartz changes to beta-quartz at 574^{0}C, then to beta-tridymite (870^{0}C) and finally to cristobalite (1470^{0}C), these changes being accompanied by volume expansion. Each of these forms have their low-temperature forms, and on cooling, changes to the low-temperature forms take place again accompanied by further volume changes. Thus repeated heating and cooling of the refractories containing silica result in cracks. Moreover, at the temperatures to which the DBM-based refractories are subjected, silica reacts with CaO to form beta di-calcium silicate which may undergo rapid inversion to gamma form with considerable expansion and thus reduce the DBM to dust. If, in addition, alumina is also present, then low-melting calcium alumino-silicate is formed below 1100^0C temperature itself. Besides, alumina forms silicates (kyanite, andalusite or sillimanite) with increase in specific gravity (from 2.7 of silica to 3.2-3.7 of the silicates) and then mullite at temperatures 1200-1600^0C, with disturbance of the eutectics and resultant deformation of texture and weakening of the refractory. Hence both silica and alumina are objectionable in DBM.

Fe_2O_3 is generally considered deleterious because it melts at a relatively lower temperature of 1100^0C. But sometimes, a little of it is desirable in DBM refractories where it is crushed and mould-pressed with the help of some binder. Fe_2O_3 combines with MgO to form magnesium ferrite ($2MgO.Fe_2O_3$) which is a binding agent.

Keeping these factors in view, a set of specifications for DBM is stipulated. Commercial DBM has been classified into 7 grades depending on the grade of the raw magnesite. The highest grade DBM (super-grade) contains over 99% MgO. But the lowest quality accepted by the industries contains *MgO 85% (min), SiO_2 6.5 % (max); Fe_2O_3 + Al_2O_3 5% (max); CaO up to 2.5 per cent.* By and large this specification is in conformity with that stipulated by the Bureau of Indian Standards (BIS) in 1972 and 1977.

Specifications of magnesite for making DBM: For achieving the above grade in the DBM, raw magnesite has to have some specific values for the chemical constituents. Moreover, for making DBM, raw magnesite is sintered at a high temperature of 1700^0C. Therefore, the same constituents namely, SiO_2, Al_2O_3, Fe_2O_3 and CaO are considered deleterious for the same reasons applicable to DBM. The Indian industries specify quality of magnesite for DBM as: *MgO 42.5% (min), up to SiO_2 4 % (but most preferably up to 2.5%); Fe_2O_3 up to 5% (but most preferably up to 2%); Al_2O_3 up to 2%; CaO up to 1.5% (but most preferably up to 1.0%).*

3. Fused magnesia: Fused magnesia is very costly and used in very special cases. The industries specify practically pure magnesite containing above 99% MgO and only nil to trace impurities. In this case, no binder is required and hence there is no need of even a minimum amount of Fe_2O_3 unlike in the case of DBM.

USES AND SPECIFICATIONS

Crude magnesite is not widely used as such. It finds industrial applications mostly in the form of caustic magnesia, dead-burnt magnesite (DBM) and fused magnesia. The chief industrial uses are:

1. Refractory
2. Rubber
3. Paper
4. Cosmetics
5. Electrical insulator
6. Chemical

7. Magnesium metal
8. Sorel (magnesium oxychloride) cement
9. Magnesium oxysulphate cement
10. Fertilizer
11. Animal feedstuff
12. Glass
13. Dust suppression
14. Water purification
15. Glazing
16. Enamel
17. Ceramic welding

These uses as well as some minor ones are discussed as follows.

1. Refractory: Refractory materials are defined as those resistant to heat and having a melting temperature of not less than 1580^0C. The function of refractory lining on a furnace wall is not only to withstand high temperature, but also to withstand temperature fluctuation, and to resist penetration, abrasion and erosion by hot gases and molten materials in the furnace; and over and above, it should not chemically react with those materials. Life of refractory lining is increasingly becoming a critical parameter in the productivity of a furnace and economics of a plant, because each time the lining fails and needs replacement, the furnace has to be shut down. Insofar as use of magnesite in refractories is concerned, except the minor use based on fused magnesia, it is mostly used in the form of DBM—either alone or mixed with some other refractory material. All refractories based on DBM are chemically basic and can be used under conditions of high temperatures ranging up to 1785^0C and their compressive strength may vary from 250-400 kg/cm^2 depending on the type of refractory.

Types of Magnesite Based Refractories

(1) Magnesite refractories

(a) *Dead-burnt magnesite refractory*: These refractories consist of only DBM and are for general purpose. They can be classified into three types:

i. Brick: DBM is first crushed to size ranging from less than 5 micron to 60 micron. Then different size fractions of the particles are mixed in the ratio 45% of 20-60 micron, 10% of 5-20 micron and 45% of less than 5 micron size. After this, by passing the mixture through magnetic separators, iron particles are eliminated from it. Finally, it is mixed with 2-5% of some binder (caustic soda or caustic magnesia) and 4-7% of water, mould-pressed into bricks by applying 16,000 psi pressure and fired at $1600\text{-}1700^0$C. Such bricks are suitable for providing basic refractory lining in open-hearth steel-melting furnace, aluminium and copper alloy melting furnace, cement kiln etc.

ii. Granules: In the industrial circle, these are referred to as *dead-burnt peas* or maintenance grade DBM. Dead-burnt pea magnesite is used for making monolithic hearths and in the ramming mixtures for furnace lining (generally mixed with ground dolomite).

iii. Mortar: This is made of very fine grained DBM of size less than 75 micron (200 mesh), and is used for repairing or fettling of damaged lining.

However, DBM refractories suffer from a tendency to spall under thermal shocks i.e., conditions of repeated heating and cooling.

(b) *Fused magnesia brick*: These are basic refractories capable of withstanding very strong chemical actions and also very high temperatures of above 2500^0C. Calcined magnesia is fused and moulded into shape. No binder is needed. These refractories are very costly to make and is used only in special cases such as electric immersion heaters and resistance heaters for melting metals and alloys.

(2) Tar bonded/impregnated magnesia bricks: To overcome the problem of spalling under thermal shocks, magnesite refractory bricks can be coated or impregnated with tar.

(3) DBM-chromite refractories: More widespread technique to overcome the tendency of spalling is to use a mixture of DBM and chromite. Such refractories have replaced DBM-based refractory bricks in many applications. The following combinations are in usage:

(a) *Magnesite-chrome bricks*: In magnesite-chrome (or mag-chrome) bricks, content of magnesite predominates that of chromite, the minimum MgO and Cr_2O_3 contents being 55% and 6-10% respectively. Generally, MgO-content of 57-76% and a Cr_2O_3-content of 13-15% are maintained by the Indian industries. The bricks may be burnt or unburnt. These are used in EAF, OHF, basic oxygen furnace (BOF), nonferrous metal furnace, rotary cement kiln, glass tank furnace, etc. Those with higher chromite content are used for roof-lining of open hearth steel-making furnaces.

(b) *Chemically bonded Magnesite-chrome bricks*: The composition is similar to that of magnesite-chrome bricks, but in this case a part of the chromite is replaced by some chemical bonding material. Such bricks must not be burnt because otherwise, the chemical may be destroyed. But their possible weakness due to not burning is generally made up by making them steel-clad (i.e., providing a protective covering of steel). The main uses are for roof-making in steel and nonferrous metal furnaces.

(c) *Chrome-magnesite bricks*: In such bricks, chromite predominates (in some bricks the Cr_2O_3 to MgO ratio may be as high as 70:30). The bricks may be burnt or unburnt. These are used in certain parts of electric arc furnace (EAF), open hearth furnace (OHF), glass tank furnace, nonferrous metal smelting furnace, etc.

(d) *Chemically bonded chrome magnesite brick*: These are also chrome-magnesite bricks. But in such bricks, a greater part of the chromite is replaced by some chemical bonding material, reducing its content to 18-22%, while that of magnesite remains at 35-48% level. These are not burnt, lest the chemical may get destroyed. These are preferred to ordinary chrome-magnesite bricks in the EAF, OHF and nonferrous metal industry.

(4) DBM-graphite (or Mag-carb) refractories: Use of mag-chrome refractories, is discouraged in countries like USA, Germany etc. because of environmental reasons (some of the chromites contain hexavalent chromium which is carcinogenic). Hence, they have now largely been replaced by mag-carb bricks containing a mixture of DBM and graphite. It was

first manufactured in USA in 1960s and its popularity picked up with advancements in steel technology such as basic oxygen converter, water-cooled electric arc furnace (EAF) and steel-refining ladle.

In mag-carb bricks, strong resistance of graphite to thermal shocks (due to the combination of high thermal conductivity and low elastic modulus) is combined with the high refractoriness of magnesite. Higher the graphite content, higher will be the number of casts (i.e., the number of heat cycles after which the brick will need replacement) and longer will be the life of bricks. However, too high a graphite content at the cost of magnesite may reduce the refractoriness as graphite is not very refractory (it conducts heat). In basic oxygen converters, the proportion of graphite used generally vary up to 20% (brick life 700-750 casts); in water-cooled EAF, from 15-20% (brick life 500 casts) to 20-25% (brick life 1000 casts) and in ladles, it is around 10% (brick life 50 casts). The water-cooled technology involves transfer of heat from the walls of the furnace to the cooling system, and the heat conductivity of graphite, particularly under enhanced heat conditions, becomes important. In this application, the mag-carb bricks allow the furnaces to be fired at high temperatures in the range of around 2000°C.

2. Synthetic rubber: Natural rubber is a processed natural vegetable gum which is present as tiny droplets in the juice called *latex*. It consists of long chains of interconnected isoprene molecules containing C, CH, CH_2 and CH_3. The normally entangled chains can straighten up when stretched, giving rubber its most important characteristic — elasticity. Synthetic rubber (or *Buna*), on the other hand consists of a mixture of butadiene and styrene approximately in the ratio 75:25. The principle involved in the manufacture of synthetic rubber involves a process of polymerization, i.e., small molecules are added successively to a molecule (monomer) to give rise to a big molecule. In industrial practice, polymerization is allowed to proceed in an emulsion of butadiene and styrene in aqueous medium containing a combination of activators (an emulsion is a dispersion of liquid in another immiscible liquid). After completion of polymerization, the resultant product obtained resembles natural latex, which is coagulated with help of hydrochloric acid and other chemicals.

Magnesite finds use in the chloroprene (or neoprene) type of synthetic rubber in which chlorine replaces the methyl group of the basic monomer. The function of magnesite is twofold as follows.

(a) *Accelerator*: Highly reactive light caustic magnesia in colloidal suspension in the aqueous medium of the emulsion acts as a catalyst to accelerate the process of polymerization. For this purpose, the purer the caustic magnesia is, the better. Further, the grain size should be very fine so as to make a colloidal suspension and to enable the particles to react most efficiently. Since the medium of the emulsion is aqueous, water-soluble matter is not desirable. Further, since the latex is treated with HCl-acid, presence of matter soluble in that acid is also not desirable. Manganese, copper, Al_2O_3, Fe_2O_3, CaO and organic matter interfere with the polymerization process and are objectionable (but after polymerization CaO, organic matter and certain other substances are added to improve workability). Silica is objectionable because it affects grindability of the magnesite.

The Bureau of Indian Standards (BIS) has stipulated in 1980 the quality of caustic magnesia as: 94% (min) MgO, 5% (max) LOI (mainly CO_2), 1% (max) water-soluble matter, 0.5% (max) matter insoluble in HCl, 0.003% (max) Mn, 0.001% Cu, 2% (max) CaO, 1% (max) Al_2O_3 + Fe_2O_3, less than 53 micron (300 mesh) size. The industries, however accept caustic magnesia containing as low as 87% MgO, up to 2.5% CaO and up to 4% SiO_2 + R_2O_3.

(b) *Stiffening agent*: Magnesite is added as filler to increase the stiffness of the rubber. Particle size should be very fine so as to make them light and free-flowing and to facilitate uniform and thorough dispersion in the medium of the molten rubber. Grit is objectionable because it is not amenable to fine grinding easily and it will hinder intimate mixing. Lime is objectionable because it is hygroscopic and will cause crumbling of the rubber product on exposure to air (but chalk i.e., $CaCO_3$ is added during processing of the latex to improve workability of the rubber).

3. Paper: In the sulphite process of paper manufacturing, caustic magnesia is used along with lime and dolomite. By mixing water, CaO is converted to slaked lime or $Ca(OH)_2$ and MgO to $Mg(OH)_2$. Then by passing SO_2 gas, they are converted to $CaHSO_3$ and $MgHSO_3$ which are acidic in nature. They together dissolve all the constituents of wood chips except cellulose, but $MgHSO_3$ being more reactive, more soluble and more stable than $CaHSO_3$, increases the efficiency of the process. With regard to the quality of the caustic magnesia, the Indian industries specify 85-88% MgO, 2.5% LOI and 125 micron (120 mesh) size.

4. Cosmetics: High-purity *light magnesia* is used in cosmetic preparations to neutralize the effect of acid in perspiration which causes irritation of skin and corrosion of fabrics in contact with the skin. Basicity, lightness and free-flowing nature of powdered magnesia are the main criteria. Arsenic and lead are injurious to the human body, and hence are objectionable. CaO has a tendency to generate heat while absorbing moisture (which it does very readily) and is considered undesirable. The Bureau of Indian Standards (BIS) has in 1977, stipulated that caustic magnesia to be used for this purpose should contain *96% (min) MgO, 2% (max) Pb, 2% (max)* As_2O_3 *and 1% (max) CaO*.

5. Electrical insulator: Rutile (TiO_2) and titanates are poor conductors of electricity and possess high dielectric strength which is an indicator of the voltage that an insulating material can withstand before breakdown (cf., titanium has electrical conductivity of 1-3% IACS, or International Annealed Copper Standard, i.e., its conductivity is 1-3% that of copper). Rutile has also the ability to stabilize electric arc by overcoming the tendency to splutter and flicker. Magnesium has weak to moderate electrical conductivity of 12.3-38.6% IACS and zirconium 3.4-4.2% IACS. When magnesium, titanium and zirconium are combined due to firing of a mixture of magnesite, rutile and zirconia (ZrO_2), a truly efficient electrical insulator suitable for use as condensers in radios —magnesium zirconium orthotitanate ($Mg_2TiO_4.ZrTiO_4$), is formed .

6. Chemicals: For manufacturing various chemicals, the magnesium (and hence MgO) of magnesite is directly utilized and so a high content of MgO is imperative. Also, since some of the uses of these chemicals relate to medicines, food and drinks, certain constituents like arsenic that are poisonous are not at all desirable. Besides, certain other constituents like silica, aluminium, copper, zinc and iron either interfere with the chemical reactions involved or are carried into the chemical products affecting their qualities, and hence are considered deleterious. The Bureau of Indian Standards (BIS) has in 1979, stipulated that magnesite to be used for making chemicals should contain *45% (min) MgO, 2% (max)* SiO_2*, 0.3% (max)* Al_2O_3*, 0.4%* Fe_2O_3 *and 1% (max) CaO*. The important magnesite-based chemicals are as follows.

(a) *Epsom salt*: Epsom salt (also called *epsomite*) is hydrated magnesium sulphate having composition $MgSO_4.7H_2O$. It is a bitter-tasting salt soluble in water. Its main uses are medicinal, as bath salt, as laxative and for applying on boils, carbuncles, etc. Originally, Epsom salt was derived from natural spring water at a place called Epsom near Edinburgh in UK. It is prepared by reacting high-purity magnesite with dilute sulphuric acid.

(b) *Magnesium sulphate (anhydrous)*: It is prepared in the same way as Epsom salt except that it has to be dried. But the tendency to form hydrate by absorbing water persists, and hence it is used as a deliquescent salt (drying agent).

(c) *Magnesium chloride*: This is made from caustic magnesia. The highly reactive MgO is first converted to a precipitate of $Mg(OH)_2$ with the help of $Ca(OH)_2$, and then HCl acid is added to yield $MgCl_2$-solution which is dried. $MgCl_2$ is hygroscopic and in excess water, it is soluble. The freezing temperature of its solution in water is lower than 0^0C.

7. Magnesium metal: Magnesite used to be the main source of magnesium metal until 1937, when seawater became more popular. Magnesium metal can be recovered from calcined magnesite by four processes as follows:

(a) *Silico-thermic process:* In this process, a mixture of calcined magnesite and 75%-grade ferrosilicon is briquetted and heated in a retort. The magnesium oxide in the calcined magnesite is reduced by silicon, producing magnesium vapour, which is condensed to crystals of magnesium. The reaction is as follows:

$$3MgO + FeSi \rightarrow 3Mg + FeO.SiO_2$$

These magnesium crystals are melted, refined (by vaporizing and condensing) and formed into ingots. Both Fe_2O_3 and Al_2O_3 are highly objectionable as both combine with silicon to form silicates and consume a portion of the silicon.

(a)Alumino-thermic process: The process is similar to the above except that in lieu of silicon, aluminium is used as the reductant.

(b) Calcium carbide process: Here, the pure carbon of CaC_2 acts as the reductant. A mixture of MgO, CaC_2 and fluorite (CaF_2) is heated. The latter is used as a flux to reduce the temperature of fusion. Alkalis (Na and K) are objectionable because they tend to combine with part of the fluorine of CaF_2 thus adversely affecting the economy of the process.

(c) Electrolytic process: In this process, first $MgCl_2$ is made from magnesite and then the former is fused and electrolyzed. In this process compounds of aluminium, copper, nickel, silicon and zinc are highly objectionable because they are reduced to their respective metals by electrolysis and also by the magnesium formed and pass wholly into the latter. Further, compounds of manganese, iron and boron are also considered deleterious because, although most of these metals get separated and go into the sludge, parts may remain in the magnesium metal.

8. Sorrel cement: Named after a chemist named Sorel who first invented it in 1853, *Sorel cement* (also called *magnesium oxychloride cement*) having molecular formula $[(MgO)_2(MgCl_2)(H_2O)_{11}]$ is a rapidly setting (sets in 3-4 hours to a hard cement). After setting, it becomes light and pleasingly brownish orange in appearance. It can be used in flooring of railway carriages, kitchens and bathrooms, in false roofing, in wall board, in plaster/stucco and in preparation of adhesive composition.

In the manufacture of sorrel cement, highly reactive caustic magnesia formed at 700-1000^0C and containing 2-7% CO_2 is the raw material, which is finely ground to less than 75 micron and then treated with a strong solution of $MgCl_2$.

CaO is undesirable because it being hygroscopic, tends to slake and form $Ca(OH)_2$ and cause cracks in the cement on exposure to moisture. Silica is not generally specified because at the calcination temperature it does not melt although if in a very fine size, some silica may combine with MgO to form $MgSiO_3$. Industries use caustic magnesia containing at least 90% MgO and 2.5% (max) CaO. The Bureau of Indian Standards (BIS) has, in 1962, stipulated the quality of caustic magnesia for this purpose as: 87% (min) MgO, 2% (max) CaO, and 2% (max) CO_2.

9. Magnesium oxysulphate cement: *Magnesium oxysulphate cement* is a quick-drying material (hardens in 10 minutes) and is useful for mending cracks in concrete roadways. It is made by first treating the calcined dolomite with calcium sulphate and water to obtain magnesium sulphate heptahydrate ($MgSO_4.7H_2O$) and then to a 50% concentrated solution of this, sodium hexametaphosphate, MgO and water are added. The $MgSO_4.7H_2O$, MgO and water combine to form a slurry of magnesium oxysulphate ($MgSO_4.5MgO.8H_2O$) or MOS in short. Its properties are similar to those of Sorel cement.

10. Fertilizer: Magnesium is an essential ingredient of chlorophyll ($C_{55}H_{70}MgN_4O_{5\text{-}6}$) and is also good for healthy growth of tomatoes, potatoes, roses. Moreover, it helps formation of healthy bones, manufactureing of proteins, releasing of energy from muscle, regulation of body temperature and slowing down of the aging process of humans. It enters the system of human body from soil through plants and vegetables. For fertilizing soil, magnesium is applied in two forms:

(a) *Caustic magnesia*: It is marketed on the basis of its MgO content. Although caustic magnesia with 95% MgO is preferred, it should have at least 90% MgO. It should be pulverized very finely and the ignition loss, which is an indicator of porosity and reactivity, should be between 3 and 5 percent. Usually magnesia is not added alone in the soil, but is introduced in the soil as a micro-constituent in super phosphates.

(b) *Magnesium sulphate*: High solubility of $MgSO_4$ in water makes it a preferred soil conditioner.

11. Animal Feedstuff: As in the case of humans, magnesium helps in the formation of healthy bones, manufacturing proteins, releasing energy from muscle and regulating body temperature of animals also. For this purpose, it is added to animal feedstuff in the form of caustic magnesia. Caustic magnesia used in animal feedstuff should have MgO content in the range of 80 to 90%. The common impurities (CaO, SiO_2, Al_2O_3 and $Fe_2O_{3)}$ are not considered critical. But, since it is used for direct consumption of animals, magnesia must be free from toxic elements.

12. Glass: Chemically, glass is a mixture of the silicates of sodium, calcium and magnesium. The composition of typical ordinary glass is [$18Na_2O.2MgO.8CaO.72SiO_2$]. Ordinary glass contains 4-5% magnesia and some special glasses (e.g., float glass) may contain up to 15% of it. While in the former case dolomite alone suffices, in the latter case it is supplemented by caustic magnesia.

Essentially, the process of manufacture of glass consists in melting a mixture of 47% silica sand, 14% soda (Na_2CO_3), 12% dolomite ($CaCO_3.MgCO_3$), 3.5% limestone ($CaCO_3$), 2.5% carbon (coke) and the balance broken waste glass (called cullet) at 1400-1500^0 C, and then cooling it first to a thick viscous liquid at 800-900^0 C. After first neutralizing the original colouring substances present in the charge by adding MnO_2, Sb_2O_3, As etc. and then forming it into different desired shapes, colours and types, this thick liquid is rapidly quenched so as to prevent devitification to a solid glass product. The function of the soda, lime and broken glass is to act as fluxes lowering the melting point of silica from 1580^0 C to 1400^0 C. However, lime has a tendency to form crystals and the addition of magnesia helps prevention of this devitrification. At this temperature, MgO does not become inert periclase, and it takes part in the reactions (also see the chapter on silicon).

Float glass is a type of sheet glass that is exceptionally smooth on both surfaces and free from internal stress. For its manufacturing, molten glass at 1100^0 C is discharged from the furnace onto a bed of molten tin, where it floats and spreads out freely in the form of a long strip. Here, the role of excess MgO is to tie up CaO and prevent it from reacting with molten tin.

Colouring substance like Fe_2O_3 is the most objectionable and industries specify its maximum limit in the caustic magnesia at 0.1 percent. MgO-content should be more than 95 percent.

13. Dust suppression: Use of $MgCl_2$ for suppressing dust of unpaved graveled road is an established practice. A preparation containing 28% $MgCl_2$ and 72% water is sprayed on the road. $MgCl_2$ being hygroscopic, not only holds the water but also absorbs more and the solution forms a layer on the gravels and binds them.

14. Water purification: Caustic magnesia has been claimed to be an efficient remover of cadmium (a divalent metal) from water. Cadmium is removed by converting it to its carbonate (*otavite*) and the higher the pH of the water, the more efficient is this conversion. In the conventional process, calcite is added to water to form $Ca(OH)_2$ which increases the pH to around 6-7, and the conversion is very slow. Sulphate reduction process with organic matter is still slower. As a result, these processes are not very suitable for treating large volumes of flowing water. In the process involving addition of caustic magnesia, $Mg(OH)_2$ is formed which increases the pH to more than 8.5. At this pH, the conversion of cadmium to otavite is fast and efficient, and consequently, it is suitable for large volumes of flowing water.

15. Glazing: The purpose of glazing is to provide a uniform firmly adhering coating on the surface of the ceramic body concealing defects such as pinholes, bubbles, etc. The glaze is made predominantly of quartz and feldspar. The ingredients are mixed, finely ground and mixed with water, and this mixture is the glaze. The moulded raw body of the product is dipped into the glaze and then fired to a temperature of about 1400^0 C. If, however, a strong dense refractory coating is required as on heat-resistant boards, then caustic magnesia is also incorporated in the mix, and the firing is done at a higher temperature of 1700^{0}C. The magnesia will fuse and recrystallize into dense inert refractory periclase. Colouring substance like Fe_2O_3 is the most objectionable and industries specify its maximum limit in the caustic magnesia at 0.1 percent.

16. Enamel: Chemically, enamel is a complex mixture of silicates, borates and fluorides of some metals like sodium, potassium, etc. It is a glaze coating on metallic surfaces so as to give protection to the latter against high temperature and corrosion. It is prepared by mixing borax ($Na_2B_4O_7.10H_2O$), quartz, fluorspar, soda (Na_2CO_3), sodium nitrate, oxides of cobalt, manganese and nickel and an opacifier substance (e.g., tin oxide, titanium silicate, antimony trioxide). The mixture is finely ground to powder and made into a slurry with water. This is called *"enamel slip"*. Metallic objects are dipped in it and fired to about 900^0 C. Two to three of such enamel coats are usually applied. Caustic magnesia is sometimes used as an inorganic heat-resistant base coating. Colouring substance like Fe_2O_3 is the most objectionable and industries specify its maximum limit in the caustic magnesia at 0.1 percent.

17. Ceramic welding: In ceramic welding, a mixture of oxidized gas and powders of some refractory substance and fuel is projected on the ceramic joint to be welded. The fuel burns fusing (or at least softening) the refractory powder as a result of which a cohesive refractory mass is built up on the welded surface. Caustic magnesia either alone or in conjunction with Al_2O_3 and Cr_2O_3 is used as the refractory material.

18. Other uses:

(a) *Asbestos products*: Caustic magnesia is often added to anthophyllite and actinolite to make hard setting compositions for lagging boilers and steam pipes and for acid filtration. It should be in the powdered form and should have 95% MgO.

(b) *Abrasive*: Finely ground caustic magnesia can be used as an abrasive due to its hardness (harder than magnesite which has hardness 3.0-4.5 on Mohs scale). Here, high purity is not required and silica is also not very objectionable. Industries specify caustic magnesia containing 85% MgO and up to 7% SiO_2.

(c) *De-icing*: $MgCl_2$ is used as a de-icing agent for paved roads on account of its lower freezing temperature than that of water. Its advantage lies in its ability to go into solution in the water as ice melts as a result of which it gets washed away with the water after de-icing.

(d) *Agriculture*: Caustic magnesia powder can be sprinkled on plants to protect them against acid rain. Basicity of MgO is the criterion.

(e) *Diet coke*: $MgSO_4$ is used as an additive to *diet coke* (magnesium ions are responsible for its typical sour taste).

(f) *Oil purification*: Porous bed of caustic magnesia can be used for filtering oil.

(g) *Electrode*: Magnesite powder (45% MgO and 2-3% SiO_2) is sometimes added to the coating mixture for stiffening.

(h) *Magnesium diboride*: MgB_2 is a potential superconductor material.

WASTE UTILIZATION

1. Low grade rejects: Low grade magnesite containing less than 45% MgO is mixed with clay to make tiles and mosaic chips.

2. Dunite Dunite is an igneous rock made up entirely of olivine ($Mg_2Fe_2SiO_4$) and its partial alteration product serpentine ($H_4Mg_3Si_2O_9$). In some vein deposits, magnesite was formed due to complete alteration of the olivine/serpentine of dunite. In such deposits, dunite constitutes the host rock of magnesite (e.g., Chalk Hills of Salem area, Tamil Nadu and of Dodhkanya of Karnataka in India), and it is generated as waste after mining and sorting of magnesite. Now, dunite is high in magnesia—typically containing 30-45% MgO. In USA, dunite has been used, to a limited extent, in refractories. Besides, its suitability as a fluxing material in pig iron manufacturing is being seriously explored. Some of the dunites can reportedly be incorporated as a component in the sinter feed. (Also see the chapter 'Rocks—Other Uses')

SUBSTITUTION

1. Seawater : Seawater, which contains 0.2 % MgO or 1.3 gm per litre magnesium metal, has been the major source of magnesia and magnesium since 1937 when, for the first time magnesia was extracted from it in UK, and thereafter, during World War II (1939-1945), its use received an impetus, virtually replacing magnesite. The magnesia obtained from seawater is practically pure.

(a) *Magnesium chloride and metal*: $Mg(OH)_2$ is first precipitated by mixing sea water with $Ca(OH)_2$ and using a seed. Then this $Mg(OH)_2$ is treated with HCl acid by which a 15% $MgCl_2$ solution is yielded, which is concentrated by drying and electrolyzed to get magnesium.

(b) *Magnesia*: For obtaining MgO, the $Mg(OH)_2$ precipitated as above is calcined. But before that seawater has to get rid of the dissolved CO_2, lest it will react with $Ca(OH)_2$ to form $CaCO_3$ and eventually contaminate the magnesia product. To eliminate CO_2, the sea water is first made acidic by treating it with sulphuric acid and then de-carbonizing. The calcined $Mg(OH)_2$ cake is dried at 1000^0 C to obtain pure magnesia. From this pure magnesia, high-grade high-density low-porosity DBM can be made by sintering at $2000\text{-}2300^0$ C. Industries are producing seawater-based high-grade DBM containing 97.8 to 98.5% MgO, 0.98-1.5% CaO, 0.1% Fe_2O_3 and 0.25 to 0.35% SiO_2 with 2% (max) porosity and 3.45 gm/cc bulk density.

2. Brine: Brine waters from certain lakes like Great Salt Lake and Dead Sea are very rich in $MgCl_2$, and can be directly electrolyzed to obtain magnesium metal. The $MgCl_2$-content of the Dead Sea is about 16 percent.

3. Salt waste: Seawater bitterns—the residual liquor left after extraction of common salt—in USA contain on an average 6.0-8.7% $MgCl_2$ and 4.2-6.1% $MgSO_4$ (those from Michigan wells contain as much as 10% $MgCl_2$). The Central Electro-Chemical Research Institute, Karaikudi, India, after a sustained research starting in 1963, developed a process in 1986 to derive magnesium metal using the waste salt water route as against seawater. Seawater becomes saturated with NaCl at density 25.5^0 $Be^/$ (equivalent to specific gravity 1.2134 at 15^0C). On progressive evaporation the density increases. When it reaches 30^0 $Be^/$

(equivalent to specific gravity 1.2609 at 15^0C), most of the NaCl is precipitated and the wastes become rich in other salts including those of magnesium.

*4. Dolomit :*Dolomite (double carbonate of calcium and magnesium) contains around 22% Mg. On calcination, the CO_2 is driven off leaving a mixture of the oxides of calcium and dolomite. Magnesium metal can be recovered from this calcined dolomite by silico-thermic process. In this process, a mixture of calcined dolomite and 75%-grade ferrosilicon is briquetted and heated in a retort. The magnesium oxide in the calcined dolomite is reduced by silicon, producing dicalcium silicate and magnesium vapour, which is condensed to crystals of 99.8% purity magnesium. The reaction is as follows:

$$2MgO.CaO + FeSi \rightarrow 2Mg + Fe(CaO)_2.SiO_2$$

These magnesium crystals are melted, refined and formed into ingots.

5. Calcium chloride: As a dust-suppressant, $CaCl_2$ which is generally obtained as byproduct from ammonia soda or other processing industries, can be used interchangeably with $MgCl_2$, and use of $CaCl_2$ liquor, for suppressing dust of unpaved graveled road is also an established practice. A preparation containing 78% $CaCl_2$ and 22% water is sprayed on the road. $CaCl_2$ being hygroscopic, not only holds the water but also absorbs more and the solution forms a layer on the gravels and binds them.

6. Spinel: Typical spinel is a practically an infusible mineral having composition $MgAl_2O_4$. It is harder and heavier than magnesite (hardness 8 on Mohs scale and specific gravity 3.5-4.1). It contains 71.8% alumina and 28.2% magnesia, both of which are highly refractory materials individually. Refractory bricks made of spinel are in use in rotary kilns for manufacturing cement by dry process.

Chapter 31

MICA

The name mica owes its origin to the Latin word "micare" meaning "to shine". Mica is a group of minerals all of which are essentially hydrated aluminium silicates, but presence of one or more of other additional elements has given rise to a host of individual mica minerals. Mineralogically, a total of nine minerals has been included under mica as follows:

1. Muscovite or potassium mica [$H_2KAl_3(SiO_4)_3$]
2. Phlogopite or potassium-magnesium mica [$H_2KMg_3Al(SiO_4)_3$]
3. Biotite or potassium-magnesium-iron mica [$H_2K(Mg, Fe)_3Al(SiO_4)_3$]
4. Lepidolite or potassium-lithium mica [$(OH, F)_2KLiAl_2Si_3O_{10}$]
5. Paragonite or sodium mica [$H_2NaAl_3(SiO_4)_3$]
6. Zinnwaldite or lithium-iron mica
7. Lepidomelane or iron mica
8. Fuchsite [$H_2K(Al,Cr)_3(SiO_4)_3$]
9. Vermiculite [alteration product of micas]

In some literature, Roscoelite and fuchsite have been considered as different species under mica. But, according to Dana (A Text Book of Mineralogy, Indian Edition, 1959), they are essentially varieties of muscovite. In Roscoelite, aluminium is partially replaced by vanadium while in fuchsite, chromium is additionally present. However, not all these species are of commercial interest. Only muscovite, phlogopite, lepidolite and vermiculite are commercially significant while biotite and fuchsite have some minor uses. Out of these, lepidolite is used as a source of lithium and is out of the scope of this book (see author's book "Uses of Metals and Metallic Minerals", New Age International, 2007) while vermiculite, being an alteration product of the micas, is nowadays regarded in industry circle more as a separate mineral than as a member of mica group and is dealt with in a separate chapter later in this book. In the present chapter, discussion will, therefore, be confined to only muscovite, phlogopite, biotite and fuchsite.

Muscovite may be found in many rocks like granite, pegmatite, syenite, gneiss, schist and crystalline limestone; but the commercially important muscovite occurs in quartz-rich pegmatite and was formed as primary deposition from magma rich in potash and alumina. Phlogopite occurs in crystalline limestone and dolomite and also in amphibole, pyroxene, serpentine, etc., and was formed due to regional and contact metamorphism. Biotite, which is of minor commercial significance, is a widely occurring mineral found in various igneous and metamorphic rocks like granite, syenite, diorite, gneiss, schist, etc, both as a primary mineral and as an alteration product of hornblende, garnet, talc, etc. However, concentration of recoverable mica in the host rocks has always been erratic and unpredictable. India, USA, Brazil are the leading producers of different types of mica.

MUSCOVITE

History

In ancient times, people understood by mica what is called today muscovite. It was known in India since ancient times. Its Sanskrit equivalent is “Abhra” (meaning cloud) which found mention in ancient Sanskrit literature as a material of divine origin and having magical medicinal properties. Besides medicine, its other ancient uses — mainly by virtue of its sparkle — were for making ornaments, for decoration of potteries, clothes, toys, etc., for painting and as special purpose glass. A number of ancient workings in and around mica-bearing pegmatite and schist rocks has been seen in Koderma region of Jharkhand state. In different parts of the world, clear sheets of muscovite were popular as lamp shades, chimney windows, etc. In Russia, its first recorded use was as window glass and the name muscovite is believed to have come from the popular reference to those types of window glass as “Muscovy glass” (cf., Moscow).

These traditional uses of muscovite continued more or less unchanged till the later part of 19th century when electricity arrived in the industrial scene. It was at that time that the strong electrical insulation property of muscovite was recognized and its splittings became popular as the most efficient insulating material. Manufacture of splittings revolutionalized muscovite industry. Still later, in the 20th century it became a highly sought after material for use in electronics for the same reason. Commensurate with this development, organized mining started. In India, the process of modernization of the old unsystematic mines of Koderma area began in around 1910, and the now-famous mica-mining belt of Bihar-Jharkhand region started taking shape. So far as other mica-mining areas of India are concerned, that of Nellore district, Andhra pradesh commenced—albeit in a small scale—in 1887 and those of Rajasthan in 1904.

For many years, India’s production of sheet mica was mainly export-oriented to serve the industries of USA, UK and Germany (in case of Germany it was till 1938, i.e., prior to the World War II). During the period 1897-1950, India’s total export was about 163,000 tons. According to the published production statistics, its total production of crude muscovite peaked in 1958 (about 32,000 tons) and thereafter has by and large been dwindling reaching 3,860 tons in the year ending March 1990. During the year ending March 2006, the production of crude muscovite in India stood at merely 1,259 tons. The reason was mainly increasing emphasis on built-up products based on splittings, scrap and ground muscovite (these types of mica are abundantly available in USA which is the largest consumer of mica) and consequent decreased demand in the export market for high-quality sheet muscovite for which India was traditionally the leader.

Industrial Classification

Crude muscovite is classified into different types and grades based on source rock, colour (during mining stage itself), presence or absence of stains, thickness, size (in terms of area) and processing undergone after mining. The scheme of classification is as follows:

1. Sheet mica: Crude crystalline mica is mined in the form of what are called "*muscovite books*" which are made up of sheets like leaves of a book. The first level classification is based on colour and is at the mining stage itself:

(1) Ruby : Pinkish buff to brown
(2) Green (also called non-ruby): Yellowish green to green

Although the term green mica is often used, the term non-ruby was standardized by the National Bureau of Standards, USA, and is used by the US Government. Rarely, the term *rum mica* is used for colours falling in the transitional zone between these two classes. Ruby and non-ruby micas differ from each other in respect of, apart from colour, certain other characteristics also. Post-mining, each of these classes of muscovite are further classified into the following commercial types based on thickness, size and processing:

(a) Block mica: Dressed mica of minimum thickness 0.007 inch. It is further subdivided into different grades according to usable area, shape and the dimensions of length and width. From the lowest grade circular shaped block of minimum area 1 square inch, the highest grade can go up to a rectangular shaped block of 100 square inch or more area (at least 12 inches X 8 inches).
(b) Film mica: It is a sheet split from a block mica with minimum thickness 0.0012 inch. Like block mica, it is also further subdivided into different grades according to usable area, shape and the dimensions of length and width. From the lowest grade circular shaped block of minimum area 1 square inch, the highest grade can go up to a rectangular shaped block of 100 square inch or more area (at least 12 inches X 8 inches).
(c) Splittings: These are sheets split from those block and film micas which have less than a 6 square inch area, and their thickness is below 0.0012 inch. Indian splittings generally have 1-3 square inches usable area, but in other countries less than 0.75 square inch area is common. An individual splitting is too thin to be used all by itself, and generally several splittings are joined in the form of *built-up* mica products.

Each of these types of sheet mica can again be classified on the basis of visual defects like spots, cracks, buckles and foreign inclusions, into:

i. Clear mica (hard, uniform coloured, flat and free from all stains and other defects)
ii. Stained mica (further graded depending on the degree of visual defects)

1 Scrap mica: It includes both: (i) the mine scrap, i.e., the sub-standard mica falling below the specifications for sheet mica which is obtained as byproduct during mining of pegmatite, and (ii) the factory scrap derived from factory wastes generated during preparation of sheet mica. This type of mica is generally used in ground form.

2 Flake mica: In contrast to scrap mica, flake mica is not a waste. It is the finely divided mica obtained as primary mineral from schists or as byproduct from feldspar and china clay beneficiation. As in the case of scrap mica, this type of mica is also used in ground form.

3 Ground mica: Ground scrap and flake micas with size ranging from 1 mm to 45 microns (16-325 mesh).

Thus, the best quality and the highest priced muscovite is that which is a rectangular shaped block or film mica of clear ruby type, free from any spot or wrinkle and having at least 12 X 8 square inches usable area.

Processing

1. Sheet mica: For obtaining the better priced sheet mica from the run-of-mine muscovite books, careful preparation – entirely based on human skill and hand labour — is necessary. A rough book is first cleaned of all adhering dirt, fragments of foreign materials like quartz and feldspar and defective mica laminae. Next, this cleaned book is split open into what are called *muscovite slabs* or *untrimmed sheet mica* which are about 1/4 inch thick. Some scrap mica may also be generated during this operation. These slabs are further reduced in thickness to irregularly shaped *dressed muscovite blocks* by trimming with the help of knives in order to remove all flawed portions. At his stage 70-80% of the original book may have become lost as scrap mica and other wastes. After this, processing for recovering various marketable grades of sheet mica is done by visual judgement. The process consists in judging the best fit largest rectangles within the limits of the full-trimmed irregularly shaped blocks and cutting them out. These rectangular block micas of different marketable sizes are then sorted into different grades according to the nature, intensity and extent of stains present. From the block micas, film micas and splitting of specified thicknesses are recovered by carefully separating thinner sheets along cleavage planes.

2. Ground mica: This is a processed product obtained by grinding scrap (both mine scrap and factory scrap) and flake mica. The processes are as follows:

a. *Dry grinding*: Impure mine scrap (not the factory scrap) and flake mica are usually subjected to this method of grinding called micronization. The fineness of grain size achieved by this method is 1 mm-150 micron (16-100 mesh) and the edges of the grains are sharp, jagged and uneven. Also the particles have relatively low aspect ratio (length to width ratio). The process consists in removal of gangue material by water jet, drying and finally grinding in hammer mills.

b. *Wet grinding*: Mainly factory scrap and also some mine scrap which are somewhat pure and relatively free of gangue materials, are subjected to this process. By this method, smooth- and round-edged lustrous flat platelets with size ranging from 100-45 micron (160-325 mesh) and relatively high aspect ratio (length to width ratio) are produced. Because of fineness and flatness of the platelets, there is less likelihood of inclusions of aqueous soluble salts to remain within them. The process consists in first grinding with simultaneous addition of water with the help of wooden rollers in a chaser-mill to form a paste, and then taking the paste in a stream of water to settling vats. There, the gritty particles settle down while the sludge of fine mica particles are carried by the over-flow water to a centrifuge for drying. After initial screening, final screening of the dried mica particle is carried out through silk cloth sieves.

Due to the differences in the size and nature of the grains, dry-ground mica and wet-ground mica have their own exclusive applications.

Criteria of Use

Different sets of criteria (apart from the basic defining characteristics like colour, clarity, shape, size and thickness) determine the uses of different types of muscovite i.e., blocks, films, splittings and ground mica. Some of these criteria are made use of in their preparation itself, while others are critical in their end-use applications. The important criteria are as follows:

1 *Cleavage:* Muscovite has a perfect cleavage. It is due to this cleavage that blocks, films and splittings with extremely smooth surfaces can be easily separated from muscovite books without using tools other than simple knives and, consequently, the cost of their preparation remains low.

2 *Lustre:* It has vitreous to pearly lustre which enables the ground mica particles to sparkle.

3 *Physico-mechanical properties :-* The sheets are flexible and resilient or elastic when bent (modulus of elasticity 25 X 10^6), yet very tough i.e., they can withstand impact force well. It can withstand pressure up to 5700 psi. Tensile strength of a sheet is high, being 37000-43000 psi. Muscovite is moderately hard with values 2-2.25 in Mohs scale. As a result, the sheets are resistant to scratch while the grinding cost of the scraps and flakes is low. Its specific gravity is about 3, and this relatively low specific gravity enables its ground particles to be separated from heavier gangue particle and be carried away by overflow water during wet grinding process.

4 *Electrical properties* - Muscovite has very high dielectric strength of 120-140 KV/cm (i.e., high insulating efficiency) and low dielectric constant of 4-12 indicating weak electrical conductivity (cf., value for air, one of the poor conductors of electricity, is 1) coupled with very high Q-factor resulting in low power factor loss (Q-factor is defined as the ratio of energy stored to energy dissipated; the higher the Q, the lower will be the energy losses). These unique electrical properties are maintained even at a high frequency of 500 MHz.

5 *Resistance to electromagnetic radiation:* Mica can resist microwave radiation.

6 *Optical propertie :-* Sheets of muscovite are transparent to translucent depending on degree of clarity and thickness. Refractive index of pure iron-free muscovite varies from 1.552 to 1.588 (cf., linseed oil 1.48, ordinary glass 1.53). Thus its birefringence is 0.028 (cf., high birefringence 0.272 in case of calcite). It is resistant to ultraviolet rays.

7 *Thermal properties:* Muscovite has a low thermal conductivity (16 X 10^{-4} cal/cm^2/sec/cm/ ^{0}C) and is resistant to thermal shocks on account of changes in

temperature. It can withstand temperatures of up to 600-700^{0}C above which it starts losing its water molecules. It is non-inflammable.

8 *Chemical characteristics:* It is not decomposed by acids, and hence, is resistant to corrosion.

9 *Nature of ground particles:* This nature depends on the process of grinding. Edges of the larger-sized grains (above 150 micron) as obtained by dry grinding process are sharp and uneven while very fine-sized particles (less than 100 micron) obtained by wet process are smooth- and round-edged.

10 *Skill and availability of labour:* This factor is important, particularly in case of block and film mica, because maximum recovery of the largest pieces of the best quality of these types of sheet mica from books depends on the visual judgemental ability and craft of labour. India was a leader in their international market mainly by virtue of cheap labour who had acquired the skill through generations.

Uses and Specifications

Traditional uses of muscovite have given way to a wide array of end-use applications after the advent of electricity and later, electronics, and in this, the USA is the largest consumer, although it is highly deficient in resources of large-sized muscovite books. In fact, the demand pattern in USA, to a very large extent, has influenced the mining and labour-intensive processing industries of India which has been the traditional supplier of block and film micas to USA by virtue of not just natural occurrence of this type of mica, but, more important, its highly skilled labour. However, the very erratic and unpredictable geological mode of occurrence of good-quality large books and consequent inconsistency in their supply has resulted in shifting in the demand in USA away from block and film mica towards products based on small-sized splittings and scrap of which there is abundant supply in that country. More recently, since the early 1980s, miniaturization of mica-based high-tech electronic products have changed the demand substantially from large blocks and films towards small-sized micas. Considered from this angle, now, the splittings and, to a lesser extent, scrap which were earlier regarded as inferior grade micas, have become strong competitors of block and film micas, and this trend of substitution coupled with unscientific mining practices has played a major role in the decline of production of muscovite in India since the 1960s. The traditional and the more modern applications of all the types of muscovite are discussed as follows.

1. Block and film micas

(1) *Capacitors and electronic tubes*: In these products, high quality blocks and films are required, either as single large-area pieces or as composites of two or more blocks or films of smaller surface areas joined by some resin binder. The primary function of these products is to store electricity without conducting it and with minimum loss. Muscovite is preferred for its high dielectric strength and high Q-factor (i.e., low power factor loss), and higher these values are, better will be the performance of the product. So, clear flat blocks and films of ruby muscovite free from any stains and other defects, which have the highest values of these parameters amongst all micas,

are most preferred, particularly if the products are for military use or for heavy electrical machines (e.g., electric motors, generators and transformers). The other important criteria are flexibility (since bending is required in tubes), high resilience and toughness that facilitate working with the sheets and also contributes to durability of the products.

(2) *Household electrical appliances*: Relatively lower-quality and smaller-sized block or film mica find use as insulating sheets in electrical appliances like flat iron, toasters, etc. In such applications, not only high dielectric strength and high Q value, but also resistance to thermal shocks (i.e., repeated heating and cooling) is the most useful and critical property. Since, here, mica is not required to be bent, flexibility is not an important criterion, but toughness is.

(3) *Radio and television tubes*: Here also, as in the case of domestic appliances, muscovite blocks and films are used for their high dielectric strength, high Q value and resistance to thermal shocks. Since the sheets are required to be bent, flexibility is an important criterion apart from toughness.

(4) *Furnace and oven door, petromax and gas lamp chimney*: These are non-electrical applications of clear, defect-free transparent block and film micas. Thermal insulation, toughness, comparable-to-glass refractive index and lightness are the common criteria for all these applications. In addition, resistance to thermal shocks is also important for doors and peepholes of furnaces, ovens and stoves.

(5) *Window glass*: This is an old use of high-quality block and film mica which used to be a fashion in Russia. Pleasing colours of both ruby and non-ruby muscovite, toughness and heat insulating power of mica were the main considerations. Both transparent and translucent varieties were used.

(6) *Silvered mica*: This is made by riveting, clamping and then sintering block/film mica. It finds application in oscillators, filters, transmission circuits, etc.

(7) *Quarter-wave plate for optical instruments*: A wave plate or retarder is an optical device that alters the polarization state of a light wave passing through it by shifting the phase of light wave between two perpendicular polarization components. A typical wave plate is simply a birefringent crystal with a carefully chosen thickness. A quarter wave plate can change polarized light to circular light and vice versa. When plane polarized light passes through this plate, it is split into two components with relative shift of one quarter wave length. This shift causes light wave to propagate in helical fashion. Thus circular polarized light is produced. Clarity coupled with low birefringence of block/film mica makes it suitable for this application in polarizing microscope, in photo-elastic stress/strain benches for modeling stress distribution in bridges and buildings, in helium-neon laser systems, as beam-splitters etc. For this purpose, plates 10-25 mm diameter and thickness around 0.025 mm are used. The exact thickness, however depends on the wave length of light selected. Blue light requires thinner plate than red light.

(8) *Other uses of sheet mica*:

(a) Gauge glasses of high pressure steam boiler (transparency and ability to withstand high pressure)

(b) Diaphragms of oxygen breathing equipments used in underground mines (flat 0.015 inch thick mica)
(c) Marker dials of navigation compasses (nonmagnetic property, mechanical strength and elasticity)
(d) Window covers and goggles for radiation pyrometers and thermal regulators
(e) Diaphragms in microwave transmitters (resistance to microwave radiation)
(f) Insulation wrappers for high tension radar coils
(g) Mica washers in computer
(h) Diaphragm in guided missile
(i) Diaphragm for detecting sound in submarines and aircrafts
(j) Windows for Geiger counters
(k) Insulation for magnetos in internal combustion engines of submarines and airplanes.

2. Splittings

Micanite: Splittings are too small in both thickness and size to be used as single pieces, although they may also possess the electrical and thermal properties like blocks and films. Hence, they are made into built-up mica called *micanite*. To manufacture micanite, first pieces of mica splittings are spread on some binder in slightly overlapping fashion, thus making a large-sized but very thin sheet, and then, these sheets and the binder are arranged in alternate layers, heated and pressed. The product is a large sized irregularly shaped micanite, which can be trimmed and cut to obtain *micanite boards*, *tapes* and *papers*. The original properties of high dielectric strength, high Q value, high thermal shock resistance and toughness are fully retained while, at the same time, allowing practically unlimited latitude in customization of the shape, size and thickness. For this reason, micanite has now replaced block and film micas as insulating medium in electric motors, generators, transformers and practically in any of the applications of block and film mica. Here, the binder is a critical component, because it not only should have ability to bond with mica, but also should possess the electrical and thermal properties of mica. Some resinous binder based on shellac, alkyl or silicone is generally used.

3. Scrap mica

(1) *Reconstituted mica:* In USA, products like *mica paper* has been developed based on abundantly available indigenous factory scrap and, to a lesser extent, mine scrap by using suitable binders. Thus made mica paper is comparable with micanite in respect of electrical, thermal and mechanical properties. The processes employed are as follows:

  (a) A slurry is prepared with a mixture containing large-sized flakes (1 mm and above size with aspect ratio i.e., length to width ratio at least 150), medium-sized flakes (0.25 mm –1.0 mm size) and small-sized flakes (less than 0.25 mm size). It is then spread in the form of a sheet and pressed and heated.
  (b) Scrap mica is ground to less than 1.18 mm (14 mesh) size and mixed with scrap thermoplastic polyester (e.g., poly-ethylene terepthalate or PET) ground to 250 micron (60 mesh) size in 75:1 ratio (may go up to 90:1). The

dry powder mixture is formed into a layer of predetermined thickness, length and width, and then heated 400-500^{0}C temperature under 300-100 psi pressure. The thermoplastic starts softening at 300^{0}C and securely bonds the mica grains to yield reconstituted mica paper of specified dimensions.

(2) *Glass-bonded mica:* In 1900, with a view to finding a way to use the mountains of scrap mica accumulated in Indian mining areas, a chemical engineer named Percy Crosley working for Micalex Corporation Limited of UK, found that when mica scrap and powdered glass were fused at high temperature under high pressure, a new material could be produced with insulation properties. In 1914, Micalex Corporation Limited of UK brand named this material as *mycalex*. In 1943, a technology was developed in USA for moulding micalex in the form of sheets and rods, and their commercial production was started in 1955. It can be used for insulation in electrical equipments.

4. Ground mica

(1) *Roofing material and wall board joint cement*: Ground mica is used in jointing cement for gypsum boards (for filling joints between plaster boards), asphalt roofing and damp proof seals. In this application, 10-12% of dry-ground uneven- and sharp-edged and relatively larger-sized particles are used to reinforce the sand-cement paste. Here, the mica particles get interlocked within the cement matrix forming a strong bond. Heat-insulating property, anti-cracking ability, toughness, acid inertness and light weight are the main criteria.

(2) *Fire protection boards*: Dry-ground mica is added to a mixture of calcium silicate and portland cement in manufacture of low-density fire boards or insulation boards (cf., asbestos cement. see chapter on asbestos). The criteria are moderate specific gravity, resistance to shrinkage, thermal stability at high temperature and strength. As in the case of roofing material, here also the mica particles get interlocked within the cement matrix forming a strong bond. Mica prevents formation of cracks that allow fire to pass through. But for this purpose, MgO-content should be less than 2 percent. MgO is highly hygroscopic and absorbs water to form $Mg(OH)_2$, which on drying gives off the water causing shrinkage.

(3) *Welding rod coating*: The main criteria are high dielectric strength, and platy structure. Relatively inexpensive dry-ground uneven- and sharp-edged larger-sized particles of mica are used in the flux composition for coating rutile electrodes for welding of mild steel. The jagged grains interlock with other grains of the mix and form a uniform coating material. For coating special electrodes, calcined muscovite is used.

(4) *Well drilling*: In both water-based (practice in USA) and oil-based (practice in North Sea) drilling muds, dry-ground uneven- and sharp-edged and relatively larger-sized particles of mica are added to the silica grains in what is called *proppant*. If there are fracture zones in the rocks of a petroleum or natural gas or ground water reservoir, then the rocks tend to cave in and block the wells, adversely affecting the recovery. Proppants are materials which are used for filling up the fracture cavities to prevent closure of the wells and also circulation loss, but without reducing the permeability

of the reservoir rock, so that flow of oil or gas or water can be sustained. For this purpose, haphazardly sized angular grains are specified. The angularity helps the grains to interlock with each other and provide a strong support for the cavities, while the haphazard sizes leave some pores and channels so as to make the fillings permeable. Mica imparts toughness to the composition. Low grade mica of size ranging from coarse (5-12 mm) to medium (1.7-1.0 mm) is used.

(5) Paint:

(a) Oil emulsion paint: An emulsion is a dispersion of liquid in another immiscible liquid. Both dry and wet ground mica are used for different purposes.

   i. Dry ground micronized mica: 10-20% of such mica is loaded into the paint. The relatively larger sized jagged plates of mica align themselves in a planar fashion and serve to impart a mat finish to the coated surface. Besides, due to the uneven boundaries of the plates, they interlock with each other forming a uniform continuous layer that firmly adheres to the coated surface. As a result, the coating becomes resistant to cracking and it inhibits ingress of water with dissolved salts. Also, this adherence combined with toughness of mica makes the coating scrub-resistant. Further, mica serves to improve resistance to chemical attack and ultraviolet light. All these factors together ensure durability of the coating even in applications which are exposed to sun and salty water. Mica is suitable for use in paints for structural steel works and in marine paints.
   ii. Wet ground mica: Emulsions loaded with wet ground ultra-fine flat smooth-surfaced plates of mica are used in small-scale industrial and fire protection paints that are exposed to hazardous environment. Such paints are not used in bulk all at a time, and are required to be stored for use as and when need arises. For this reason, they should have long shelf lives. Presence of aqueous soluble salts tend to shorten the self life, and since there is less likelihood of inclusions of aqueous soluble salts to remain within the ultra-fine flat platelets of wet ground mica, self lives of such emulsion paints are relatively long. In case of the substrate catching fire, the layer of mica serves as an insulating barrier between the fire and oxygen while allowing the volatiles to escape in zigzag paths through the boundaries between the particles. Toughness, resistance to chemical attack, heat endurance and non-inflammability of mica are the main criteria.

In either case, mica gives an aesthetically attractive sparkling effect to the texture of the painted surface by virtue of its pearly to vitreous lustre.

(b) Pearlescent pigment: A pigment is a dry insoluble colouring matter which has to be mixed with a liquid to produce a paint and, besides colouring, they serve various other functions. Due to the combined effect of light transmission, reflectance and interference (due to two light wave systems uniting together at varying phases), a combination of mica and TiO_2 pigments in a paint produces a nacreous effect like that of mother of pearl, which is called *pearlescence*. Pearlescence is produced when light ray passes through specified thickness of a medium of higher refractive index into one of lower refractive index and interference effects are generated at the interface between the two media. In the case of TiO_2-mica paint, the translucent platy mica with lower refractive index of 1.55 is used as a substrate upon which a thin coating of TiO_2 with higher refractive index of 2.40 is laid. For the best effect, the thickness of the TiO_2 coating should be half the wave length of incident light. The thickness of the mica substrate should be less than 500 micron and may be varied to give different intensities of the effect. Thickness of less than 20 micron gives a satin lustre, that of 20-50 micron gives pearly lustre and that of more than 100 micron gives a sparkling effect. The important applications of pearlescent paint are: (i) on automobiles, (ii) as undercoat in household paint, (iii) on roof tiles (used in Japan), (iv) on household plastics, (v) on computer cabinets, and (vi) on PVC sheaths (for metallic effect).

(6) *Wall paper, plaster, stucco*: Here also, the white, smooth, rounded and ultrafine particles obtained by wet grinding process are applied to the surface to give a sparkling effect without modifying its colour while, at the same time, providing strength, anti-cracking property and insulation against heat. Pearly to vitreous lustre, neutral white colour, transparency (by virtue of refractive index that is almost equal to that of ordinary transparent glass), toughness, smooth surface of the platelets (by virtue of which the latter adhere to the surface and resist cracking) and thermal insulating property are the important criteria.

(7) *Filler in rubber, lubricants and greases*: The smooth, rounded and ultrafine particles obtained by wet grinding process are added as a filler mainly for increasing toughness and heat-tolerance. Both these properties assume importance when the rubber is used for manufacture of tires. The smoothness and roundedness of the particle serve to increase the efficiency of the lubricants and greases.

(8) *Thermoplastics and thermo-sets*: Mica improves certain properties of these two types of polymers. Thermoplastics (e.g., polypropylene) are made by injection, extrusion etc. processes and are used in automobiles (headlight surrounds, dashboard components, air conditioner and heater valve casings, bumpers, moulded rear seat backs), in microwave ovens, in dish washers, in fan blades etc., while thermo-sets (e.g., resin-based phenolics such as bakelite type materials) are used in fuse and junction boxes. The beneficial effects of mica are:

   i. It increases tensile and flexural strengths of the polymer by virtue of high strength and elasticity of the plates.
   ii. Its plates resist expansion on heating and shrinkage on cooling by virtue of their heat tolerance and also increases the heat distortion temperature (HDT) by virtue of resistance to thermal shocks.
   iii. Its plates orient themselves in a planar fashion thereby improving impermeability of the polymer to liquids and gases.
   iv. It imparts resistance to ultraviolet light and microwave radiation and also resistance to attacks by chemicals.

v. It increases dielectric strength (particularly important for fuse and junction boxes).

The first two functions together give dimensional stability to the polymer. Wet ground mica is preferred to dry micronized mica because the former has high aspect ratio (length to width ratio), smooth flat platelets which orient themselves along parallel planes and distribute all the above properties uniformly throughout the polymer matrix. Besides the linear orientation of the elongated platelets facilitate unidirectional flow of the thermoplastics during their making by injection or extrusion process. Muscovite coated with silane and organo-silane compounds improve the performance of mica further (silane is silicon tetrahydride (SiH_4) which has the ability to form effective coupling between mica surface and surrounding polymer at elevated temperature, see also the chapter on silicon).

(9) *Fiber glass reinforced plastics*: Fiber glass is glass formed into fine fibers (thinner than human hair) by drawing molten glass through tiny holes. It is resistant to heat and fire. Fiber glass reinforced plastics (FRP) are extremely strong and light, finding application in furniture, car and boat bodies, rail carriage components and many other objects. Silane or silicon tetrahydride (SiH_4) has the tendency to break up into silicon and hydrogen at 420^0 C and this characteristic has made it useful as a silicon coupling agent to bind glass fibers with polymer matrices in fiber-reinforced plastics. In manufacture of such plastics, silane-treated wet ground mica can be added to the plastics to combine the advantages of silane and mica (see also the chapter on silicon).

(10) *Nickel-coated mica*: It has very good ability to shield microwave and other electromagnetic radiation and to reduce electromagnetic interference. It finds application in computer cabinets and microprocessor casings.

(11) *Sealant*: A sealant is an organic substance soft enough to pour or extrude into an opening in an object, and capable of subsequent hardening to form a permanent bond with the object. Wet-ground ultra-fine mica is used as a filler in some sealants to perform certain functions as follows.

a. The fine-sized powder of mica can uniformly disperse throughout the sealant
b. It prevents them from sticking to the container tubes
c. By virtue of their perfect laminated structure and smoothness of the surfaces, the mica particles facilitate the sealant to extrude into the openings.
d. It gives protection to the sealant against ultraviolet light.
e. Due to transparency, mica does not modify the colour of the sealant.
f. Mica imparts strength to the sealant by virtue of its toughness.
g. It imparts thermal endurance and electrical insulation properties to the sealant

(12) *Christmas-tree snow*: The main criterion is pearly to vitreous lustre, particle size (should not be too fine) and the cost. Generally, the comparatively inexpensive dry-ground uneven- and sharp-edged larger-sized particles serve the purpose.

(13) *Other uses of ground mica*:

a. Small quantities of dry ground mica powder is used in cosmetic application.
b. Wet ground mica powder is used for sprinkling over crops and plants to control aphids infestation.
c. Small quantity of ground mica is also used in industries like foundry as coating cores and moulds.
d. In the form of aluminium-mica alloy (coated with Ni or Cu with addition of Mg) is a good solid dry lubricant which can be used in bearings to enable them to tolerate heat of friction.
e. A thin coating of ground mica can be applied under pressure on plywood to make attractive decorative panels that are resistant to boiling water, as well as to acids.
f. Ground mica has been used as an additive to the raw material mix for manufacturing *mica insulation bricks* which are suitable in steel furnace, petroleum refinery, thermal power plant etc.

Substitution

The natural block and film micas have long been substituted by splittings-based micanite which in its turn, has been partially substituted by scrap-based mica paper. But, in 1947, intensive research for developing synthetic substitute of muscovite was started in a few laboratories in USA, some progress has been reported since then. The processes involve:

(1) Manufacturing synthetic mica by internal electrical resistance melting
(2) Synthesis of micas by solid state reactions
(3) Manufacture of synthetic mica dielectrics by hot-pressing and phosphate bonding
(4) Manufacture of synthetic mica ceramics
(5) Manufacture of reconstituted mica based on synthetic mica
(6) Growing synthetic fluorine mica or fluorophlogopite [$KMg_3(AlSi_3O_{10}F_2)$] in the laboratory.

But there is no single substitute in which all the electrical, thermal, optical and mechanical properties of natural mica, particularly block and film micas,—are present. Of these, only the last named one, i.e., fluorophlogopite, comes nearest to muscovite although it is expensive to make. Chemically, fluorophlogopite is essentially like phlogopite except that the (OH) molecule is replaced by F. Large book-like crystals of fluorophlogopite have been grown from chemicals at high temperature by Bridgman-Stockbarger method using platinum crucibles with seeds, and from these books it has been possible to get thin sheets. This synthetic mica has high chemical stability,, transparency, high electrical insulation with dielectric strength 180 KV/cm (c.f., muscovite-120-240 KV/cm), high heat tolerance up to 1100^0C (c.f., muscovite – up to 800^0C, and phlogopite – up to 1000^0C), high flexibility, cleavability and high mechanical strength.

Synthetic mica sheets have been found suitable for a variety of applications like heat-resistant glass in stove windows, glass and paper for certain kinds of capacitor, monochromator for X-ray, water gauges of high pressure boilers, microwave and optics, neutron diffraction, etc. From ground powder of fluorophlogopite, synthetic mica paper has been successfully made.

PHLOGOPITE

Phlogopite is yellowish brown to brownish red coloured mica. Phlogopite invariably contains foreign inclusions and due to regularly arranged inclusions of acicular rutile or tourmaline, it disperses transmitted light in the form of six-rayed stars. These stars can be seen when candle light passes through a thin sheet of phlogopite. the colour and this unique dispersion gives it a fire-like appearance, and because of this, it is also called *amber mica*.

Phlogopite is formed due to regional and contact metamorphism and is most commonly found in crystalline limestone and dolomite and also in serpentine and pyroxene (cf., muscovite in pegmatite). The leading producers are Madagascar and Canada. In India, although there are some sporadic occurrences in Kerala, there is no commercially deposit known.

Like muscovite, phlogopite also shows perfect cleavage enabling thin sheets to be separated with ease, pearly to vitreous lustre, transparency of thin sheets (refractive index 1.54-1.6), toughness and elasticity, while its heat insulating power is even superior to that of muscovite, and it can withstand temperatures of up to 800-1000^{0}C above which it starts losing its water molecules (the corresponding temperature for muscovite is 600^{0}C). However, it has lower dielectric strength and Q-factor and consequently, higher power factor loss than muscovite. Further, due to the presence of inclusions, the splittability of phlogopite is affected and it is not possible to get good quality large-sized blocks and films comparable to muscovite. The thin sheets, as supplied from Madagascar and Canada are in the form of irregular shaped small-sized splittings of not more than 0.0012 inch thick.

Due to its superior thermal insulation ability, phlogopite is preferable to muscovite in heating elements as in electric irons, in military search lights and in aircraft spark plugs. But, because of high power factor loss, it is not used in capacitors. In pearlescent pigment (see ‘paint’ under muscovite), phlogopite can also be used if deep body hue is desirable. Phlogopite can be used as a filler in thermoplastics if its colour is acceptable (see ‘thermoplastics’ under muscovite).

BIOTITE

Biotite is a dark coloured mica containing iron and magnesium and is widely found in igneous and metamorphic rocks like granite, syenite, diorite, gneiss and schist, etc. It generally occurs as scales, both in disseminated form and in the form of massive aggregations, and consequently, it does not yield sheets even though it has perfect cleavage. Biotite is of very minor commercial significance and small quantities of it are ground for use as fillers and coatings.

FUCHSITE

Fuchsite [$H_2K(Al,Cr)_3(SiO_4)_3$] is a variation of muscovite in which part of aluminium has been replaced by chromium imparting a bright green colour to the mica. It is named after the German geologist Fuchs who studied it during 1835-45. Its powder is associated with some mystical power of healing various diseases.

Chapter 32

OCHRE

Ochre is essentially a naturally occurring mixture of haematite (Fe_2O_3), limonite ($2Fe_2O_3.3H_2O$) and clay. Powdered haematite is red while powdered limonite is yellow. So depending on the their relative predominance ochre is classified into two broad types — red ochre and yellow ochre. Red ochre (locally called “Geru mitti” in India) consists of a clay base, permeated by ferric oxide, i.e., haematite, while in yellow ochre (locally called “Rangraj” in India), the clay base is permeated with hydrated ferric oxide, i.e., limonite. The common denominator is its earthiness, natural ultra-fine particle size (less than 4 micron) and softness due to the clay which gives ochre a separate identity (both haematite and limonite as such are hard minerals having Mohs hardness around 5.5 and are unable to yield such ultra-fine particles). In other words, ochre combines in it the properties of clay and the colours of haematite/limonite.

Ochre was known to prehistoric men as long back as 6000 BC. Petroglyphs or rock-paintings of that time have been discovered in rock shelters in some parts Australia, South Africa and India (Uttar Pradesh and Uttarakhand) in which natural colours red, black, white etc. were used. Analyses have revealed that the colours were made by mixing different earthy mineral matter including ochre.

Official statistics of production of ochre in India is available since 1906. During the period 1906-1946, about 230700 tons were produced. The production history since 1947 is as follows.

Year	Production (tons)
1947	11,579
1950	12,178
1960	20,177
1970	39,504
1980	92,938
1990	153,439
Year ending March 2001	390,409
Year ending March 2006	920,600

Bulk of the production comes from Rajasthan, Madhya Pradesh, Karnataka and Andhra Pradesh. The phenomenal increase in production after 2000-2001 is despite the increasing trend of its substitution by synthetic ferric oxide pigment.

CRITERIA OF USE

1 *Colour:* The natural red and yellow pigments by virtue of the haematite/limonite content are the key to most of the uses of ochre.

2 *Particle size:* The size of particles of the clay component in ochre is ultra-fine — less than 4 micron and generally of the order of 2 micron. On account of this, the particles tend to remain in colloidal suspension in water or oil.

3 *Particle structure:* In clay, the clay minerals are in the form of platelets arranged in parallel and separated by micro-pores (it is these micro-pores in which the absorbed water resides). The inter-lamellar pores are filled up with single-molecule layers of water. This inter-lamellar water is higher in viscosity and density than free water.

4 *Specific gravity*- Specific gravity of haematite is 4.9-5.3 and that of limonite, 3.6-4.0. With regard to the clay component, the specific gravity is generally above 1 due to the inter-lamellar water as explained above. On the whole, therefore, ochre is heavier than both water and oil.

5 *Hardness and fracture:* While the clay component is soft, ochre is harder, because the haematite and limonite components impart some degree of hardness to it. Mohs hardness of both haematite and limonite is around 5.5, and the average hardness of ochre, therefore, becomes less than this. The fracture pattern of haematite is subconchoidal with fairly sharp edges.

6 *Opacity:* The wavelengths of red-yellow and blue-ultraviolet colours lie in the opposite end of the visible spectrum. Hence ochre with its strong red/yellow colour is opaque to ultraviolet colour. Further, very finesized particles of clay scatter ultraviolet light. Thus, ochre can shield the ultraviolet rays effectively.

7 *Resistance to weathering:* Weathering is effected by oxidation. Both haematite and limonite are stable end products of oxidation and are saturated with oxygen. Clays are also end products of weathering of rocks. Consequently, ochre is immune to oxidation and weathering.

8 *Solubility:*-All the components are insoluble in both water and oil and so is ochre.

9 *Chemical characteristic*:-Ochre is chemically inert.

USES

1. Colouring matter: Both red and yellow varieties of ochre are natural pigments characterised by their permanence of colour, opacity to ultraviolet light and their covering power. They produce high impervious paint films which resist weathering, give good protection to wooden or metal structure and can be used in either oil or water media.

Insolubility of ochre in both water and oil makes it suitable for use in both water and oil paints (a paint is made of a pigment and an a medium). The ultra-fine particles of clay stained red or yellow by haematite or limonite tend to remain in colloidal suspension in the medium for a long time so as to facilitate painting with the help of a brush — a requisite property for a good paint. But the particles are also heavier than water or oil, and after application on a surface, they settle down. At this stage, the platelet-like molecular structure of the clay particles come into play. These extremely fine-sized platelets provide a large and flattish surface due to which the particles, after settling down, firmly adhere to the coated surface. This gives a sort of permanence to the paint coating. Further, the fine particles stick to each other making a compact and impervious film.

The ability of ochre to shield ultraviolet rays and strong resistance to weathering enable it to be used in open areas. The strong rich colours impart an excellent covering power.

By mixing ochre with kaolin and other pigment materials, a wide variation in colours and shades can be achieved. Red and yellow ochre are extensively used for colouring roofing tiles, concrete and slabs, cement flooring tiles, glass, ceramics, paper etc. Ochre-based colours are also mixed with cement, linoleum, rubber, glasses, enamels, plastic etc. to impart colour and opacity to them. They are traditionally used in some parts of India for decoration of houses and temples. A mixture of red ochre and some starch (e.g., powdered tamarind seed) to serve as glue is a popular material for use as a protective coating on copper and brass utensils in many Indian villages.

With regard to specifications, according to an old standard recommended by the Bureau of Indian Standards (BIS) in 1950, the content of Fe_2O_3 should be at least 70% in red ochre pigment and 35% in yellow ochre pigment; volatile matter 1.0% (max), water-soluble matter 2.0% (max), oil absorption low and CaO 5.0% (max). Volatile matter when escaping can leave holes on the paint coating. Water-soluble matter and oil absorption should be low because the medium in the paint is water or oil. CaO is objectionable because it is hygroscopic and when the painted surface is exposed to atmosphere, it will absorb moisture with volume expansion resulting in cracks on the surface.

2. Polish:- Purified red ochre known as *rouge* is used for polishing plate glass. This red ochre is rich in hard haematite which makes the average hardness of this variety of ochre quite hard. Moreover, the fractured haematite particles with subconchoidal surfaces and sharp edges make this variety of ochre effective as a polishing agent.

Chapter 33

PERLITE

Perlite is an igneous rock. It is a glassy mass of volcanic origin that is chiefly made up of rhyolite with variation towards andesite and that has a relatively high water content. It shows unique concentric fracture lines developed during cooling and contraction of the lava (*perlitic fracture*). On account of this fracture, megascopically, perlite appears as an aggregate of small onion-like nodules each of which looks like a pearl (a pearl is also made up of similar concentric layers). In fact, the name perlite has come from “pearlite” (i.e., “pearlstone”). It is distinguished from other natural glasses by its siliceous composition and chemical water held within the glass structure.

In 2005, Greece was the top producer of perlite with at least one-third world share followed by China, USA, Japan, Russia, Hungary, Mexico and Turkey, reports the British Geological Survey.

All commercial deposits of perlite are of Tertiary age. In India, the known and only commercial deposit is located at Patanvav, in Rajkot district of Gujarat. It is associated with volcanic (basalt) eruption of upper Cretaceous to Eocene age. Perlite occurs here as horizontal bands varying in thickness from few metres to a maximum of 12 metres.

CRITERIA OF USE

1 *Chemical characteristics* Chemically, perlite is inert. Typical analysis of perlite is:

- 70-75% SiO_2
- 12-15% Al_2O_3
- 3-4% Na_2O
- 3-5% K_2O
- 0.5-2.0% Fe_2O_3
- 0.2-0.7% MgO
- 0.5-1.5% CaO
- 3-5% H_2O

Perlite, sometimes, occurs in nature in impure form mixed with non-glassy rhyolite.

2. Megascopic structure: Perlite is nodular.

3. Colour: Perlite is greyish black to jet-black in colour. The colour depends on the amount of water trapped within it, which in turn, depends on the rhyolite (devoid of water) impurity.The more the water, the less will be its reflectivity and the more black the colour. Thus the highest grade perlite is jet-black and the lowest grade is greyish with significant content of rhyolite.

4. Expansion: When perlite is heated to 700–1260°C, it softens. Its body-water vaporizes and part of it escapes through this softened mass, the remaining water getting scattered in the form of bubbles within the perlite. This causes expansion of its grains 7-35 times its original volume depending on the amount of original water and the temperature. The expanded material becomes brilliant snow white, due to a decrease in the volume of water and diffraction of the light incident on the trapped bubbles. A high-temperature expanded and milled to (-) 100 size product of perlite is sold under trade names *Carlita* (Mexican product). When it is milled to still finer sizes of (-) 150 mesh and (-) 325 mesh, it is sold under the name *Dicalite*.

5. Bulk density: The bulk density of unexpanded (raw) perlite is 1100 kg/m^3 (1.1g/cm^3). This value decreases as the same mass of perlite is expanded and its volume increases. Bulk density of expanded perlite may be as low as 30 kg/m^3.

*6. Porosity:*After the escape of water, the expanded perlite becomes a porous mass.

7. Thermal insulation: The air in the pores within the grains of expanded perlite traps heat and thus imparts to the latter thermal insulation capability.

8. Sound insulation: The pores provide zigzag interconnected paths for the air to pass through, thus slowing down the propagation of sound waves and imparting acoustic insulation.

USES AND SPECIFICATIONS

Perlite is a low-priced rock used in three forms as:

1 Crushed (less than 3.4 mm size) perlite rock as it occurs in nature (raw)
2 Expanded Perlite
    (a) Milled (powdered) to sizes ranging from (-) 325 mesh to (-) 100 mesh
    (b) Granules

The key to most of its industrial uses are its high expandability and the related properties of low bulk density and high porosity. The principal uses are:

A. Raw perlite rock

1 Slag granulation
2 Special casting sand

B. Milled expanded perlite
1 Filtration

2 Cleaning absorbent
3 Horticulture and hydroponics
4 Insecticide
5 Building material
6 Portable ice box
7 Chemical containers
8 Refractory materials
9 Foundry
10 Boiler and pipe covering
11 Paint
12 Abrasive

C. Expanded perlite granules

1 Oil well drilling
2 Nuclear fuel element

These uses are discussed as follows.

A. Raw Perlite Rock

1. Slag granulation: Slag is processed to yield granulated slag, the major use of which in India is as a substitute (partial or full depending on the composition of the slag) for clinker in cement making. The granulation has to be done before the slag cools down to a solid mass, because the cold solid slag is very hard and its granulation will be cost-prohibitive. To granulate slag, nodules of raw perlite rock are dispersed in the cooling slag. As the slag cools, it coagulates as granules around these perlite nuclei. The nodular structure of perlite and its chemical inertness are the main criteria. Besides, the chemical composition of slag and perlite vis-à-vis that of ordinary portland cement are quite complementary as shown below:

Ingredient	Typical Indian slag (%)	Typical perlite (%)	Ordinary portland cement (%)
CaO	35-55	0.5-1.5	60-65
SiO_2	15-40	70-75	20-22
Al_2O_3	2-15	12-15	3-6
Fe_2O_3	1-20	0.5-2.0	2-5
MgO	4-12	0.2-0.7	---

2. Special casting sand: By virtue of the high silica-content coupled with inertness, high thermal insulation, crushed raw perlite rock is used as foundry lining. The inter-granular space allows the gases to pass through.

B. Milled expanded perlite

1. Filtration: Ground expanded perlite is used in both pressure and rotary vacuum filters for filtering colloidal liquids such as beer, wine, fruit juice, sugar syrup, citric acid, drugs, vegetable oils, swimming pool water, etc. The porosity, chemical inertness and chemical composition of perlite suit this application.

The milled expanded perlite (Dicalite) for this application should be of sizes ranging from (-) 150 mesh to (-) 325 mesh with bulk density ranging from 180-250 Kg/m^3. Carbonates of calcium and magnesium are objectionable when the diatomite is intended for filtering acidic liquors such as lemon juice that will dissolve them, but not in case of neutral liquors. Clay and organic matter are undesirable because they will be left in the residue blocking the pores and lowering the filtering efficiency. NaCl is objectionable because it will dissolve in the filtrate and contaminate it. Iron oxide may also react with some chemicals to be filtered and contaminate them. Industries specify not more than 6% clay.

2. Cleaning absorbent: Its porosity and consequent absorbent qualities make it useful for cleaning up toxic liquid spills and controlling pollution. It is used for this purpose in oil refineries, garages, etc.

3. Horticulture and hydroponics: Perlite is high in silica — an important ingredient of plant-bodies, with the remainder containing, inter alia, Fe, Ca, Mg and K which are also essential nutrients for plant growth. It has high ability to absorb and hold fluids for the requirement of plants. The silica stimulates self-acquired resistance (SAR) in plants thereby increasing their resistance to disease. Besides, expanded perlite is a lightweight, porous, non-toxic cost effective mineral. The microscopic porous structure of each particle provides effective thermal insulation to plants and root zones, and also makes composts more open to air. All of these unique factors make perlite an efficient and cost-effective horticultural growth promoting medium for all growing applications.

Perlite, by virtue of the absorbed and stored water, can also be used as a growing medium in *hydroponic* gardens (hydroponics is a technique of growing plants without soil, in water containing dissolved nutrients).

Expanded perlite for these kinds of application, is milled to (-) 100 mesh size and should have bulk density of 60-150 Kg/m^3.

4. Insecticide: By virtue of its high porosity, absorbent quality, low bulk density and chemical inertness, expanded perlite can be used as a carrier of insecticide and herbicide chemicals.

5. Building material: Expanded perlite finds major use as lightweight plasters and mortars with thermal and acoustic insulating properties. Its high porosity and absorptive power effect a strong bondage of the mix, and its high silica serves to supplement the sand. It is preferred for application in chimney lining. Due to the brilliant snow-white colour of the expanded perlite, it finds application in roof-decking, wall boards, floor tiles, etc.

In retarded hemihydrate gypsum plaster, gypsum is first partially calcined at 150-180^{0}C to its hemihydrate form ($CaSO_4.1/2\ H_2O$, which is the starting material for making plaster) and ground. But instead of mixing it with water alone, it is mixed with sand, expanded perlite, some retarder and water, and then applied — generally on gypsum-based boards. The role of perlite is to hold the water, to impart thermal and acoustic insulation, render a brilliant snow-white colour and to make the board light.

Expanded perlite for these kinds of applications is milled to (-) 100 mesh size and should have bulk density of 60-150 Kg/m^3.

6. Portable ice-box: Thermal insulation of expanded perlite makes it useful for lining of such boxes.

*7. Chemical containers:*Expanded perlite can be used for safe handling, transportation and storage of cryogenic chemicals like liquid oxygen and nitrogen due to its thermal insulation qualities, absorptive and holding power and chemical inertness. Expanded perlite for these kinds of applications is milled to (-) 100 mesh size and should have bulk density of 60-150 Kg/m^3.

8. Refractory materials: Thermal insulation properties of perlite enable it to be used as the barrier material in some fire resistant safes, and also as an additive to firebrick aggregates. For these kinds of applications, expanded perlite is milled to (-) 100 mesh size and the powder is sprayed with hot asphalt and dried. The expanded milled perlite should have bulk density of 60-150 Kg/m^3.

9. Foundry: Perlite, by virtue of its high thermal insulation efficiency, is used in foundry, especially in ladle topping and in core lining to slow down the cooling rate and thus minimize shrinkage. It also serves the purpose of keeping the cast in molten state in case of delay in pouring.

*10. Boiler and pipe covering:*Perlite, by virtue of its high thermal insulation efficiency, is used in the form of quilted mattresses for covering boilers and pipes. Expanded perlite for these kinds of applications, is milled to (-) 100 mesh size and should have bulk density of 60-150 Kg/m^3.

11. Paint: The main function of perlite is as an extender in wall paints. The properties made use of are chemical inertness, low bulk density, high absorption of liquid (in this case oil) and brilliant snow-white colour. CaO and MgO are considered deleterious because they have a tendency to absorb water and increase in volume thereby producing cracks in the paint film over a period of time. Iron oxide and organic matter have colouring effect and are undesirable.

12. Abrasive: Expanded perlite has been used in some hand soaps and cleaners and also in polishing wheels. The main criteria are its chemical stability, medium hard silica content and inertness.

13. Other uses:

a. In ceramics as a clay additive for reducing weight and for increasing thermal insulation.

b. In plastic as a lightweight filler.
c. As a lightweight porous carrier of fertilizers.

C. Expanded perlite granules

1. Oil well drilling: In rotary core drilling, mud water is pumped through the space between the wall of the hole and the drill rod. It comes out through the outer annulus of the drill. The main function of the mud water is:(i) to cool the drill rod, (ii) to lubricate the drill and (iii) to support and prevent caving of the wall of the bore hole. Depending on the nature of the wall rocks, various materials are added to the mud water for increasing its efficiency for performing these functions, and expanded granular perlite is one of them which is used if the wall rock is pervious. Perlite holds the water and also, by virtue of its low density, it decreases the density of the mud water and reduce the pressure on the wall rock. Both these roles serve to prevent the mud water from seeping into the rocks, thus maintaining its viscosity.

2. Nuclear fuel element: Fuel element is a sort of container or matrix within which the fuel is placed. Fuel element may be of two types – container type and dispersion type. In the container type, the fuel embodied within the container is generally in the form of plates, sheets, bars, billets, rods, tubes and bunches of wires. In the dispersion type of fuel elements, the fuel (uranium metal or compound) is distributed in discrete particles throughout a matrix of metal, glass etc., with which the particles must not chemically react at the operating temperatures. Perlite granules can be a potential material and have been tried. Chemical inertness is the main criteria. Besides, the inter-granular spaces can allow the heat generated inside due to the fission to flow outward while the granules themselves remain unaffected by virtue of thermal insulation property.

Chapter 34

PHOSPHORUS AND ITS MINERALS

Nitrogen, phosphorus and potassium — commonly referred to as NPK — are the trio of ingredients essential for plant life, and phosphorus, along with calcium, is central to life. The word phosphorus comes from the two Greek words — ‘phos’ meaning light and ‘phoros’ meaning ‘to carry’ (Greek *phosphoros* was the ancient name for the planet Venus). Phosphorus occurs in small amounts in practically all kinds of rocks, but, being highly reactive, it is never found as a free element. The commercially significant natural sources of phosphorus are:

1 Bedded deposits of phosphorite occurring as continuous layers with phosphate pellets, grains, organic remains, etc., bound by a cement which may be calcareous, sandy, etc.
2 Kind of excreta of birds called guano which are found in coastal areas, sea islands and caves. The composition of a typical fresh guano was analyzed to be 7.3% nitrogen, 1.5% phosphorus, 60% moisture and 31.2% other substances.
3 Animal bones
4 Nodular phosphorite comprising a wide array of phosphatic material ranging from tiny particles to pebble size, in a matrix of clay, quartz, carbonates, etc.
5 Apatite, which is an igneous mineral occurring as veins in granite.

All these are essentially calcium phosphate [$Ca_3(PO_4)_2$]. Of all these, only apatite , which is the primary source of calcium phosphate, has a definite chemical composition. It is of two types, i.e,. chlor-apatite having a composition $3Ca_3(PO_4)_2.CaCl_2$ and fluor-apatite having a composition of $3Ca_3(PO_4)_2.CaF_2$. Apatite occurs in rocks of all types and ages, but is most common in igneous rocks which contain an average of 0.6% apatite (i.e., 0.1% P). The other main component of rock phosphate is phosphorite. The phosphatic mineral in it is usually a carbonate-fluorapatite though locally francolite, dahllite, wavellite and augelite — all having complex chemical composition — have been reported.

One or more of these together constitute the natural rock called rock phosphate, which is the most important industrial source of phosphate today. In legislation and trade, rock phosphate is usually regarded as a mineral (cf., limestone, coal). Rock phosphate is a widely occurring mineral. The primary source mineral of phosphorus, i.e., apatite is responsible for this widespread deposition. The salts in the fallen leaves form acids. On decaying, the acids dissolve and release phosphorus from the minerals, thus soil gets phosphorus from the minerals, the plants get it back from the soil, animals get it from the plants, the soil gets it back in the form of bones and excreta of the animals and then, these bones and excreta are dissolved and carried into the sea from which phosphorite beds are finally deposited. The amorphous calcium phosphate thus formed from its crystalline forms is also called *bone phosphate of lime (BPL)*. The grade of rock phosphate is expressed in terms of P_2O_5. In order to be economic, a deposit of rock phosphate should contain at least 20% P_2O_5 (i.e., 43.61% BPL). But it does not have a definite chemical composition.

There are various theories about how this deposition took place. The earliest theories, proposed by various authors during the period 1873-1919, attributed the source of phosphate to accumulation of biological remains (e.g., coprolites or a kind of impure calcium phosphate, planktons, fish remains). According to one school represented by Mansfield (1920), Emigh (1958, 1967) and Pevear (1966), the formation of phosphate beds took place by progressive replacement of calcareous oolitic deposits by phosphate present in sea water in dissolved form. Kazakov (1937) and McKelvey et al. (1953) have put forth the theory that the cold phosphate-rich waters from the deeper levels of the ocean rose to shallower levels by what is known as *oceanic upwelling*, which caused an increase in pH (i.e., increase in alkalinity) accompanied by reduction in the partial pressure of CO_2 and finally, precipitation of phosphate. There are other theories linking phosphate deposition to climate, to submarine volcanism, to algal stromatolites, etc. However, the theory of Kazakov and Mckelvey has found the most widespread acceptance. But it is still a mystery where terrestrial animals got its phosphorus from because phosphorus is much rarer in environment than in life. Research in the University of Arizona in 2004 has pointed towards the possibility that many of the meteorites —, particularly the iron meteorites, might have provided the initial supply of phosphorus. For example, *schreibersite* having the composition iron-nickel-phosphide is rich in phosphorus.

Morocco is the most important producing country followed by China, USA, South Africa, Jordan, Russia and many other countries. So far as India is concerned, low to marginal grade, but still commercially important rock phosphate occurs in Jhamarkotra area of Udaipur district of Rajasthan, Lalitpur area of Uttar Pradesh and Jhabua district of Madhya Pradesh, and vein type deposits of apatite occur in Beldih area of Purulia district in West Bengal and in Kasipatnam area in Andhra Pradesh. Mining is carried out mostly by opencast method and there are only a few underground mines as in USA.

HISTORY

The attractive glow of the element phosphorus led to its discovery by a German alchemist called Hennig Brand in as early as 1669, when he succeeded in isolating it from urine which naturally contains significant amounts of dissolved phosphates. But it took more than 300 years to fully understand the mechanism of the glow. Initially, during the 1680s, it was attributed to consumption of oxygen. By the 19th century, it was found out that the glow does not occur in pure oxygen, and it does so only within a limited range of partial pressure. In the latter part of that century, phosphorus was made commercially for the first time by a process involving treating ground bone with strong acids. In the year 1681, an Englishman named Robert Boyle dipped a splinter of wood treated with sulphur into a mixture of sulphur and phosphorus. The wood splinter caught fire easily. Although it did not immediately catch up with the people, it laid the foundation of the match industry. It was only as recently as in 1974 that R.J. van Zee and A.U. Khan discovered that a slow reaction takes place at the surface of phosphorus forming short-lived molecules of HPO and P_2O_2 both of which emit light.

So far as phosphate rock is concerned, greater part of the phosphate produced in the world is used for manufacturing chemical fertilizers, and the history of use of this mineral is synchronous with that of fertilizers. The primitive men in USA used to bury dead fish under maize fields indicating that they were aware of the relation between bones of dead animals and crop growth. During ancient times, the Chinese used to mix soil with human and animal wastes. Much later, in 1769, the association of phosphorus with bones was scientifically established by a Swedish mineralogist Johan Gottlieb Gahn. The practice of using phosphorus-rich bones and guano (besides nitrogenous farm manure) in agriculture continued till the early 19th century. In 1804, Nicolas de Saussure of Peru demonstrated for the first time the link between plant growth and inorganic chemical compounds containing nitrogen and phosphorus and thus laid the foundation of modern fertilizer industry. In 1835, the guano and nitrate were brought from Peru to England for experimentation. In 1840, Justus von Liebig, the pioneer of the science of agricultural chemistry worked out that treating bones with sulphuric acid makes them easier for plants to assimilate the contained phosphorus. Based on this principle, the first phosphatic fertilizer plant was set up in 1842 in England. By the end of the 19th century, cheap high-calcium high-phosphorus slag from British iron industry became popular for use in agriculture as a source of phosphorus.

The phosphate industry in the USA began in 1867 with production of just two tons of contained P_2O_5 which increased to 457,000 tons in 1900 and to about four million tons in 1953.

The estimates of world production of phosphate rock made by the US Bureau of Mines (USBM) indicate that from 10.48 million tons in 1929 it increased to 25.5 million tons in 1953. By 2000, it has reached 136 million tons.

In India, although geological occurrences of apatite and rock phosphate were known and there was enough awareness about the importance of phosphorus in agriculture and also about the serious state of phosphorus deficiency in the soil over a large area—in the Indo-Gangetic plains, in the coastal areas and in the deltaic tracts) there was no serious thinking in terms of large scale mining and beneficiating whatever low grade deposits nature has endowed, till 1953. In that year a report of the Indian Council of Agricultural Crops brought the matter into focus. Prior to that year bones crushed in the form of meal, called *bone meal*, was the main source of phosphorus and large quantities of it even used to be exported, and only apatite was being mined erratically, the quantities mined between 1947 and 1952 varying from 423 tons to 3,074 tons. The production of apatite peaked at 38,000 tons only once in 1976, declining to about 12,000 tons in the year ending March 2002 and to 9000 tons in that ending March 2006. The real impetus, however, came in 1965 when for the first time rock phosphate mining started with a production of 7,000 tons. This maintained by and large an increasing trend reaching 656,000 tons in the year ending March 2002 and to 1.37 million tons in that ending March 2006. However the largest of the deposits, namely, Jhamarkotra in Rajasthan being dolomitic and calcareous in nature, the problem of beneficiation for manufacturing chemical fertilizer (otherwise it can be used for direct application to soil) continued. Some breakthrough was achieved in 1981 when a technology was developed by the Indian Bureau of Mines (IBM) on laboratory and pilot plant scales. Based essentially on this technology, a commercial plant of 421,000 tons capacity has been set up.

VARIETIES OF PHOSPHORUS

There are three allotropic forms of phosphorus, white or yellow, red and black, out of which the yellow and the red ones are useful and more commonly talked about. Each molecule of all the varieties contain four atoms. These atoms in both the yellow and the red varieties are arranged in somewhat unstable tetrahedral structure, but the manners of arrangement are different, relatively more stable in the latter. In the black phosphorus molecules, the atoms are in very stable orthorhombic structure and hence it is practically non-reactive with air, producing no glow. The three basic varieties differ in specific gravity—1.82 for the yellow, 2.34 for the red and 2.69 for the black ones. Besides, there are differences in certain other properties of yellow and red varieties which determine their industrial uses (the black phosphorus has no commercial utility as yet). Some authors have mentioned about a fourth variety, namely, violet phosphorus, but according to others, the colour of violet variety is actually due to mixing of black and red colours.

PROCESSING OF PHOSPHATE

The beneficiation techniques depend upon the nature of objectionable impurities in them. There are three distinct types of rock phosphate — siliceous, calcareous/dolomitic and ferruginous. The beneficiation processes for these are described as follows.

(a) *Siliceous rock phosphate*: Natural rock phosphate mined from most of the deposits across the world, invariably contains 70-90% of sand and clay. Amongst the Indian deposits, the Maton deposit of Rajasthan containing 22-28% P_2O_5 and 20-40% SiO_2, falls in this class. After mining, the rock is deposited in a pit, thoroughly mixed with enough water so as to get a slurry which is processed by washing, spinning, crushing and screening. As a result, the coarse phosphate grains and pebbles (1/32-3/4 inch) are separated from the remaining mixture containing fine phosphate particles, sand and clay suspended in water. The coarse phosphate fraction is sent for manufacturing fertilizer. The other fraction containing a mixture of water, sand, clay and fine particles of phosphate are fed into a flotation cell where reagents are added so that the phosphate particles float and the other substances sink. In case of Maton deposit, the phosphate has been upgraded to 35% P_2O_5 and 8% SiO_2 with a recovery of over 90 per cent.

(b) *Calcareous/dolomitic rock phosphate*: This type of rock phosphate deposits containing 13-20% P_2O_5 with calcite and dolomite as the predominant gangue minerals (around 41% CaO and 9-10% MgO), is exemplified by Jhamarkotra deposit of Rajasthan and Mussorie area of Uttarakhand in India. A beneficiation technique developed by the Indian Bureau of Mines (IBM) in 1970-1971 involved initial heating of the rock to about 1000^0C for decomposition of the carbonates and then attrition scrubbing and classification. But this process turned out to be expensive due to high cost of oil and poor recovery. Later, during 1980-1981, the IBM has developed a technique adopting a straight flotation route which involves use of two reagents for selective depression of phosphorite and flotation of calcite. By this technique, rock phosphate containing as low as 13.19% P_2O_5 could be upgraded to a concentrate containing as high as 35.1% P_2O_5 with 82.7% recovery.

(c) *Ferruginous rock phosphate*: This type is best exemplified by Jhabua deposit of Madhya Pradesh in India. A typical analysis shows 27.2% P_2O_5 and 18% Fe_2O_3. By adopting a flotation route, a concentrate containing 37.2% P_2O_5 with 59.5% recovery could be produced.

The developments of the beneficiation techniques has made it possible now to utilize many so-called useless rock phosphate deposits for various industrial purposes. However, attempts to beneficiate apatite has not met with encouraging results because, first, it is harder than weathered or even fresh rock phosphate (hardness of apatite is 5 on Mohs scale) which makes the grinding cost high, and secondly the apatite of Beldih mine in India contains magnetite as a trace element in the crystal lattices which have not been found amenable to liberation.

CRITERIA OF USE

A. Elemental Phosphorus

1 *Red phosphorus*: Red phosphorus is relatively more stable and hence relatively less reactive. It boils at 280^0C and also ignites at the same temperature.

2 *Yellow phosphorus*: It is a soft waxy substance. The important properties making it industrially useful are as follows:

(a) Reactivity: Yellow phosphorus is very unstable and highly reactive. It forms a number of organic and inorganic compounds. It has a very strong affinity for oxygen and exhibits a faint glow upon exposure to air (this is the reason it used to be referred to as “morning star”). On heating, it quickly catches fire at a low temperature of only 40^0C, even below its melting point (44.2^0C). Due to this vulnerability to fire hazard, it is kept under water.

(b) Phosphorescence: The spontaneous glow and ignition at ordinary temperature have inspired people to associate phosphorus with phosphorescence. All light comes from atoms. It is produced when an atom has gained energy, by absorbing light from another source or by being heated or by being struck by another atom, and then gives it off. In other words, it is first excited and then it de-excites. Many substances easily gain energy and emit light without being heated very much. They do this through a process called *luminescence*. Atoms of some luminescent materials stay excited for some time before they de-excite and consequently, they glow in the dark long after they have received extra energy. They are called *phosphorescent*, and those emitting light only during their exposure to exciting energy are called *fluorescent*. Some people call the ability of yellow phosphorus to shine in the dark under conditions of mild heat, *chemo-luminescence* (the name phosphorescence was coined first by a 17th century alchemist Vincentinus Casciarolo of Bolgnia, Italy who found a heavy crystalline stone, known later to be barytes with glass at the foot of a volcano and fired it in a charcoal oven intending to convert it to a noble metal. Although he obtained no noble metal, he found the sintered stone emitted red light in the dark after exposure to sunlight. He named this phenomenon *phosphorescence*).

(c) Solubility: It is insoluble in water, but soluble in CS_2.

(d) Poisonous Nature: Yellow phosphorus is extremely poisonous. Upon ingestion, it causes severe liver disease known as *smoking stool syndrome*. Prolonged yellow phosphorus poisoning leads to necrosis of jaw called *phossy jaw*. Its contact with skin can cause severe burns. This is the reason it is always advised to handle yellow phosphorus with forceps. Many of its organic compounds are extremely toxic. In contrast, most of its inorganic compounds are non-toxic.

(e) Nutrient value: In the form of trivalent inorganic phosphate (particularly of calcium), it has great nutrient value and it forms the backbone of DNA and RNA because it connects the genetic bases of these molecules to enable them to form long chains. Its compound adenosine tri-phosphate (ATP) is the fundamental fuel providing energy for growth and movement of living beings, and so it is vital to metabolism. Phosphorus is a part of the bones of vertebrae and also of phospho-lipids that make up cell walls. Further, it plays an important role in root development and in the synthesis of proteins, fats and carbohydrates.

(f) Alloyability: Phosphorus is one of a few nonmetals capable of forming alloys with certain metals.

B. Minerals of Phosphorus

1 *Optical properties and form*: The mineral apatite shows variations in colour and crystalline form. Its different varieties and their colours are:

(a) Asparagus stone — colourless, green, blue, yellow and flesh-red
(b) Moroxite — Greenish blue to bluish
(c) Lasurapalite — Sky blue
(d) Manganapalite — Dark bluish green (contains MnO_2).

With regard to crystal form, it is hexagonal-tripyramidal and the crystals may be long or short prismatic, or tabular. Refractive index varies from 1.63 to 1.648 (cf., ordinary glass 1.53 and diamond 2.42)

1 *Hardness*: Apatite is a medium hard material having hardness 5 in the Mohs scale.

2 *Chemical characteristics*: Content of phosphorus and also of calcium are the key to the uses of both apatite and rock phosphate. So the percentage of bone phosphate of lime (BPL) or $Ca_3(PO_4)_2$ is the yardstick for the nature of its use. This amorphous BPL, unlike crystalline calcium phosphate, is soluble in water and more easily so in acids, and in the process, it breaks down to release phosphorus.

USES AND SPECIFICATIONS

The principal uses of rock phosphate are as follows:

1 Manufacture of phosphoric acid
2 Recovery of elemental phosphorus
3 Fertilizer

  (a) Ordinary or single super phosphate (SSP)
  (b) Triple super phosphate (TSP)
  (c) Mono-ammonium phosphate (MAP)
  (d) di-ammonium phosphate (DAP)
  (e) Ammonium phosphate sulphate (APS)
  (f) Nitro-phosphates (NP)
  (g) Urea ammonium phosphate (UAP)
  (h) NPK fertilizers

4. Direct application to soil
5. Poultry and live stock feed
6. Bone China
7. Gemstones
8. Alloy

These uses along with specifications of the rock phosphate are discussed in details.

1. Phosphoric acid:

(a) Manufacturing process:

(1) Wet process: Rock phosphate or apatite is first ground and then treated with an excess of 33% dilute H_2SO_4 acid to produce a mixture of phosphoric acid and gypsum which is insoluble. The mixture in the form of slurry is filtered so as to remove the gypsum. The chemical reaction involved is:

$$Ca_3(PO_4)_2 + 3H_2SO_4 + 6H_2O \rightarrow 2H_3PO_4 + 3(CaSO_4.2H_2O)$$

or

$$3Ca_3(PO_4)_2.CaF_2+10H_2SO_4+20H_2O \rightarrow 6H_3PO_4+2HF+10(CaSO_4.2H_2O)$$

This process is more common, particularly in India.

(2) Dry process: Phosphate rock is first sintered at 1300^0C. Then the sintered phosphate is fused in an electric furnace along with dry coke and silica. Elemental phosphorus vapour mixed with CO is liberated and collected while calcium silicate is left behind as slag. This mixture is cooled so that only phosphorus vapour liquefies, and not the CO which escapes. The phosphorus is then converted to P_2O_5 by burning which, when dissolved in water, forms phosphoric acid.

(b) *Specifications:*

(1) Wet process: The Bureau of Indian Standards (BIS) has recommended in 1985 a set of specifications for rock phosphate/apatite for manufacturing phosphoric acid by wet process, which is common in India. According to it, the parameters are *P_2O_5: 32% (min); SiO_2: 5% (max); F: 4% (max); CO_2: 3%; Al_2O_3+Fe_2O: 3.5% (max); Moisture: 1.5% (max) ; MgO: 0.5% (max); Cl: 0.05% (max); Organic matter and combined water: 1.5% (max)*. But, before this, in the 1970s, the Government of India constituted a committee under Kasturirangan which surveyed the preferences of the industries and laid down a set of specifications with respect to certain parameters. These two sets of specifications differ from each other very little. All these parameters along with their limits are discussed in the following paragraphs.

Phosphorus is the important constituent in the product and it is analyzed in terms of P_2O_5. So, its content should obviously be as high as possible. Sometimes it is specified in terms of CaO/ P_2O_5, in which case this ratio should be as low as possible. The industries prefer not only a minimum of 32% P_2O_5-content but also a maximum CaO/P_2O_5 ratio 1.5.

Silica should be low, because it increases the grinding cost and its grains may abrade the lining of the reactors and the surfaces of other equipments. Further, silica being resistant to the H_2SO_4 acid, it hinders spreading of the latter throughout the mass of the phosphate thus increasing what is called curing time and slowing down reaction. However, if fluorine is present, then a little silica is desirable. Fluorine by itself is objectionable because it is liberated as HF which is extremely corrosive to the plant equipments. But if both silica and fluorine are present, then HF will react with silica to produce fluoro-silicic acid [H_2SiF_6] as shown below.

$$4HF + SiO_2 \rightarrow SiF_4 + 2H_2O$$
$$3\,SiF_4 + 4H_2O \rightarrow Si(OH)_4 + 2H_2SiF_6$$

Proven material for construction of plant is available to withstand the corrosive action of this fluoro-silicic acid, but on the other hand, the latter is a valuable byproduct. It is used in manufacture of synthetic cryolite by treating it with clay and bauxite, and also for production of sodium silicofluoride and of ammonium-magnesium-zinc fluorosilicates. The industries specify three parameters — SiO_2: 2.5-5.0%, F: 4% (max) and SiO_2/F ratio: 60/76 (this is the ratio in which they can react fully with each other to form H_2SiF_6 without leaving any free fluorine to be emanated as HF which is objectionable). But in that case, the contents of sodium/potassium salts should be nil because otherwise sodium/potassium fluorosilicates will be formed instead of fluoro-silicic acid. These fluorosilicates, precipitating along with gypsum not only interfere with the growth of crystals of the latter, but also affect its purity. Besides, they may form scales on the walls of the equipment.

So far as $CaCO_3$ (which is expressed in terms of CO_2) is concerned, although the escaping CO_2 generated due to reaction between the carbonate and the H_2SO_4 acid, makes the grains of the rock phosphate/apatite porous so as to facilitate availability of larger surface area for more efficient chemical reactivity, the disadvantages of its presence on three counts far outweigh this advantage. First, too high a content will mean a corresponding lowering of the P_2O_5-content. Second, it means a higher consumption of H_2SO_4 acid, a part of which goes into reaction with the calcium to produce some extra gypsum unnecessarily. Third, when the carbonate reacts with the H_2SO_4 acid, CO_2 starts escaping upwards and continues to do so even during the filtration of phosphoric acid from the slurry, and this upward escaping CO_2 not only slows down the downward movement of the acid through the filtration bed but also blocks the pores of the bed.

Fe_2O_3 and Al_2O_3 (together referred to as R_2O_3) consume a part of the P_2O_5 to form Fe- and Al-phosphates which are insoluble. Thus: (i) part of P_2O_5 becomes unavailable for the production of H_3PO_4 and hence wasted; (ii) the Fe- and Al-phosphates being insoluble, remain in the residue along with gypsum on the filter bed, rendering the useful byproduct gypsum relatively impure; and (iii) by precipitating from the solution along with gypsum, they interfere with the growth of the latter's crystals. The industries prefer a maximum of 3% R_2O_3.

MgO is objectionable on two counts. First, it reacts with a part of the H_2SO_4 acidwhich is thus wasted. Second, water is added to the H_2SO_4 acid to maintain some degree of dilution in order to facilitate smooth flow as well as easy filtration of the slurry, and MgO increases the viscosity of the slurry by absorbing this very water. Both the BIS and the industries specify the maximum limit of 0.5% for MgO.

As a result of reaction between chlorides and H_2SO_4 acid, chlorine gas emanates causing corrosion of the plant equipment. While the BIS has specified the maximum limit of 0.05% for chlorine content, the industries' specifications tend to be more stringent, often as low as 150 ppm.

So far as organic matter is concerned, it is considered deleterious on three counts. Firstly, it reacts with a part of the H_2SO_4 acid which is thus wasted. Second, (as in the case of $CaCO_3$) when the carbon reacts with the H_2SO_4 acid, CO_2 starts escaping upwards and continues to do so even during the filtration of phosphoric acid from the slurry, and this upward escaping CO_2 not only slows down the downward movement of the acid through the filtration bed but also blocks the pores of the bed.. Third, the residual organic matter left after this reaction makes the phosphoric acid coloured, which in its turn, will have a colouring effect on the product (triple superphosphate fertilizer) based on it generating consumer resistance. While the BIS has specified the maximum limit of 1.5% for both organic matter and combined water taken together, the industries often specify this limit for organic matter alone.

Moisture present in the raw mineral itself hampers grinding and it also adds to the weight of the mineral, and hence it is considered objectionable by the buyers. Calcium sulphate is not objectionable, because it is insoluble and gets filtered out along with gypsum formed by the action of the H_2SO_4 acid during manufacturing of phosphoric acid.

(2) Dry process: Insofar as the dry process is concerned, relatively lower grade phosphate rock can be used and the specifications are the same as that applicable for manufacturing elemental phosphorus (discussed later) since the process is to a large extent the same, the latter forming an intermediate product.

(c) *Uses*: Phosphoric acid is used for manufacture of some fertilizers like mono- and di-ammonium phosphates and triple superphosphate fertilizers (elaborated later). The other uses based on it are as follows:

(1) Phosphates are utilized in the making of special glasses that are used for sodium lamps.

(2) Based on phosphoric acid, various food grade sodium phosphates like sodium tri-poly-phosphate, sodium pyrophosphate, di-sodium phosphate, tri-sodium phosphate, tetra-sodium pyrophosphate, sodium mono-phosphate, etc. are made. These are used in processing of meat and cheese, in toothpaste, in water softening, etc.

(3) Sodium tri-poly-phosphate (STPP) is used in laundry detergents, but it is banned in several countries. This and other sodium phosphates are also regarded as food grade phosphates.

(4) Phosphoric acid made from elemental phosphorus is used in soda beverages and other soft drinks to give a mild intoxicating feeling. It also serves to prolong their shelf lives by increasing the acidity level (i.e., lowering the pH value).

(5) Sodium tri-poly-phosphate (STPP) have been used extensively in heavy duty industrial detergents. They combine with hardening metals (calcium and magnesium) to form a soluble complex which is removed with the wash water. They also sequester dissolved iron and manganese which can interfere with detergency.

(6) Sodium ammonium hydrogen phosphate [$Na(NH_4).HPO_4.4H_2O$] is a microcosmic salt used in bead tests for metals. When heated to redness, this compound forms sodium hexa-meta-phosphate or *calgon* [$Na_2\{Na_4(PO_3)_6\}$] which is used for preventing scale-formation in boiler tubes, pipes etc.

(7) Phosphoric acid, by virtue of its ability to selectively allow hydrogen protons to pass through while blocking hydrogen electrons and oxygen ions, is used as the electrolyte in *phosphoric acid fuel cell* . The operating temperature of such fuel cells is 150-200^{0}C and output of a single cell can be up to 200 KW (for details about fuel cells, see the chapter on graphite).

2. Recovery of elemental phosphorus:

(a) *Manufacturing process*: Yellow phosphorus is made by electro-thermal process. Phosphate rock is first sintered at 1300^{0}C. Then the sintered phosphate is fused in an electric furnace along with dry coke and silica. Elemental phosphorus vapour mixed with CO is liberated and collected while calcium silicate is left behind as slag. This mixture is cooled so that only phosphorus vapour liquefies (boiling temperature 280^{0}C), and not the CO which escapes. The yellow phosphorus so obtained is refined. To make red phosphorus, the yellow variety is heated to 240^{0}C in an inert atmosphere or it is exposed to sunlight to bring about the required alteration in the arrangement of atoms.

(b) *Specifications*: The Bureau of Indian Standards (BIS) has recommended in 1985 a set of specifications for rock phosphate/apatite for this purpose. According to it, the parameters are *P_2O_5: 30% (min); SiO_2: 10% (max); F: 2% (max); Cl: 0.015% (max); CO_2: 2%; Al_2O_3+Fe_2O: 3% (max); Moisture: 1.5% (max); Organic matter and combined water: 2% (max), MgO: 0.5% (max)*. Industries in India, however, are known to use rocks containing as low as 24% P_2O_5 and as high as 23% SiO_2 with 3% iron and 7% alumina. Phosphorus is the important constituent in the product and it is analyzed in terms of P_2O_5. So, its content should obviously be as high as possible. SiO_2 should not be very objectionable because in any case it is addedto the furnace charge. But excessive silica will react, at the sintering temperature (1300^{0}C), with the calcium of the phosphate rock to form a fused mass of calcium silicate (which goes into the slag), and also will create difficulties in maneuvering the quantity of silica that is to be added to the charge. Fluorine and chlorine are objectionable because both are corrosive to the plant equipments. So far as $CaCO_3$ (which is expressed in terms of CO_2) is concerned, too high a content will mean a corresponding lowering of the P_2O_5-content, and the CaO left after heating at 1300^0C will increase slag volume. Fe_2O_3 and Al_2O_3 (together referred to as R_2O_3) consume a part of the P_2O_5 to form Fe- and Al-phosphates. Both moisture and organic matter will consume energy for heating. MgO is highly refractory and will increase the sintering temperature. Besides, $CaCO_3$, $MgCO_3$ and R_2O_3 are all slag-forming components and therefore should be as low as possible. High content of these slag forming impurities will require excessive SiO_2 resulting in the dilution of P_2O_5 content in the charge. The rock should be hard and compact so that it can directly be charged into the furnace.

(c) Uses:

(1) Match industry: This is the first and the most important use of red phosphorus. It forms an ingredient of the mixture of substances applied on the striking surface of safety matches. The proneness to catch fire easily in air is the main criterion. The heat of friction is enough for it to catch fire. Originally yellow phosphorus was used, but it proved to be hazardous and unsafe to handle due to its low ignition temperature (40^0C). Nowadays, red phosphorus is used which is safer due to its higher ignition temperature (280^0C). Also, the compound phosphorus sesqui-sulphide (P_4S_3) is a component of the mixture forming the heads of strike-anywhere matches.

(2) Chemical and pharmaceutical industry. Phosphorus finds application in the manufacture of its tri-chloride, penta-chloride, penta-sulphide and sesqui-sulphide which in turn are used for making saccharine, sulpha-drugs and vitamins. The chrorides are also used to make various organo-phosphorus compounds which have application in flame-retardants, pesticides, etc.

(3) Poison:- Yellow phosphorus being a strongly poisonous substance is used to make pastes for destroying vermin. The product *glyphosate* is traded as a herbicide.

(4) Bombs and ammunition: The tendency of yellow phosphorus to catch fire has been made use of in making bombs, incendiary shells, smoke screens, tracer bullets and Molotov cocktails of benzene and phosphorus. Red phosphorus which is safer to handle, is used in cap-gun caps.

(5) Deoxidizing agent: Due to the strong affinity of yellow phosphorus for oxygen, it is used to remove oxygen from copper. But for this purpose, it is added to the molten copper in the form of the alloy phosphor-copper.

(6) Semiconductor:: In trace amounts, phosphorus is used as a dope in certain type of semiconductors.

3. Fertilizers: Phosphorus along with calcium, nitrogen and potassium is essential for plant growth. These four principal elements are so interrelated that deficiency of even one of them in the soil affects the ability of a plant to assimilate the others. Generally, it has been found that 1 ton of wheat removes about 18 Kg of nitrogen, 3.65 Kg of phosphorus and 4 Kg of potassium from the soil; 1 ton of beets removes about 25 Kg of nitrogen, 7 Kg of phosphorus, 1.4 Kg of potassium and 12 Kg of calcium from the soil. Their respective amounts for 1 ton of corn are 37 Kg, 7 Kg, 29 Kg and 7 Kg. Phosphorus is a natural ingredient in many soils and micro-organisms comprising some bacteria and fungi make available insoluble phosphorus to roots of plants. But generally, this natural phosphorus needs to be supplemented in the form of fertilizers. The fertilizers containing this (and the other three) elements have to be soluble in water so as to enable the plants to slowly assimilate them. However, more quantities of them in the form of fertilizers have to be added to the soil because part of them combine with iron, aluminium, etc. of the soil to form insoluble chemical compounds which are of no use to the plants. Various technologies have been developed for controlled release of the elements as per the rate of assimilation by the plants and for minimizing their losses due to chemical reactions. These technologies include: (i) use of slowly dissolving compounds, (ii) enclosing the soluble nutrients in slowly decomposing wax, resin, sulphur or plastic, and (iii) chelation, i.e., adding chemicals to the fertilizer which would prevent the nutrients from dissolving rapidly thus protecting them against attack by metals. Different phosphorus-containing fertilizers are discussed as follows:

(a) Ordinary or single superphosphate (SSP): The name superphosphate has been given to the mixture of mono-calcium phosphate [$CaH_4(PO_4)_2$] and calcium sulphate [$CaSO_4$]. The idea behind converting the rock phosphate into superphosphate is that the former is insoluble in water while the latter is soluble and phosphorus can be assimilated by plants if it is in the form of some salt which is soluble in water.

For manufacturing SSP, rock phosphate is first ground, then treated with about its own weight of 66% concentrated H_2SO_4 acid, cured and finally dried and mechanically disintegrated. The following reaction takes place:

$$3Ca_3(PO_4)_2 + 6H_2SO_4 \rightarrow 3CaH_4(PO_4)_2 + 6CaSO_4$$

Although the reacting substances are the same as in the case of phosphoric acid, their inter se ratios and the degrees of concentration of the H_2SO_4 acid are different, and that makes all the difference to the end product. The total phosphate-content (in terms of P_2O_5) in SSP is 16% the whole of which is water soluble.

So far as the specifications of rock phosphate are concerned, P_2O_5 is the most desirable constituent and sulphates are also not objectionable because SSP is valued for the contents of these two components. In India, the industries prefer more than 30% P_2O_5-content. Al_2O_3, Fe_2O_3, SiO_2, F, $CaCO_3$, MgO, Chlorides, organic matter and moisture are considered deleterious for the following reasons:

(1) Al_2O_3 and Fe_2O_3 (i.e., R_2O_3):- Fe_2O_3 and Al_2O_3 (together referred to as R_2O_3) consume a part of the P_2O_5 to form Fe- and Al-phosphates which are insoluble in water. Thus, while the aim is to have the entire phosphorus in the form of soluble phosphate, a part of it remains in the form of insoluble Fe- and Al-phosphates. In a sense higher R_2O_3 may tend to reversion of available P_2O_5 (water soluble P_2O_5). As a result a part of the phosphorus is lost so far as its utilization as a fertilizer is concerned. The industries prefer a maximum of 3.5% R_2O_3.

(2) SiO_2 and F: - Silica should be low, because it increases the grinding cost and its grains may abrade the lining of the reactors and the surfaces of other equipments.

Further, silica being resistant to the H_2SO_4 acid, it hinders spreading of the latter throughout the mass of the phosphate thus increasing what is called curing time and slowing down reaction. However, if fluorine is present, then a little silica is desirable. Fluorine by itself is objectionable because it is liberated as HF which is extremely corrosive to the plant equipments. But if both silica and fluorine are present, then HF will react with silica to produce fluoro-silicic acid [H_2SiF_6] as shown below.

$$4HF + SiO_2 \rightarrow SiF_4 + 2H_2O$$
$$3\,SiF_4 + 4H_2O \rightarrow Si(OH)_4 + 2H_2SiF_6$$

Proven material for construction of plant is available to withstand the corrosive action of this fluoro-silicic acid, but on the other hand, the latter is a valuable byproduct. It is used in manufacture of synthetic cryolite by treating it with clay and bauxite, and also for production of sodium silicofluoride and of ammonium-magnesium-zinc fluorosilicates. In Indian industries, SiO_2 upto 8% is tolerated.

(1) $CaCO_3$ - Both too low and too high contents of it are objectionable. The escaping CO_2 generated due to reaction between the carbonate and the H_2SO_4 acid, makes the grains of the rock phosphate/apatite porous so as to facilitate availability of larger surface area for more efficient chemical reactivity. On the other hand, too high a content will mean a corresponding lowering of the P_2O_5-content but a higher consumption of H_2SO_4 acid (for reaction with the carbonate). Carbonate upto 5% is considered optimum.

(2) MgO: After the superphosphate is manufactured, MgO may be added for (i) absorbing excess water and acid from it by forming $Mg(OH)_2$ and $MgSO_4$ and (ii) supplying magnesium to the plants growing in magnesium-deficient soil. But if there is MgO as impurity in the rock phosphate itself, then it is objectionable because (i) it reacts with a part of the H_2SO_4 acidwhich is thus wasted and (ii) calculated amount of water is added to the H_2SO_4 acid to maintain the required degree of concentration for the reactions to be complete and MgO will disturb that concentration by absorbing this very water.

(3) Chlorides: As a result of reaction between chlorides and H_2SO_4 acid, chlorine gas emanates causing corrosion of the plant equipment.

(4) Organic matter: First, it reacts with a part of the H_2SO_4 acid which is thus wasted. Second, the residual organic matter left after this reaction makes the phosphoric acid coloured, which in its turn, will have a colouring effect on the product that may generate consumer resistance.

(5) Moisture: Moisture present in the raw mineral itself hampers grinding and also free flow of the material on the conveyor belt will be hampered.

(b) Triple superphosphate (TSP)::It is also known as concentrated superphosphate and its phosphate-content is about three times that of SSP. The total phosphate-content (in terms of P_2O_5) in TSP is 46% out of which 92.4% is water soluble. In this case phosphoric acid instead of sulphuric acid is used. Chemically, it is mono-calcium phosphate mono-hydrate [$Ca(H_2PO_4)_2.H_2O$]. For making it, rock phosphate is treated with concentrated phosphoric acid (52-54% P_2O_5). The following reaction takes place:

$$3Ca_3(PO_4)_2 + 12H_3PO_4 + 9H_2O \rightarrow 9[Ca(H_2PO_4)_2.H_2O]$$

The specifications of rock phosphate are the same as in the case of SSP.

(c) Mono-ammonium phosphate(MAP): It is a rich source of phosphorus and it supplies both phosphorus and nitrogen to the soil. It contains about 55% P_2O_5 and 11-12% N. About 82% of the phosphate is water soluble. For manufacturing it, phosphoric acid (45-52% concentration) and ammonia in the ratio 1:1 are allowed to react. Solid MAP and steam are produced.

(d) Di-ammonium phosphate(DAP): It also supplies both phosphorus and nitrogen — but more of the latter compared to MAP — to the soil. It contains about 46% P_2O_5 and 18% N. Over 89% of the phosphate is water soluble. For manufacturing it, phosphoric acid (40-54% concentration) and ammonia in the ratio 1:2 are required . The reaction takes place in two stages. First, a mixture of DAP and MAP is produced which is further ammoniated to produce DAP.

(e) Ammonium phosphate sulphate (APS): Its basic composition is 60% ammonium sulphate and 40% ammonium phosphate. This mixture contains 20% P_2O_5 and 16% N. Practically whole of the phosphate is water soluble. The raw materials required for its production are ammonia, phosphoric acid and sulphuric acid. There are two processes:

i. A mixture of sulphuric and phosphoric acids is directly neutralized by ammonia and then the resultant APS is granulated.
ii. First, ammonium carbonate is reacted with gypsum to form ammonium sulphate solution which is then added to phosphoric acid and finally, the mixture is ammoniated.

(f) *Nitro-phosphates (NP)*: The term nitro-phosphate covers a range of fertilizers containing P and N obtained by treating rock phosphate (34% P_2O_5 and 1.5:1 CaO/P_2O_5) with nitric acid (53-60% concentration) and ammonia. A typical nitro-phosphate contains 20% N and 20% P_2O_5 out of which only 27% is water soluble.

(g) *Urea ammonium phosphate (UAP)*: This group of fertilizers are manufactured by using urea, ammonia and phosphoric acid. First, phosphoric acid is neutralized by ammonia to form ammonium phosphate to which more ammonia and urea are added to augment the nitrogen content. A typical UAP contains 24-28% of each N and P_2O_5. Of the P_2O_5, only about 90% is water soluble.

(h) NPK fertilizers: These contain all the three nutrients, N,P and K in different customized proportions. The basic raw materials are phosphoric acid, ammonia and potash. Urea may be added to increase nitrogen content if necessary. Generally, the ranges of N, P (in terms of P_2O_5) and K are 10-19%, 17-35% and 14-26% ,respectively. Over 80% of the P_2O_5 is water soluble.

4. Direct application to soil: Experimental studies undertaken by various agricultural laboratories in India, to determine the relative efficiency of low to medium grade phosphorite for direct application in the field have been quite successful. The direct application in the field in combination with nitrogenous fertilizers can be best in the lateritic, acidic and upland soils of Gangetic region. Calcium phosphate is soluble in acids and for this reason, finely ground low grade rock phosphate and apatite, which cannot otherwise be converted to chemical fertilizer economically, are directly sprinkled on acidic soils. The weakly phosphatic limestone of Palamou district of Jharkhand state has also been found useful for direct application to acidic soils. The phosphate is slowly dissolved in the soil and it becomes available for the plants to assimilate. Silica should be as low as possible because it tends to increase grinding cost. Other impurities that are critical for superphosphates are not of relevance. However, the use of rock phosphate for direct application as fertilizer depends on its level of solubility in the acidic soil, which in turn is dependent upon the structure and chemical composition of the rock. It is believed that carbonate radical is responsible for the reactivity of directly applied P_2O_5 in the rock. The parameters specified by the Pyrites and Phosphates Corporation Limited (PPCL), one of the important producers of rock phosphate for this purpose in India, are absolute citrate solubility index: 7 max; CO_2/ P_2O_5 ratio: 0.035; PO_4/ H_2O ratio: 2 (this indicates hydroxyl ion in crystal lattice); P_2O_5: 16% (min); Fe_2O_3: 5% (max); CaO : P_2O_5 ratio: 1.8; and size of rock phosphate: 100 mesh.

5. Poultry and live stock feed: For this purpose, rock phosphate is ground and mixed with food in order to supplement the intake of both calcium and phosphorus which are vital for strength of bones and overall health. Fluorine is highly objectionable because it is hazardous to health.

6. Bone china: Bone china is a special translucent variety of porcelain first introduced in England in 1794. It is a sophisticated fine product using tri-calcium phosphate [$Ca_3(PO)_2$] as the dominant component. The preferred source of this phosphate is the ash of cattle bone because it is iron-free. The raw material mix consisting of 45-50% bone ash, 25-30% china clay, 25-30% feldspar (flux) and about 5% ball clay (plasticizer) is first mixed with water and ground; then the slurry is de-watered by filter-pressing, shaped according to the product desired and slowly dried, and finally biscuit fired at a temperature lying within a carefully controlled shortrange of 1250-1300^0 C. The firing temperature is very critical in case of bone china. Under-firing leaves open pores and cannot bring the all-important translucency, while over-firing produces blisters on the surface. After this, it is glazed at a temperature 1050-1100^0 C. The bone ash in the right proportion acts as a flux, but when in excess, it increases refractoriness. Some of the lime of bone first reacts with china clay to form anorthite, while the P_2O_5 reacts with other compounds to form glass. For making bone ash, cattle bone isfirst crushed, washed and then subjected to heating in a highly oxidized condition by slowly increasing the temperature to 900-1000^0 C, whereby most of the organic matter is removed. The calcined bone is ground with water to very fine size, allowed to age for a few days, and then dried to a moisture content of 10-15%. This bone ash contains a little organic matter which, combined with fine size, gives it some plasticity.

7. Gem: Some of the clear crystals of apatite with attractive colours (e.g., asparagus stone, moroxite, lasurapalite, manganapalite) are used as semiprecious stones. Besides colour, moderate hardness, moderate refractive index (greater than ordinary glass) and crystalline form are the criteria. In fact due to its colours and crystal forms, apatite was initially confused with aquamarine, amethyst, tourmaline — all gemstones.

8. Alloys:

(a) *Phosphor* bronze: Alloy of copper, tin and phosphorus known as *phosphor bronze* is the most important alloy of phosphorus. A typical phosphor bronze contains 87.75-89.5%Cu; 10-12% Sn and 0.25-0.5% P which finds application in bearings under heavy load. Bronze with less than 0.3% P and 4-6% Sn are suitable for springs and electrical contact mechanisms where nonmagnetic properties, resistance to rust and high resilience are important requirements. If P and Sn increase to 2.5% and 10-13% respectively, then hard firm wear-resistant and corrosion-resistant casting alloys are obtained which are suited to heavy duty rolling mill bearings, gun mountings and different kinds of valves.

(b) *Phosphor-copper*: It is added to molten copper as a deoxidizing agent for removing oxygen from copper.

(c) *Ferro-phosphorus (or iron phosphide)*: It is made of 23-28% P; 2% (max) Si and balance Fe. It is made by heating iron, rock phosphate, silica and coke. A little amount of phosphorus is added in this form to pig iron meant for casting, to increase fluidity. A type of ferro-phosphorus containing 45-63% Fe, 20-35% P, 2-10% V and 1-10% Cr can be used in paint.

(d) *Indium phosphide*: It is a strong semiconductor suitable for use in high speed diodes such as the laser diodes used in optical fiber junctions. Also it is under active research to make *laser chips* by bonding a layer of light-emitting indium phosphide on to the surface of a standard silicon chip etched with special channels that act as light wave guides. The resulting sandwich has the potentiality to create on a computer chip, thousands of tiny bright lasers that can be switched on and off billions of time a second.

9. Other uses:

(a) Phosphated coatings are used to prevent rusting of iron and steel surfaces and for helping cold-drawing of wires screw threads etc.

(b) Phosphates are used in special glasses meant for sodium lamps.

(c) Calcium phosphate is an opacifying agent for glazes, and due to ability of such phosphor-glazed glass to block ultra-violet light, they are used in household lamps.

WASTE UTILIZATION

1 *Fluorie:* Fluorine occurring in rock phosphate is considered a deleterious constituent because, during manufacturing of phosphoric acid, HF gas is liberated. But, if both silica and fluorine are present in the rock phosphate, then HF will react with silica to produce fluoro-silicic acid [H_2SiF_6] as elaborated earlier under specifications. Thisis a valuable byproduct. It is used in manufacture of synthetic cryolite by treating it with clay and bauxite, and also for production of sodium silicofluoride and of ammonium-magnesium-zinc fluorosilicates. Further, rock phosphate is regarded as an important source of fluorine in USA (which is deficient in fluorite), because it is useful for manufacturing aluminium, for formulating toothpaste and for fluoridating drinking water.

2 *Uranium:* Some rock phosphate deposits contain significant quantities of uranium oxide (yellow cake). In the 1980s and 1990s, a plant was in operation in Florida, USA for recovering uranium oxide from rock phosphate.

3 *Phospho-gypsum:* During manufacture of phosphoric acid by the wet process, gypsum is produced as a byproduct. This gypsum is called *phospho-gypsum*. In some plants as much as 3-5 tons of gypsum are produced for every tonne of phosphoric acid.

4 *Phosphorus slag:*: Phosphorus slag is obtained in the dry process of manufacture of phosphoric acid and elemental phosphorus. It is tapped out of the furnace in molten state at 1500^0C (which is the same temperature at which glass melts). It is basically calcium silicate having composition 40-45% SiO_2, 45-50% CaO, 3-6% Al_2O_3, 1.5-2.0% MgO and trace Fe_2O_3. It can be use in the raw material batch for glass-making in order to: (i) get more draw, (ii) reduce the seed count, (iii) avoid using equal quantity of calcite, and (iv) increase fuel efficiency. Due to negligible iron content, it can also be used for making flint glass.

SUBSTITUTION

In addition to the natural sources, the basic slag generated from iron industries also contains significant quantities of both calcium and phosphorus depending on the phosphorus content of the iron ore. This is an important source of phosphorus in countries like Belgium, Germany, Luxembourg, etc. In India, an average LD furnace slag contains around 30% calcium and 1.4% phosphorus. However, insofar as the uses of phosphorus on the basis of its nutrient value are concerned, there is no substitute.

Chapter 35

POTASH

Nitrogen, phosphorus and potassium — commonly referred to as NPK — are the trio of ingredients essential for plant life. While potassium is made available to plants in the form of some minerals, potash is not the name of any of them. The name originally came from "pot-ash" from the early method of producing potassium cabornate or K_2CO_3 by boiling and evaporating a solution obtained by running water slowly over wood ash in iron-pots, leaving behind a mass of white solid residue which was called potash (cf., soda ash, Na_2CO_3). This was one of the methods resorted to in USA during World War II when the then main natural sources of potassium compounds — France, Germany, Poland, Russia, Spain and Middle-East countries — were cut off due to blockade of sea-routes. Later on, the name potash came to stand for the oxide of potassium, K_2O, which is the standard compound for expressing the potassium-content of all potassium compounds. Now, in industry and trade circle, this term is generally used also to denote the water-soluble compounds of potassium suitable for use as fertilizer, potassium chloride (KCl) and potassium sulphate (K_2SO_4), excluding the insoluble ones.

SOURCES OF POTASH

Potassium forms a constituent of a host of minerals like feldspars, micas, glauconite, etc. It has been estimated that 3.11% of the lithosphere and 0.04-0.07% of the ocean water is potassium oxide. But commercial minerals containing potash are only five in number. They are:

1 Sylvite [KCl]
2 Sylvinite [NaCl.KCl]
3 Carnallite [$KCl.MgCl_2.6H_2O$]
4 Kainite [$MgSO_4.KCl.3H_2O$]
5 Langbeinite [$K_2SO_4.MgSO_4$]

Beds of sylvite, carnallite, langbeinite and sylvinite occur in New Mexico and Texas, USA, some of which are mined like coal. Occurrences of various minerals are known in France, Poland, Spain and Russia. In addition, brine (subsoil and lake) is an important commercial source of potash. The brine of the Dead Sea located in Israel and Jordan contains

1.20% of KCl and is the richest single commercial source of this compound with an estimated resource of about 2 billion tons. The other ones are the Great Salt Lake of USA, Salar De Atacama desert of Chile and Da Chaidan lake of China as well as some reservoirs in Canada, France, Greece and Italy.

In India, there is no known commercially exploitable source of potash, though there is an occurrence of sylvite in Ganganagar basin of Rajasthan and investigations were carried out for its recovery from both seawater bittern (as byproduct of NaCl) and from the subsoil brine of the Great Rann of Kutch besides some unconventional mineral and non-mineral sources (feldspar, husks, flue dust and saltpeter industry waste).

The world production of potash in terms of equivalent K_2O was 27.7 million tons in 2000. Canada was the leading producer followed by Russia, Belarus, Germany, Israel and others.

RECOVERY OF POTASH

Presently, potassium chloride is the most common forms of potash being recovered from brine and the chloride mineral sylvite. There have also been attempts to recover KCl from some unconventional sources. The recovery processes are as follows.

1. Brine: The most important source is the Dead Sea brine, but seawater and subsoil brines are also processed for its recovery. The processes are essentially the same and are described as follows.

(1) *Dead Sea brine*: Dead Sea brine has a density of 1.23 gm/cc (8 times that of seawater) and has a concentration of 370 gramme of total salt per kilogramme of water. The brine is first pumped into a salt pond where, due to solar evaporation, most of the NaCl is deposited and the water-content of the brine is reduced bringing the density up to 1.298 gm/cc. This water is taken to and further evaporated in a pre-carnallite-pond where the part of the remaining NaCl is deposited increasing the density of the brine further to 1.303 gm/cc and its KCl-concentration becomes 2 per cent. This overflow brine is subjected to evaporation in a series of carnallite-ponds to deposit the salts KCl and $MgCl_2$ in the form of a bed of carnallite ($KCl.MgCl_2.6H_2O$) with the remaining NaCl. The residual brine having density 1.34 gm/cc and containing 0.3% KCl is discharged back into the Dead Sea and the final deposit containing 84% carnallite and 16% NaCl is harvested in the form of slurry with the help of mechanized harvesters. Further processing of this carnallite slurry is carried out by either of the following methods.

(a) Hot leach process: The carnallite slurry is dewatered and decomposed by water in stages while simultaneously agitating it. After this process, the $MgCl_2$ is leached away leaving behind a cake comprising sylvinite (NaCl.KCl). The sylvinite cake is mixed with water, agitated and heated in a tank under controlled temperature so as to dissolve the KCl and precipitate most of the NaCl. The hot brine, rich in dissolved KCl but with some NaCl, is thickened and cooled in stages in vacuum from 93^0C to 49^0C, as a result of which the KCl crystallizes. The slurry containing these potash crystals is dewatered, dried and granulated by adding some anti-caking agent to make it free-flowing

(b) Cold crystallization process: The crude carnallite slurry is wet-screened to separate the coarse high-grade and fine impure fractions. The latter, which contains NaCl as impurity, is treated with some reagent in a flotation cell to float the NaCl. The concentrated carnallite from the flotation cell and the coarse high grade carnallite are both decomposed in presence of water in a crystallizer, where KCl crystals are formed. In order to remove adhering $MgCl_2$, the KCl crystals are leached and dewatered in a centrifuge. Finally, they are dried and cooled to get a commercially pure potash containing 0.5% $MgCl_2$ and 0.1% moisture.

In both the processes, the waste brine consisting of NaCl and $MgCl_2$ are discharged as tailings.

(2) *Seawater brine*: The average concentration of major elements in seawater is:

Chloride	19350 ppm
Sodium	10760 ppm
Magnesium	1290 ppm
Sulphur	810 ppm
Calcium	410 ppm
Potassium	390 ppm
Bromine	67 ppm

By solar evaporation of seawater (density 3.5^0 Be′, approximately equivalent to specific gravity 1.025), common salt (NaCl) is harvested between 25.5^0 Be′ and 30^0 Be′ (approximately equivalent to specific gravity 1.20-1.26) , and the end liquor obtained after this stage is called *bittern* or *mother liquor*. The KCl-content increases from 0.07% in seawater to 2-2.5% in bittern. On further concentration of the bittern by solar evaporation process to $35\text{-}36^0$ Be′, a potash-enriched solar evaporite referred to as *mixed salt* is obtained. The average composition of the bittern and the mixed salt are

Constituent	Bittern	Mixed salt
NaCl	14-16	15-20
KCl	2.0-2.5	18-20
$MgSO_4$	6-8	2-6
$MgCl_2$	6-8	2-6

There are processes to recover potash both from the bittern directly and from the mixed salt.

(a) Bittern: The processes include:

i. Desulphation process: This involves precipitation of the $MgSO_4$ from the bittern using $CaCl_2$ to obtain a mixture of carnallite or sylvinite from which pure potash is obtained by fractional crystallization. The process involves handling of large volumes of bittern and precipitant chemical.

ii. Flotation process: This involves use of reagents for selective precipitation/floating. The reagents that have been used are chloro-platinic acid, perchloric acid, sodium altraphenyl-boron, tri-sodium cobalti-nitric acid and dipicrylamine. But employment of this process is limited by the high costs of the reagents.

(b) Mixed salt: There are two processes as

i. Hot extraction process: This process is based on *phase rule chemistry* of the oceanic salt system. Mixed salt is extracted from bittern at 110^0 C. The slurry is filtered hot to remove the residue known as *sels mixtes* containing 50-52% $MgSO_4$ and 12-15% NaCl. While the filtrate comprises impure potassium chloride. For separating potassium chloride from it, it is treated with saturated KCl- NaCl solution and heated to 110^o C, when potassium chloride dissolves while sodium chloride is. left as solid residue. The slurry is filtered and allowed to cool to room temperature when pure crystallized potassium chloride is separated by centrifuging, dried and packed. The filtrate, on cooling to 20^0C, yields a precipitate of carnallite from which 96-98% pure KCl is recovered by hot leach or cold crystallization process as in the case of Dead Sea brine. From the residue, Epsom salt ($MgSO_4.7H_2O$) or sodium sulphate can be recovered as byproduct. However, this process consumes high energy.

ii. Flotation process: A process was developed by the Central Salt and Marine Chemicals Research Institute (CSMCRI), India which is suitable to the high-$MgSO_4$ bittern generated by Indian salt industry. By this process potassium schoenite which is a hydrated double sulphate of potassium and magnesium having composition $K_2SO_4.MgSO_4.6H_2O$ (cf., langeibite, $K_2SO_4.MgSO_4$). The mixed salt mixed with bittern is made into a slurry and subjected to flotation using some suitable reagent (e.g., otadecylamine acetate, highly sulphonated castor oil). NaCl is depressed and the remaining salts are floated in the form of kainite ($KCl.MgSO4_. 3H_2O$).The higher $MgSO_4$ in the Indian bittern favours formation of kainite instead of carnallite which is the flotation product from the low- $MgSO_4$ bittern in many other countries. This kainite is converted to potassium schoenite by treating it with water and centrifuging the mixture at room temperature. The product contains 20-23% K_2O and 8-10% MgO with 1.0-1.5% NaCl as impurity, and the yield is about 75 per cent. Unlike in case of carnallite, KCl recovery from schoenite is energy-intensive, and so, recovery of K_2SO_4 (95% purity) is preferred. This is done by reacting the schoenite with excess KCl.

(3) *Subsoil brine*: Brines from Great Salt Lake of USA, Salar De Atacama desert of Chile and Da Chaidan lake of China as well as from some sources in France, Greece and Italy are regularly processed for recovery of potash in the form of K_2SO_4.

After evaporation and harvesting of the brine, main product from the Great Salt Lake is a mixture of potassium salts — kainite and carnallite. Both products are converted to schoenite by lixiviating with hot water, as a result of which spontaneous reconstitution of salts in solution and crystallization of potassium sulphate take place. For achieving this, schoenite is separated and treated with fresh water in crystallizer. $MgCl_2$ and some of the KCl dissolves leaving potassium sulphate. Sodium Sulphate is also recovered as a byproduct.

In case of the brine from the Atacama desert of Chile, the product after evaporation is mixed shoenite and sylvite (predominantly KCl) salts. The shoenite is beneficiated by spontaneous endothermic reaction with the sylvite to make a highly pure potassium sulfate and magnesium chloride.

$$K_2\,SO_4.MgSO_4.6H2O + 2KCl \rightarrow K_2\,SO_4 + MgCl_2$$

The $K_2\,SO_4$ is separated by a band filter and then dried.

The subsoil brine occurring at depths ranging from 1 cm to 3.35 m below the Great Rann of Kutch of Gujarat, India has the typical composition vis-a-vis that of seawater in terms of weight percentage of *total dissolved salts* or *TDS* as:

Constituent	Subsoil brine	Seawater
NaCl	78.40	80.83
KCl	1.83	1.89
MgSO4	0.60	6.19
MgCl2	15.68	9.72
CaSO4	3.55	1.71

The Central Salt and Marine Chemicals Research Institute (CSMCRI), India has developed a process to recover potash from this brine, but it has remained a non-starter due to poor infrastructure in the area.

2. Langbeinite: Langbeinite ($K_2SO_4.MgSO_4$) is a double salt that contains potassium sulfate and magnesium sulfate, and because of the magnesium-content, it is not usable in its mined form. Potassium sulfate can be produced from langbeinite by the removal of magnesium sulfate through addition of $MgSO_4$ and KCl involving the following reaction:

$$K_2SO_4.MgSO_4 + MgSO_4 + 4KCl \rightarrow 3K_2SO_4 + 2MgCl_2$$

3. Sylvite: Sylvite (KCl) is used either directly or after converting it to potassium sulphate. There are several processes to convert sylvite to K_2SO_4, a few of which are as follows:

(a) Kieserite ($MgSO_4$) and sylvite (KCl) that are mined separately, are purified, put in solution, electrolyzed and crystallized at temperatures up to 120°C.

$$2KCl + MgSO_4 \rightarrow K_2SO_4 + MgCl_2$$

Potassium sulphate made by this process is widely used in the Europe and Australia.

(b) Potassium chloride is passed over an anion exchange resin (R) laden with sulphate to produce K_2SO_4 as per the reaction

$$2KCl + R_2SO_4 \rightarrow K_2SO_4 + 2RCl$$

(c) Sulphur is burned to form sulphur dioxide and is passed over potassium chloride to produce potassium sulphate and hydrochloric acid as below:

$$2KCl + SO_2 + H_2O + O_2 \rightarrow K_2SO_4 + 2HCl$$

(d) Potassium chloride is acidulated with sulphuric acid to make potassium sulphate and hydrochloric acid:

$$2\ KCl + H_2SO_4 \rightarrow K_2SO_4 + 2\ HCl$$

(e) In the *trona* process, the double salt *burkite* ($Na_2CO_3.Na_2SO_4$) is reacted with potassium chloride brine to produce potassium sulphate with sodium carbonate (Na_2CO_3.) and common salt as the by-products.

$$(Na_2CO_3.\ Na_2SO_4) + 2KCl \rightarrow Na_2CO_3. + K_2SO_4 + 2NaCl$$

4. Organic wastes: These include paddy/groundnut husks, trunks, millet straw, bamboo scrap, etc. The fallen leaves from plants and trees decay and make an acid called *humus*, with the help of which the roots continually bring up mineral salts (including potash) naturally present in the subsoil. Some of these salts get into the blades of paddy and groundnut (and ultimately into their husks), trunks, straw, etc. According to analyses of typical samples of paddy husk, millet straw and bamboo scrap from India done during 1975-1976 by the Central Salt and Marine Chemicals Research Institute (CSMCRI), India, the values of water-soluble K_2O in their ashes as 0.16%, 0.56% and 0.25%, respectively, with the balance made up by silica and other constituents. Banana trunks and groundnut husks are particularly rich in soluble K_2O, its content in their ashes being 41.26% and 39.5%, respectively. Groundnut husk is widely used in India for direct application to soil, but the economic feasibility of extraction of potash from these sources has not been established.

5. Furnace flue gas: The dust collected from the flue or exhaust gases of furnaces is known as *flue dust*. Since the late 19th century it is well known that alkali metals are carried along with flue gases emitted by iron furnaces. The potassium comes chiefly from the coal and iron ore. Most of this potassium in the form of complex silicates gets fixed in the slag while a small part is volatilized and after condensation, becomes flue dust.

During the World War I (1914-1918), a plant was set up in UK to produce 2,500 tons of potash per year. Subsequently, in USA, it was found that by using *electrostatic precipitator*, larger amounts of potassium could be trapped in the flue dusts. In India, no serious attempt seems to have been made for commercial recovery of potash from this source.

In 1976, the Central Salt and Marine Chemicals Research Institute (CSMCRI), India analyzed the flue dusts emitted from some iron and cement furnaces and studied the technical feasibility of recovering potash from them. According to the analyses, the flue dusts are a complex mixture of silicates with water-soluble K_2O varying from 0.05-1.57 percent. However, in electrostatic precipitators, enhanced values can be obtained even though they are much lower than the reported 7-8% values in the flue dusts collected in some European countries and USA (perhaps condensation of gases is more efficient there due to cold climate). In the experiments conducted by the CSMCRI, flue dust was treated with simple water, with water heated to 800^0C and with sodium chloride solution. The recovery of K_2O in the first case was 1%, in the second case slightly more while in the third case it was 2 percent.

6. Feldspar:- K_2O-content in feldspars varies from 5-12%, but it is in insoluble silicate form. The methods of extraction of potash from them that have been tried are as follows:

(a) Feldspar was heated with $CaCO_3$ in conjunction with $CaSO_4$ and $CaCl_2$. In one experiment carried out by Sanda Lupan, feldspar containing 11% K_2O, $CaCO_3$ and $CaCl_2$ were mixed in the ratio 1:2.5:1, heated for two and half hours in a rotary kiln at $800\text{-}850^0$C, cooled, ground, water-leached and filtered. A mixture of KCl and $CaCl_2$ was obtained from which KCl was separated by fractional crystallization. Recovery of KCl was 85%, but the process was energy-intensive and the raw materials were costly.

(b) In an experiment conducted in the Central Salt and Marine Chemicals Research Institute (CSMCRI), India in 1979-80, a mixture of feldspar containing 12.22% K_2O, $CaCO_3$ and waste 36^0 Be′ bittern containing $MgCl_2$ is mixed and heated for 3 hours at $800\text{-}850^0$C. The product is cooled, ground, leached with hot water and filtered. The filtrate was rich in KCl. Up to 77% recovery could be achieved. But this process was also energy-intensive.

Recovering potash from feldspar is not economically viable.

7. Glauconite: As in the case of feldspar, glauconite is also insoluble in water, and recovery of potash from it is cost-prohibitive.

8. Saltpetre industry waste: Crude saltpetre (KNO_3) contains NaCl, KCl, K_2SO_4, $CaSO_4$, and $MgSO_4$ as impurities. After KNO_3 is recovered from crude saltpetre, all these impurities and a little KNO_3 go into the waste. The Central Salt and Marine Chemicals Research Institute (CSMCRI), India conducted experiments in 1964-65 with an sampl,e containing 53.1% NaCl, 31.6% KCl, 8.7% K_2SO_4, 0.8% $CaSO_4$, 1.1% $MgSO_4$, 1.4% KNO_3, 1.3% insolubles and 2% moisture. This material was boiled at 112^0C with a saturated NaCl-KCl solution. The KCl of the waste material went in solution and rapidly filtered in vacuum while the other constituents were left in the residue. On cooling crystals of pure KCl were obtained. The mother liquor was recycled for a repeat of the experiment. Since now the material has a higher concentration of K_2SO_4, crystals of this salt along with that of the unrecovered KCl were obtained at the end of the second experiment.

USES AND SPECIFICATIONS

1. Fertilizer: This is the main use of potash. Nitrogen, phosphorus and potassium (commonly referred to as N-P-K) along with calcium are essential for plant growth. These four principal elements are so interrelated that deficiency of even one of them in the soil affects the ability of a plant to assimilate the others. Generally, it has been found that 1 ton of wheat removes about 18 Kg of nitrogen, 3.65 Kg of phosphorus and 4 Kg of potassium from the soil. 1 ton of beets removes about 25 Kg of nitrogen, 7 Kg of phosphorus, 1.4 Kg of potassium and 12 Kg of calcium from the soil Their respective amounts for 1 ton of corn are 37 Kg, 7 Kg, 29 Kg and 7 Kg.

For this use, the most important requirements are the potassium (i.e., K_2O) content and water-solubility of the potash so as to enable the roots of plants to absorb it. Since both KCl and K_2SO_4 are water-soluble, either of them can be suitable. But the former is the most popular and widely used. Potash does not require any processing and is either simply blended with chemical fertilizers (see the chapter on phosphorus) or directly applied to soil. Agriculture grade KCL from Dead Sea marketed worldwide by the Arab Potash Company of Jordan contains *KCl 95% (min), K_2O 60% (min), $MgCl_2$ and $CaCl_2$ each 0.5% (max), NaCl 3.5% (max), moisture 0.5% (max), Br 0.1% (max), anti-cake/amine 2 ppm*.

Potassium sulphate (K_2SO_4) or potassium schoenite ($K_2SO_4.MgSO_4.6H_2O$) is specially suitable for crops that do not tolerate chlorine such as tobacco, potato, sugarcane, etc.

2. Caustic potash: Caustic potash or potassium hydroxide (KOH) is manufactured from KCl. For manufacturing KOH, potassium chloride brine is electrolyzed in electrolytic cells. When the brine is fed to the electrolytic cell, the process yields a solution of potassium hydroxide and co-products of chlorine and hydrogen. Caustic potash, is used in a wide variety of industrial applications. The major uses are:

(1) *Potassium carbonate:* The largest single use is in the production of potassium carbonate, which is used in the manufacture of specialty glasses, including television tubes. Other applications of potassium carbonate include: food, soaps, dyes and pigments, boiler compounds, electroplating baths, extraction of carbon dioxide from the industrial gas streams, dehydrating agents, titanium enamels, vat dyeing and textile printing, fire extinguishing powders, and in the production of several potassium chemicals including potassium acetate, bicarbonate, bi-sulphite, ferrocyanide, fluoride, metasilicate, and others. Potassium metasilicate (K_2SiO_3) is prepared by fusing silica sand or quartz powder with potassium carbonate at 1200^0C to 1400^0C. It is a transparent and corrosion resistant. It is applied as a covering on welding rod, on cathode ray tube of black and white television, on inorganic paints etc. to protect them against corrosion.Potassium fluoride (KF) is used for production of potassium metal. the process consists in its thermal reduction by calcium carbide (CaC_2).

(2) *Potassium phosphate:* The phosphates, which have buffering chelating and cleaning effects, are used in applications where their excellent solubility is of value, and find markets primarily as builders in industrial detergents and cleaners, and in water treatment chemicals. Potassium phosphates are also used in making soluble casein (a milk protein used in making plastics, adhesives and paints) and antifreeze substances. It is also used in the production of liquid fertilizers. These fertilizers can be used for crops that are sensitive to chloride ions (e.g., tobacco, potato, sugarcane). It is a source of both potassium and phosphorus.

(3) *Soaps and detergents:* Potassium soaps and detergents are made from coconut oil fatty acid, vegetable oil and toluene sulphonic acid.

(4) *Other uses:* Other end uses of potassium hydroxide include electroplating, herbicides, greases, catalysts, oxidizers, medicines, and alkaline-electrolytic batteries

and manufacture of several potassium chemicals like cyanide, aluminate, formate, fluosilicate, borohydride, bromate, bromide, gluconate, laurate, manganate, oleate, and titanate.

Chapter 36

PYROPHYLLITE

The mineralogical status of pyrophyllite is a subject of debate. Some authors have regarded it as a member of the clay family because of its chemical composition (hydrous silicate of aluminium), but according to some of them it belongs to the montmorillonite group (now called smectite group) while Dana's Text Book of Mineralogy (first published in 1898 and first Indian edition, 1959) places it in the kaolin division. On the other hand, in some literature its similarity with talc (rather than clays) with respect to both physical properties and usage has been emphasized, the two minerals being isomorphs of each other (i.e. they share the same monoclinic structure but have different chemistries). In fact, the two minerals are so similar that, till the 1950s, pyrophyllite was being mined and sold in many countries in the name of talc and after the confusion was cleared, industrialists have been regarding it as a separate entity. In this book, this commercial connotation is adopted and pyrophyllite is recognized as a separate mineral commodity and not one of the clays.

The chemical composition of pyrophyllite is $Al_2O_3.4SiO_2.H_2O$ (cf., talc, $3MgO.4SiO_2.H_2O$). The name, given by R. Hermann in 1829, has been derived from the Greek words "pyr" meaning "fire" and "phyllo" meaning "tissue-thin wafer" referring to the tendency of some variety of pyrophyllite to break into leaf-like scales when heated. In occurs in two more or less distinct varieties — crystalline folia and compact masses (cf., steatite). For the latter, however, local names are in vogue like *agalmatolite* (mined in Brazil, China and South Korea), *pagodite* (both mined in China and South Korea) and *wonderstone* (mined in south-west Africa).

Pyrophyllite is an early-stage metamorphic mineral and occurs in slate, phyllite and schist, often associated with kyanite ($Al_2O_3.SiO_2$), of which it is an alteration product (incidentally, the name "phyllite" is derived from "pyrophyllite"). Pale green foliated masses are found in the Urals (Russia) and in Switzerland while extensive deposits of the compact variety occur in USA (the Deep River region of North Carolina, South Carolina and Georgia), South Africa and China. The leading producer is South Korea followed by Japan, India, Brazil, Thailand and others.

So far as India is concerned, although pyrophyllite was being mined for a long time, its production used to be reported as talc till 1959 and separate production data started becoming available only since 1960. From that year its production history is as follows.

Year	Production
1960	925 tons
1970	13,922 tons
1980	35,077 tons
1990	85,230 tons
Year ending March 2001	148,346 tons
Year ending March 2006	181,328 tons

The production comes from the states from Andhra Pradesh, Jharkhand, Madhya Pradesh, Maharashtra, Orissa, Rajasthan and Uttar Pradesh.

CRITERIA OF USE

(1) *Chemical characteristics*: Pyrophyllite ($Al_2O_3.4SiO_2.H_2O$) contains 66.7% silica, 28.3% alumina and only 5% water compared to 65.5% SiO_2, 31.7% MgO and 4.8% H_2O in talc. Thus, as far as silica and water are concerned, their contents are comparable in the two minerals. Chemically, it is inert.

(2) *Crystal structure*: Crystal of pyrophyllite may be either platy or fibrous (asbestine). When ground, the crystals break down into plates/flakes or fibers depending on the structure. Each flake or folium has a sheet-like structure consisting of two silicate layers being sandwiched between gibbsite [$Al(OH)_3$] layers.

(3) *Hardness and surface feel*: Pyrophyllite is very soft having Mohs hardness varying from 1-2 (cf., 1 of talc) and its surface feels smooth and soapy.

(4) *Colour and optical properties*: Colour of pyrophyllite varies from white to apple green or brownish green depending on the content of impurities like iron oxide. Its foliated variety has a bright pearly lustre while the massive one is dull. Its refractive index varies from 1.55-1.60 (cf., linseed oil 1.48, ordinary glass 1.53, talc 1.54-1.59, titanium dioxide 2.40, diamond 2.42).

(5) *Specific gravity*: For its softness it has a remarkably high specific gravity — 2.85.

(6) *Mechanical properties*: The thin folia constituting the crystal of pyrophyllite, although flexible, are not elastic. Consequently, pyrophyllite possesses good mechanical strength, and for this reason, the structures and articles made up of it are durable.

(7) *Electrical properties*: It is a poor conductor of electricity having high dielectric strength (dielectric strength is a measure of the electrical insulation, and is the voltage that an insulating material can withstand before breakdown).

(8) *Non-plasticity*: It is hydrophobic (i.e., averse to water) and hence does not form a plastic mass when mixed with water. This nature is due to the slipperiness of its surface as water tends to slip away instead of adhering to it.

(9) *Oil absorption*: Ground pyrophyllite has fairly high oil absorption ability. This ability depends on the interfacial tension, shape of particles (fiber or plate), specific surface (total area of surface of particles per unit mass) and particle size distribution. More

interfacial tension means the particles will tend to hold together leaving less space for the oil to occupy and hence oil absorption will be lower. While the interfacial tension is the same for all types of pyrophyllite particles, it depends on the other three factors. The total surface area provided by the particles is more in case of plates than fibers, and hence both the specific surface and the tension is more in case of plates than in case of fibers. Again, uniform particle size means larger interstitial pore space for oil to occupy than non-uniform particles, and hence in case of the former, oil absorption ability is higher. Summing up, uniformly ground fibrous or asbestine type pyrophyllite will have higher oil absorption ability than platy type.

(10) *Thermal properties*: In pyrophyllite are combined the advantages of both metals and water as far as thermal properties are concerned. Like a metal, it gets heated quickly and then, like water (and unlike a metal), it retains the heat for a long time, slowly radiating it over many hours. This apparently anomalous behaviour is due to a combination of high specific heat and poor thermal conductivity. High specific heat means for a unit rise in temperature a mass of pyrophyllite can absorb a large amount of heat, while poor thermal conductivity means the absorbed heat does not flow out of it quickly. The thermal conductivity decreases even more when the pyrophyllite is fired.

(11) *Fired properties*: At 400^0C water molecules start being driven off and at $700\text{-}800^o$C pyrophyllite becomes completely dehydrated and breaks or exfoliates into leaves. On further heating to 1100^0C, part of the silica also breaks off as free silica which is in a stable glassy form (cristobalite) and the pyrophyllite gets converted to *mullite* (cf., the corresponding temperature for talc is 1300^0C, but instead of mullite, it gets converted into *clinoenstatite*). Mullite is an aluminium silicate having composition $3Al_2O_3.2SiO_2$ and containing 71.8% Al_2O_3 and 28.2% SiO_2. The part of the silica released from the pyrophyllite remains intimately mixed with the mullite to form a glassy composite material which is stable up to 1810^0C. It is resistant to chemical attacks by many gases, silicates, oxides etc., resistant to thermal shocks, decrepitation and abrasion and it possesses high electrical resistivity, tensile strength, compressive strength and impact strength. The low water content of 5% in pyrophyllite ensures low shrinkage on firing.

USES

The important uses are:

1 Ceramics
2 Refractory
3 Rubber
4 Paint
5 Insecticide
6 Crayon
7 Plastics
8 Cosmetics

9 Statues and decorative artifacts
10 Glass

These uses are elaborated as follows.

1. Ceramics: The word "ceramic" derived from Greek "keramos" originally meant fired and fused common clays. The original ceramic products (e.g., bricks, potteries) made only of clay were hard and resistant to heat and chemicals, but at the same time coloured, porous and brittle. Today, the product range has gone much beyond bricks and potteries to include a host of high quality white products which are not only hard and resistant to heat and chemicals but also nonporous and strong materials. In addition, glazed ceramic products are now available (the purpose of glazing is to provide a uniform firmly adhering coating on the surface of the ceramic body concealing defects such as pinholes, bubbles, etc., and the glaze is made of the same ingredients but with predominance of quartz and feldspar). For manufacturing them, a mixture of quartz or silica sand, one or more types of clay, feldspar and some flux (soda) with 30-40% water is ground, thoroughly agitated, filter pressed, moulded into the required shape, dried and then fired to a temperature ranging from 1200-1500^0 C depending on the product hardness required. Different ceramic products can be prepared by varying the types of clay, their proportion in the mixture and the firing temperature. Pyrophyllite, by virtue of its ability to be converted to mullite below the firing temperature, is one of the materials in certain types of products. The ceramic products containing pyrophyllite include white ware, sanitary ware, tiles and electrical components (e.g., resistors, transducers, vacuum gaskets, insulators).

The general criteria of this usage are the white colour, low thermal expansion, low shrinkage on cooling after firing (which in turn minimizes *crazing*) i.e., cracking of the glaze), chemical resistance, mechanical strength (compressive, tensile and impact strengths), resistance to thermal shocks and decrepitation, and high dielectric strength (for electrical insulator products) of mullite. Besides, it also supplements silica in the raw material mix. Further, its ability to become heated quickly and get converted to mullite at a lower temperature (1100^{0}C) than in some comparable materials allows faster firing cycles. The thermally massive variety, which is soft and amenable to machine-cutting and -shaping, is used for electrical components. Blocks of it are cut and shaped and then fired.

The most deleterious constituent is $CaCO_3$. On firing, while the CO_2 escapes leaving holes in the body, the CaO remains in the product which, being strongly hygroscopic, increases the chance of crumbling of the product over a period of time. Besides, iron oxide, titanium oxide and alkalis are also objectionable. Fe_2O_3 has a colouring effect on the product. Also, with TiO_2, it forms low-melting iron-titanate glass causing blisters in the products and consequent increase in porosity. Alkalis are deleterious because sodium and potassium in the form of carbonates combine with silica at the firing temperature to form silicates which are water soluble and presence of these silicates in the ceramic product, obviously, will not be desirable. Moreover, the ions of alkalis are electrically conducting.

The Bureau of Indian Standards (BIS) has recommended in 1985 the following specifications for white ware and electrical insulators: *1.0% (max)* Fe_2O_3 *and* TiO_2 *each (max 1.5%* $Fe_2O_3 + TiO_2$*), 0.5% CaO and 0.5%* $K_2O + Na_2O$. For other products like tiles etc., the specifications are: *1.5% (max)* Fe_2O_3*, 1.0% (max)* TiO_2 *(max 2.0%* $Fe_2O_3 + TiO_2$*), 0.5% CaO and 0.5%* $K_2O + Na_2O$. In addition, the Indian industries specify up to 0.5% MgO, which, like CaO. is also hygroscopic.

2. Refractory: Refractory materials are defined as those resistant to heat and having a melting temperature of not less than 1580^0 C. The function of refractory lining on a furnace wall is not only to withstand high temperature, but also to withstand temperature fluctuation, and to resist penetration, abrasion, and erosion by hot gases and molten materials in the furnace, and over and above, it should not chemically react with those materials.

Pyrophyllite is suitable for making relatively inexpensive refractories because of its ability to get converted to mullite which can withstand temperature of up to 1810^0C and also because this mullite is resistant to chemical attacks by many gases, silicates, oxides etc. and also resistant to thermal shocks, decrepitation and abrasion besides possessing high electrical resistivity, tensile strength, compressive strength and impact strength. There are three ways in which pyrophyllite-based refractories are made.

(a) Crushed pyrophyllite pieces (massive variety) are bonded by sodium silicate and moulded into bricks and fired.
(b) Small quantities of it (along with bentonite, kyanite, sillimanite, diaspore etc.) can be combined with bauxite, fireclay or zirconia for making high-alumina refractories. The mixture is thoroughly mixed with water and extruded under high pressure of 1500 lbs/m^2, into columns which are cut into bricks and fired.
(c) Monoliths are made by cutting blocks from massive pyrophyllite and firing them.

Pyrophyllite-based refractories find use in iron and steel furnaces.

In the pyrophyllite used for making refractories, the most deleterious constituent is $CaCO_3$, which has a strong fluxing effect. Besides, after firing, while the CO_2 escapes leaving holes in the refractory, the CaO remains in the product which, being strongly hygroscopic, increases the chance of crumbling of the product over a period of time. Alkalis are also deleterious because sodium and potassium in the form of carbonates combine with silica at the firing temperature to form silicates which are water soluble and presence of these silicates in the refractory product, obviously, will not be desirable. The Indian industries specify the maximum limit of alkalis at one percent.

3. Rubber: The purpose here is to use pyrophyllite as a dusting agent for lubricating moulds and for preventing surfaces from sticking together during manufacture. Chemical inertness, platy structure and smooth greasy feel are the main criteria. As it is used in the form of dust, fineness of size is obviously important and grit is highly objectionable. The platy structure has a smoothening effect on the surface of rubber tyres.

4. Paint: Pyrophyllite is not used much as a primary pigment in either oil or water paints. It is not suitable in oil paints owing to its high oil absorption and its poor opacity in oil due to the refractive indices of pyrophyllite (1.55-1.60) and that of linseed oil (1.48) being close to each other (that of the best pigment, i.e., titanium dioxide is 2.40). As regards water paints, its hydrophobic nature (owing to extreme slipperiness) prevents water from adhering to the surfaces of its particles. It is, however, used as an extender and suspending agent in oil paints. Since amount of pyrophyllite used for these purposes is small compared to that of the pigment, its high oil absorption does matter much. On the other hand, the white colour and bright lustre of its flakes are helpful. In both these applications, iron oxide, volatile matter and moisture are objectionable. Iron oxide has colouring effect. Volatile matter and moisture may render the painted surfaces liable to develop cracks due to their escape on drying. The preferred maximum size of powder is 53 microns (300 mesh), but for very high quality paints industries specify a maximum limit of 2 microns. Water soluble sulphates are considered deleterious because they will adversely affect the durability of coatings. On exposure to water, the sulphates will go into solution and after drying reappear on the surface of the coating as scum. So far as brightness is concerned, the industry prefers 87% value as measured in terms of reflectance from blue light wave, length of which is 457 micron (cf. the value of 97-98 for fresh TiO_2, which is the bench mark for brightness).

(a) *Extender*: An extender is a slow-drying medium with which a paint is mixed primarily for increasing its volume so as to facilitate its application with a brush. But, at the same time, its colouring property and hiding efficiency must not be compromised, and its viscosity should be maintained at a working level. Refractive index, platy structure, white colour, pearly lustre, durability (due to the combined effect of chemical inertness and mechanical strength), smooth surface and softness are the principal criteria.

(b) The refractive indices of pyrophyllite and linseed oil being similar, addition of the former does not modify the opacity or hiding power of the composite paint. Due to its platy structure, the powders of pyrophyllite are made up of micro-flakes with large total surface area enabling the flakes to securely stick to the surface coated and allowing the paint to level out after application. This is called in industrial parlance *flatting effect*. This effect along with smooth surface of the flakes, pearly lustre and their durability, ensures a smooth, even, pleasing and durable finish of the painted surface. Due to its white colour, pyrophyllite does not affect the colour of the main pigment component of the paint, while its softness facilitates easy brushing without any abrasive effect. Due to these advantages, pyrophyllite make a good low-cost substitute of some expensive materials like titanium dioxide and some resins.

(c) *Suspending agent*: In this application the fibrous crystalline type of pyrophyllite in powder form makes a good low-cost substitute of some expensive materials like china clay. Fine-sized fibers of pyrophyllite trap and hold the primary pigment particles enabling the latter to remain in suspension long enough to facilitate brushing. White colour and close match between the refractive indices of pyrophyllite and linseed oil ensure that addition of pyrophyllite does not modify the colouring and hiding properties of the paint. Smooth surface, pearly lustre and durability of pyrophyllite will ensure a smooth, even, pleasing and durable finish of the painted surface.

5. Insecticide: It is used as a carrier by virtue of its low water content, inertness and high specific gravity. For this application, high quality pyrophyllite is not required, and there is more consideration for low cost. Low water content ensures dryness of the insecticide powder.

6. Crayon: It is one of the traditional uses of pyrophyllite, for which it acquired its popular name *pencil stone*. It is used by tailors for marking cloths for alteration purpose and by metal workers for making marks on metals. Lumps of massive pyrophyllite are first sawn into blocks with square or rectangular shaped sides. These blocks are then cut into thin slabs equal in thickness to the desired width of the crayons, and finally, these thin slabs are cut to final size of crayons. White colour, softness, mechanical strength and platy structure are the basic criteria. In addition, poor thermal conductivity facilitates using such crayons for marking on hot metal sheets. Due to the platy structure, when a crayon is rubbed on a surface, the powders produced are made up of micro-flakes with large total surface area enabling the flakes to securely stick to the fabric and metal surfaces. Consequently, unlike ordinary chalk, the marks made with pyrophyllite crayons do not go off easily, and those made on metal sheets have the unique characteristic of remaining visible when a cold metal is heated or when a hot metal is cooled.

7. Plastics: Plastics are basically oleo-resinous materials. Pyrophyllite is used as a filler in polypropylene (PP), high density polyethylene (HDPE), low density polyethylene (LDPE), polyvinyl chloride (PVC) etc. In this application, its properties like high specific heat (ability to take heat without much increase in temperature), high electrical resistance, good mechanical strength, greasiness, platy structure, chemical inertness and high oil absorption are made use of. These improved plastic materials find use in automobile dashboards and bumpers requiring mechanical strength and computer bodies and garden chairs requiring high specific heat and electrical resistance. In all these applications, smoothness and greasiness of pyrophyllite are carried to the product and platy structure gives smooth finish. High oil absorption ensures excellent mixing of pyrophyllite with the oleo-resinous materials and inertness prevents chemical reaction between them. For uniform dispersion within the matrix, industries specify ultra-fine particle size and for high-quality sensitive products the size is as small as one micron.

8. Cosmetics: High-quality pyrophyllite is used as a base in body and face powders, creams, etc. after adding deodorant and perfumes, and also as a polishing agent in tooth pastes and powders. Hydrophobia of pyrophyllite prevents it from adsorbing the sweat and causing stickiness. Natural white colour, softness, smoothness, hydrophobic property and chemical inertness are the principal criteria.

Colour should be very white and hence iron which is a colouring substance, is considered deleterious. Grit and calcite affect smoothness. Complete chemical inertness will demand total absence of both acids and alkalis. But a slight alkalinity (pH higher than 7) is not objectionable because bacteria forming in human body sweat and teeth tend to increase the acidity level in them. Lead and arsenic, being highly toxic and poisonous substances, are highly objectionable. Salts (e.g., sulphates) soluble in water should be minimum. These salts go into solution into the water with which pyrophyllite powder is mixed (as in creams, pastes etc.), and later on, when the water evaporates, the dissolved salts form scum on the surface due to by capillary action.

9. Statues and decorative artefacts: Pleasing colour, smooth surface, durability (due to the combined effect of chemical inertness and mechanical strength) and above all, softness making it highly amenable to work on, make pyrophyllite one of the popular materials for statuary and decorative showpieces. Massive machine-amenable block pyrophyllite is required in this application.

10. Glass: In glass industry, pyrophyllite is used instead of feldspar as a source of aluminium. High alumina content (at least 20%) is the criterion.

Chapter 37

ROCKSALT (HALITE)

Sodium chloride (also known as *common salt* or *table salt* or, by common people, as simply salt) is a chemical compound with the formula NaCl which is the salt most responsible for the salinity of the ocean and of the cell-fluid of many multi-cellular organisms. Pure NaCl contains 39.33% Na and 60.67% Cl. One of the sources of salt is rock salt which is also called halite, but it is currently supplemented by widespread production of salt from seawater or brine. Both the words salt and halite have come from the Greek word “hals”.

Halite occurs as massive underground sedimentary evaporite deposits formed by drying of ancient lakes and seas, and, in nature, anhydrite, gypsum, native sulphur and sylvite (KCl) and borates may be associated with it. Very often, halite occurs in the form of: (i) salt domes which are vertical diapirs or pipe-like masses of salt that have been essentially squeezed up from underlying salt beds by mobilization due to the weight of overlying rock (*salt tectonics*) and may or may not be associated with petroleum deposits (e.g., Gulf coasts of Texas and Louisiana, USA, Germany, Spain, the Netherlands, Romania, Iran, off the coast of Brazil), (ii) *salt glaciers* where the salt has broken through the surface at high elevation and has flowed downhill (e.g., Iran); (iii) fibrous vein fillings (e.g., France); (iv) *halite flowers* which are rare stalactites of curling fibers of halite (e.g., certain arid caves of Nullarbor Plain, Australia and Quincy copper mine of Hancock, Michigan, USA); and (v) massive bedded deposits (e.g., Poland). Some of the salt domes may be over 6 km in diameter and 1-2 km in vertical length and some of the bedded deposits may have thickness of several kilometres. One such deposit is mined since 1288 in Wieliczka near Krakow in Poland which is now 65 m deep with 200 km of galleries and which has been included by UNESCO in 1978 in its World Heritage List and is presently also a tourist attraction because of the underground structures (e.g., church, sanatorium, auditorium, restaurant etc.) carved out of salt by the miners through the centuries.

In Indian subcontinent, the Salt Range extending across northern parts of Pakistan and India is where most of the rock salt is concentrated. After independence of India in 1947, there is only one area with rock salt deposits in Mandi district, Himachal Pradesh. Presently, there is a mine working in this area. Its production was 4605 tons in 1947 which came down to 3,585 tons by the year ending March 2001, and has further decreased to 1,871 tons in the year ending March 2006.

So far as the world production is concerned, the available statistics includes salt from all sources (rock salt, sea, brine) and in 2002, it was estimated at 210 million tons, the top three producers being the USA, China and Germany.

CRITERIA OF USE

Halite is typically colourless to yellow, but may also be light blue, dark blue, and pink. It crystallizes with typical cubic close packed (ccp) arrangement of sodium and chlorine ions held together firmly by an ionic bond and electrostatic forces (halite structure). But its most important properties from the industrial point of view are as follows.

(1) *Water-solubility:* Water-solubility of NaCl is high, being 36 gm/100 gm, and this makes salt a highly hygroscopic substance.
(2) *Freezing temperature of its solution in water:Freezing* temperature of the solution is -21°C under controlled laboratory conditions, but in practice, it can melt ice down to about -9°C.
(3) *Indispensability to life:*Salt is responsible for maintaining fluid balance in human and animal bodies and is essential to lives of human and animal beings. The indispensability of salt for health and growth of human population was recognized since long. It is believed that one of the reasons for shifting the capital of Roman empire to Byzantia in Turkey was the availbility of relatively more abundant salt supply.

USES

Salt is not only essential for sustaining both human and animal lives, but it is also an important industrial material. The important uses are:

1 Edible salt
2 Cattle feed
3 Preservative and disinfectant
4 De-icing of roads
5 Chemicals
6 Sodium metal
7 Soaps and detergents
8 Explosives

These uses are elaborated as follows.

1. Edible salt: Salt is not only an essential ingredient for maintaining fluid balance of human bodies but is also commonly used as a flavour enhancer for food (cooked or uncooked) and has been identified as one of the basic tastes — salty taste like sweet, bitter, etc.). But its main disadvantage is its highly hygroscopic nature because of which it absorbs moisture and becomes sticky on exposure. There are two widely marketed edible products of salt:

(a) *Table salt (free-flowing salt)*: Due to hygroscopic nature, pure salt is not free-flowing. Salt readily absorbs water and becomes sticky. Table salt sold for consumption today is not pure sodium chloride but is with some additive to make it free-flowing. In 1911 magnesium carbonate was first added to salt to prevent it from getting sticky and to make it flow more freely. Now-a-days, in USA calcium silicate, which is an anti-caking substance, is the preferred additive for this purpose.

(b) *Iodized salt*: In 1924 trace amounts of iodine in the form of sodium iodide, potassium iodide or potassium iodate were added for the first time, to increase iodine intake by common people prone to incidence of simple goiter. In India, iodized salt is manufactured by dry-spraying of potassium iodate in the ratio 1 part to 40000 parts of common salt which is equivalent to 15 ppm of iodine in the product. A small quantity of borax is also added to act as a stabilizer.

However, consumption of excess salt is associated with health risks for some people. The common risks are elevated levels of blood pressure, i.e., hypertension (which in turn is associated with increased risks of heart attack and stroke) and dehydration of the human body.

2. Cattle feed: Lower grade rock salt not suitable for human consumption is generally used as a cattle feed. A typical example is the rock salt produced from Mandi area of Himachal Pradesh, India where rock salt mined contains on an average 67.81% NaCl, 31.23% insoluble matter, 0.33% calcium bicarbonate, 0.4% $MgSO_4$, 0.26% $CaSO_4$, and 0.31% Na_2SO_4.

3. Preservative and disinfectant: Many microorganisms cannot live in an overly salty environment because water is drawn out of their cells by osmosis by the hygroscopic salt. For this reason salt is used to preserve and cure some foods (smoked bacon, fish), hides and leather and wood. It can also be used to detach leeches that have attached themselves to feed. It has also been used to disinfect wounds (although it causes a great deal of burning sensation).

4. De-icing of roads: Sometimes referred to as *road salt*, about 51% of its world output is now used by cold countries to de-ice roads in winter, both in grit bins and spread by winter service vehicles. This works because salt dissolves in water form a solution having freezing temperature lower than that of ice, (-) 9^0C under practical conditions. Salt sprinkled on ice will result in its progressive solution in the water at the surface of the ice and the solution remains liquid at the temperature of the ice. This process progresses continuously till the entire ice becomes a liquid saline solution which flows away. To improve the effectiveness of the salt for de-icing, up to 100 ppm of sodium hexacyanoferrate is commonly added as an anti-caking agent. Sand is often added to the salt so that after the ice is melted, the wet road does not become slippery.

Rock salt is also used in homes for managing ice. It is common for homeowners in cold climates to spread rock salt on their walkways and sometimes driveways after a snow storm to melt the ice.

However, it will not be effective if the atmospheric temperature drops below the freezing temperature of saline water.

5. Chemicals: Salt is the raw material for producing elemental chlorine which itself is required for the production of many modern materials including PVC and pesticides. Industrially, elemental chlorine is usually produced by the electrolysis of sodium chloride dissolved in water. Along with chlorine, this chlor-alkali process yields hydrogen gas and sodium hydroxide, according to the chemical equation

$$2NaCl + 2H_2O \rightarrow Cl_2 + H_2 + 2NaOH$$

Besides chlorine, NaCl is used for manufacturing some basic chemicals containing sodium or chlorine such as sodium carbonate or soda ash (Na_2CO_3), caustic soda (NaOH), hydrochloric acid (HCl), bleaching powder [CaO(OCl)Cl], calcium chloride (CaCl), sodium sulphate or *salt cake* (Na_2SO_4) and various chlorates (e.g., sodium chlorate, sodium perchlorate, sodium hypochlorite, etc.)

6. Sodium metal: Sodium metal is a highly reactive hazardous metal having lighter-than-water (specific gravity 0.97 at 0^0C temperature) which decreases with temperature. It melts at 97.5^0C. It boils at 883^0C under atmospheric pressure. Thermal conductivity of solid sodium at about 21^0C is 0.32 cal/sec/$cm^2/^0$C, but it increases with increasing temperature, and that of liquid sodium at 200^0C is considerably high – 0.93 cal/sec/$cm^2/^0$C (cf. the figure for copper is 0.941).

The metal was earlier produced by an expensive method of electrolyzing sodium hydroxide. But nowadays, it is produced commercially through the electrolysis of fused sodium chloride (melting point 800^0C). This is done in a *Down's cell* in which sodium chloride is mixed with calcium chloride to lower the melting point to about 580^0C. As calcium is more electropositive than sodium, no calcium will be formed at the cathode.

The metal is used to manufacture tetraethyl lead (now discontinued), as coolant in nuclear reactor (pure liquid sodium) and in sodium vapour lamp.

7. Soaps and detergents: By mixing fat with soda ash (a chemical made from salt) soaps and detergents can be made. In medieval times, salt was used for rubbing household surfaces as a cleansing agent.

8. Explosives: An explosive is made up of a mixture of chemicals which, when heated due to blow, friction or ignition, develops a very rapid generation of gas under tremendous pressure resulting in a sudden shattering effect. A common type of explosive is dynamite which is made up mainly of nitroglycerine or glycerol trinitrate (a liquid), nitroglycol, ammonium nitrate, saltpetre (KNO_3) etc. In some formulations (emulsion explosive with liquid ammonium nitrate as the primary component), NaCl is added (up to 40%) as a coolant to moderate the shattering effect and make it safer to use in underground mines.

9. Other uses:

(a) *Food processing*: Salt is used for processing yeast in bakery, for de-boning chicken, for removing oyster from shell, for stabilizing wine, etc.
(b) *Ceramics*: Soda ash (Na_2CO_3) and sodium sulphate (Na_2SO_4) are used.
(c) *Glazing*: Rock salt finds use in sodium glazing.
(d) *Paper-pulp processing*: Caustic soda (NaOH) is used in the soda process of paper manufacturing.
(e) *Refrigeration*: Frozen solution of salt in water (freezing point -9^0C to -21^0C depending on conditions) is used where deep-freezing is required (e.g., frozen food).

(f) *Agriculture*: Rock salt is added for top-dressing of the soil before harvesting of sugar-beets, provided there is enough rainfall to decrease the concentration of harmful chlorine ions as otherwise rock salt will add to the latter's concentration and will be counter-productive.

(g) *Water treatment*: Soda ash (Na_2CO_3) can be used for softening water.

(h) *Rubber*: It is used for coagulating artificial rubber during its manufacture.

SUBSTITUTION

1. Seawater salt:- The average concentration of major elements in seawater is:

Chloride	19,350 ppm
Sodium	10,760 ppm
Magnesium	1,290 ppm
Sulphur	810 ppm
Calcium	410 ppm
Potassium	390 ppm
Bromine	67 ppm

Total salts dissolved in seawater is 3.7 percent. This saline matter contains on an average 77.76% (may go up to more than 80%) NaCl.

Density of seawater varies from $2.5\text{-}3.5^0$ $Be^/$ (approximately equivalent to specific gravity 1.025). On progressive solar evaporation stage by stage in a series of condensers or reservoirs, the density increases. In the first stage density reaches 10^0 $Be^/$ and volume becomes 37% of the original, when FeO and $CaCO_3$ separates out. In the stage when density reaches 25^0 $Be^/$, $CaSO_4$ separates out, and NaCl separates at density 25.5^0 $Be^/$-30^0 $Be^/$ (or equivalent specific gravity 1.20-1.26).

The crystal habit of the salt obtained by crystallization from seawater is cubic. The large areas of contact between the salt cubes and a surface do not allow the salt to flow freely. Research has been conducted to modify the crystal habit of salt from cubic to dodecahedral by adding glycine of 10-25% concentration to the saturated brine. On evaporation, dodecahedral crystals of this *glycine-rich salt* containing 0.5-1.0% glycine is precipitated. The dodecahedrons having small areas of contact with a surface, can roll freely.

2. Subsoil brine salt: The subsoil brine occurring at depths ranging from 1 cm to 3.35 m below the Great Rann of Kutch of Gujarat, India has the typical composition vis-à-vis that of seawater in terms of weight percentage of *total dissolved salts* or *TDS* as:

Constituent	Subsoil brine	Seawater
NaCl	78.40	80.83
KCl	1.83	1.89
$MgSO_4$	0.60	6.19
$MgCl_2$	15.68	9.72
$CaSO_4$	3.55	1.71

The process of recovery of salt from this brine is similar in principle to that from seawater.

3. De-icing: Alternative de-icing chemicals have been used. Chemicals such as calcium magnesium acetate are being produced. These chemicals are environment-friendly, but are costlier than salt.

Chapter 38

RUTILE

Rutile is theoretically 100% TiO_2, but, in nature, the presence of iron oxide up to 10% is not uncommon. The mineral ilmenite (FeO, TiO_2,;52.6% TiO_2 and 47.4% FeO) very often occurs together with and more abundantly than rutile in heavy mineral sands. However, being abundant, it is now the main source of titanium metal and, to underscore this metallurgical use, it is classified as a metallic mineral (see the author's book "Uses of Metals and Metallic Minerals", New Age, 2007). As for rutile, although it is richer in TiO_2-content, it is scarce and costlier compared to ilmenite and finds use mostly in direct industrial applications for which ilmenite is either not suitable or not available at an economic cost.

Rutile, anatase and brookite are all polymorphs, having the same chemical composition TiO_2, but different crystal forms. Their difference is due to the temperature of formation. Anatase formed at the lowest temperature, brookite at an intermediate temperature and rutile at the highest temperature. Consequently, anatase and brookite, after their formation, have been found in many places, to have been modified to rutile which is definitely the most stable amongst the three. As a result, primary rutile is today found most widespread in igneous rocks like diorite, syenite, granite, amphibolite, etc, albeit in small amounts and mostly in the form of microscopic sizes of crystals. Rarely, large crystals are also encountered. But economically recoverable amounts occur as a secondary mineral in heavy mineral sands. The name rutile has come from the Latin word "rutilus" meaning "reddish brown" emphasizing the characteristic colour of this mineral. Anatase also occurs in a similar manner. Brookite is a rare mineral.

Large usable grains of rutile occur in heavy mineral sands in the beaches. Australia is the leading producer of rutile. The beach sands of Florida (USA) contains about 0.3% rutile (7% of the total heavy minerals). In India 1-4% of rutile occurs in the beach sands of Kerala, Tamil Nadu and Orissa as one of the heavy minerals while in those of Sri Lanka, the rutile content is around 2 percent.

HISTORY

The sand deposit of Kerala in India was discovered in 1909. Coir workers of that region used to rub their hands in sand to get a grip of the coir. Some sand used to stick to the wet coir. Eventually, some sand found its way to Germany along with the exported coir. One day, in 1909, C. W. Schomberg, a chemist, by chance, stumbled upon this glistening sand. He could identify that the sand contained monazite, an important material in those times, not for its thorium value but as an incandescent material for gas light mantle. He came to India and located the deposits. He established a separation plant in 1911, and in that year exploitation of monazite also commenced. Now the monazite sand was very rich in a number of heavy minerals like ilmenite, rutile, zircon, garnet, etc. Of these the most abundant was ilmenite. So, in the plant, ilmenite concentrate also started being separated. The British took over it during World War I (1914-1918). After independence (1947), in 1951, the Government of India created a new undertaking, namely the Indian Rare Earths Ltd (IREL) for mining and processing the heavy mineral sand resources of India in the states of Kerala, Tamil Nadu and Orissa for recovering different heavy minerals and rare earth metals. Initially, IREL operated a plant for processing monazite and produced some rare earth chemicals. Later on, in 1965, it took over the plant for separation of the different heavy mineral fractions which included rutile.

The world production of rutile in the year 2000 was 486,000 tons with Australia (as leading producer), South Africa and USA together accounting for over 95 percent. With regards to India, its production in the year ending March 2001 was about 19,000 tons.

CRITERIA OF USE

Rutile is practically 100% TiO_2. But manufactured TiO_2 is a pure, soft, powdery chemical. Therefore, although many properties of this chemical and that of mineral rutile are common, yet the rutile in its natural form has some exclusive properties by virtue of it crystal structure, which determine its industrial use directly without converting it to the chemical compound of titanium. The properties of natural rutile that are useful from the point of view of industrial use are as follows.

1 *Crystal form*: Rutile has tetragonal crystal structure, commonly prismatic. It does not have very well-developed cleavages and generally occurs in massive form. This gives it some degree of toughness, i.e., resistance to breakage.
2 *Hardness*: It is medium hard with hardness 6.0-6.5 on Mohs scale.
3 *Colour and optical properties*: The most common colour is reddish brown, but sometimes, depending on the presence of impurities, attractive and rich variations of violet, green, bluish and even black colours are come across.
4 *Opacity*: Rutile may be transparent, translucent or opaque.
5 *Refractive index*: The most characteristic optical property is its high refractive index with a high degree of double refraction. Double refraction occurs when a ray of light enters the crystal and is split into fast and slow beams. As these two beams exit the crystal they are bent into two different angles because the angle is affected by the speed of the beams. The refractive index of rutile is in the range 2.616-2.903 (cf., diamond – 2.42) and the double refraction gives it a phenomenally high dispersion resulting in an effect of changing colours in a well-developed crystal.
6 *Specific gravity*: Rutile is heavy having specific gravity varying up to 5.2.

7 *Chemical characteristic*: Rutile is very high in TiO_2-content — 90-100% (cf., that of ilmenite, also a titanium mineral valuable for its TiO_2-content, is 52.67%). Rutile is insoluble in acids.

8 *Electrical property*: Dielectric constant of rutile is about 12, indicating high efficiency to store electrical charge in a capacitor (dielectric constant is the ratio of the capacitance of a specific sample of the material between two plates and a vacuum between the same plates; the value for air, one of the poor conductors of electricity, is 1). By virtue of this high dielectric constant, it has the unique ability to stabilize an electric arc and to prevent its tendency to sputter and flicker caused by fluctuations in the frequency of an electric current. Rutile can momentarily store the excess charge and release the same to make up momentary shortfalls, thus stabilizing the arc.

USES AND SPECIFICATIONS

The important uses of rutile are:

1. Titanium dioxide pigment
2. Titanium metal
3. Welding rod coating
4. Gem

These are elaborated as follows.

1. Titanium dioxide (TiO_2): Although the chemical composition of rutile is TiO_2, yet it contains some impurities, most commonly Fe_2O_3. So manufacturing TiO_2 from rutile, in essence, consists in removal of this Fe_2O_3 and other impurities. There are two processes for this purpose as follows.

(a) *Sulphate process*: In the sulphate process, finely ground rutile is digested in concentrated sulphuric acid (98% concentration) to yield a liquor containing the sulphates of titanium and iron along with impurities containing Al, Si, P and Mg. When this liquor is progressively diluted with water in a controlled manner, at first, while the titanium and iron sulphates remain in solution, those other impurities precipitate, which are removed by filtration. Further dilution makes the sulphates also to precipitate, which are recovered by filtration. The mixture of sulphates is then dissolved in water at elevated temperature with seeds of pure TiO_2 crystals (rutile) added. As a result, titanium hydrate crystallizes and precipitates, while the iron sulphate remains in solution, which is decanted off. The titanium hydrate is washed. But this titanium hydrate still contains some titanium sulphate as impurity, and it is then calcined at $600\text{-}650^0$ C, as a result of which both the water and SO_2 get removed leaving solid TiO_2. If the seeds are of rutile, then the TiO_2 produced is of purer grade than if anatase seeds are used. The main disadvantage is that the dilute sulphuric acid cannot be recycled and has to be disposed. Due to this reason, the process is not popular nowadays.

(b) *Kroll process or chloride process*: In the chloride process, rutile (95-96% TiO_2) is chlorinated to produce $FeCl_2$ and titanium tetrachloride ($TiCl_4$), which being soluble in water, can be separated by filtration. For producing high purity TiO_2, this tetrachloride is hydrolyzed with seeds of pure TiO_2 to precipitate titanium hydroxide, and finally to the product TiO_2 in the same way as in sulphate process described above. Part of the hazardous chlorine is recaptured and recycled making the process environment-friendly and popular.

This manufactured pure titanium dioxide has many unique properties. These are as follows.

1 *Colour and brightness:* Titanium dioxide is a bright white substance with refractive index of 2.7 (cf. 1.0 of vacuum and 2.42 of diamond) and high dispersion (dispersion is the rate of change of refractive index with change in wavelength of the incident light). The high refractive index combined with high dispersion gives it an adamantine lustre and a brilliant appearance. The colouring parameter 'L' value of fresh TiO_2 is 98-100 and is the bench mark for whiteness. The brightness of TiO_2 as measured in terms of reflectance from blue light (wave length 457 micron) is 97-98 and is the bench mark for brightness.

2 *Opacity and light reflectivity:* It has the highest white hiding power amongst all the known white pigments. In fine particle size, it reflects both visible and ultraviolet light rays. The thumb rule is that the particle size should be half of the wave length of the light ray to be reflected. The wave length of the violet light is 0.4-0.5 micron, which is the shortest for the visible light rays. So, particle size of less than 0.2 micron will reflect and scatter ultraviolet light also.

3 *Toxicity:* TiO_2 is non-toxic.

4 *Hardness:* It is extremely hard.

5 *Refractoriness:* It is highly refractory and can withstand up to 1800^0C temperature (a refractory material is defined as one resistant to heat and having a melting temperature of not less than 1580^0 C and the function of refractory lining is not only to withstand high temperature, but also to resist temperature fluctuation, slag and metal penetration, abrasion, and erosion by hot gases and molten slags and metals).

6 *Resistance to chemical:* It has a strong ability to resist attacks by acids.

The important industrial uses of titanium dioxide are:

(1) *Paint:* White colour, lightness, adamantine lustre, brilliant appearance, excellent hiding power, high reflectivity and scattering ability for both visible and ultraviolet light, non-toxicity, hardness, refractoriness and strong ability to resist attacks by acids make TiO_2 an excellent high-performing pigment that is used in white paint after mixing with some suitable media, and by far the bulk of the consumption of all ilmenite is in this industry. When finely ground TiO_2 powder (particle size less than 0.2 microns) is capable of remaining evenly distributed and in suspension in the medium. Also, at this particle size, the powder scatters both visible and ultraviolet light. This increases its value as a pigment. It can also be mixed with other chemicals to yield coloured pigments. For this purpose, even the coloured impurities present in

the ore can be taken advantage of. However, it tends to yellow over a long duration of time, and to increase durability, it is used in combination with some filler (e.g., 5-20% of ZnO_2).

(2) *Enamels and glazes:* TiO_2 is used as an opacifying agent in enamels mainly due to its lustre, hiding power, hardness and resistance to acids. Titanium dioxide enamel finds application on steel and cast iron goods like stoves, refrigerators, etc. It is also used (to the extent of 8-12%) to impart pleasing glazes on porcelain, sanitary ware etc., as well as in ivory finish of artificial teeth. It is also used in lacquers.

(3) *Paper, rubber, textile fabric, floor covering:* Here, the use of TiO_2 is as a coating material on account of its white colour, lightness, adamantine lustre, brilliant appearance, excellent hiding power and strong ability to resist attacks by acids.

(4) *Pharmaceuticals:* Ability of finely ground TiO_2 (290-700 nano-metres) to scatter ultraviolet light and its non-toxicity are the main criteria for its use in dermatological preparations for protection against sun, particularly in tropical regions. It is also used as an opacifier and whitener in the films and sugar coatings on tablets.

(5) *Hydrogen production:* According to some Australian scientists, sunlight can be harvested to generate hydrogen from water with the help of titanium dioxide. For this purpose, a rod made of TiO_2 and another made of platinum are immersed in a solution containing water and a little caustic soda, and the two rods are interconnected at the top end. Then ultraviolet light is allowed to fall on the TiO_2-rod. An electrolysis-like effect is produced, splitting the water into hydrogen and oxygen ions, the former going towards the platinum rod and the latter towards the TiO_2-rod. The effect becomes more pronounced if the TiO_2 is replaced by strontium titanate.

(6) *Self-cleaning fabric:* Titanium dioxide in the presence of ultraviolet light acts as a catalyst to facilitate oxidation of a wide range of organic materials. This property has been made use of by a group of researchers from Hong Kong Polytechnic University in laying the foundation of making *"self-cleaning fabrics"*. The key to the breakthrough lay in powdering titanium dioxide to extremely small particles of 20 nanometres size (2500 times smaller than the width of a human hair), and then developing anatase crystal structure (tetragonal titanium dioxide crystals in octrahedral habit) in these tiny particles. Such nano-particles act as catalysts that help break down, in presence of sunlight, carbon-based molecules of dirt, grease, etc. In the process developed, a cotton fabric is dipped into a liquid slurry made of these particles for just half a minute, removed, padded dry, and then heated to 97^0C for 15 minutes.

(7) *Self-cleaning car windscreen:-* An ultra-thin coating comprising nano-particles of titanium dioxide on top of the windscreen can act as filter for ultraviolet rays and also can stop raindrops from obscuring the driver's view by spreading out the water as a thin film. Research is underway in Itali to make self-cleaning car windscreen using this principle.

(8) *Chemicals:* Titanium tetrachloride ($TiCl_4$), a straw-coloured liquid, was used as a smokescreen in military operations during World War-II. It has also been used for sky-writing for advertisement or other purposes. Further, it has a strong affinity for sulphur and can absorb H_2S gas to yield TiS_2 and release hydrogen. A titanyl chloride antimony trichloride complex , which was found to be effective as a fire-

retardant, has been applied to some types of cellulose fabric. The alkyl titanates derived from the reaction between titanium tetrachloride and alcohols were found to be good waterproofing agents and have been used as water repellant finish to paper, wool, rayon, nylon, silk, wood, etc. Both titanous chloride and sulphate possess strong iron-removing and colour-reducing properties, and are used for de-staining paper, wool, textile prints, leather, sugar and silica sand that is meant for use in manufacture of optical glass.

(9) *TiALON:* It is the acronym for titanium, aluminium, oxygen and nitrogen which are combined into a composite material called titanium-aluminium oxy-nitride. This ceramic material having unique electrical properties was developed by the US Bureau of Mines during the late 1980s and early 1990s. This TiALON can be either a conductor or a semiconductor depending on the ratio between the conducting and non-conducting phases.

Later on, its modified version has been developed which is a light-weight, tough, corrosion-resistant, insulating ceramic material capable of being applied to a surface by vapour deposition to form an extremely thin uniform coating.

It is used in a more advanced form of *electrode boring* called *“electrochemical boring”*. These are techniques of making very fine bores (diameter may be as small as 0.004 mm). In conventional electrode boring, a fine platinum wire electrode is inserted within a glass tube, and positive and negative electrical charges from a DC source are applied to the object to be bored and to the electrode tube respectively. Due to flow of electrons, molecules of the object are eroded in the point of its contact with the platinum wire. In electrochemical boring, an electrically conductive thin metal tube containing an electrolyte is used in place of the platinum-glass electrode. Here, the role of TiALON is to provide a very thin insulating coating on the metal tube with a view to preventing electrochemical corrosion of the object around the contact point.

(10) *Ceramic titanates:* These have been finding increasing use in electronic industry. These are characterized by very high dielectric constant (making them excellent conductors of electricity), excellent piezoelectric effect and pyroelectric properties (piezoelectric crystals can change alternating mechanical strains into electrical impulses and vice versa; pyroelectric materials converts heat energy into electric impulses). Some of the titanates are characterized by development of positive temperature coefficient of resistivity (or PTC, i.e., the resistivity increases with increase in temperature, and the increase is very large at curie temperature which is the temperature at which a substance loses its magnetism). Titanates are used for manufacturing dielectric ceramics, piezoceramics, pyroelectric sensors and PTC resistors. Dielectric ceramics include ceramic capacitors in disc, tubular and multiplayer shapes. Piezoceramic devices comprise all kinds of electrochemical transducers, high voltage generators, electromechanical resistors, filters in telecommunication and sensing devices in information technology. Pyroelectric properties provide a basis for uses in infrared detection and thermal imaging. Application of PTC resistors include semiconductors used in current regulators, self-regulating heaters, overheat protectors and demagnetizers in colour television receivers. The electrical properties of titanate ceramics depend on the porosity and the ceramic microstructure. These are prepared by special forming (such as casting

and pressing) and sintering techniques. Examples of dielectric ceramics are barium titanate ($BaTiO_3$) and solid solution of barium and strontium titanate [$(Ba,Sr) TiO_3$]; those of piezo-ceramics are $BaTiO_3$ and solid solution of lead titanate and lead zirconate [$Pb(Ti,Zr)O_3$ or PZT]; those of pyroelectric ceramics are [$Pb(Ti,Zr)O_3$] and solid solution series lead-lanthanum-zirconate-titanate (PLZT); and those of PTC resistors are also $BaTiO_3$ but made semiconductive by substituting lanthanum or neodymium for barium ions. These properties make them suitable for use in television set capacitors, microphones, phonograph pickups, high frequency sound generators and radiators for generation of ultrasonic energy.

(11) Transparent PLZT ceramics are also manufactured. These are used in goggles for thermal and flash protection, in linear electro-optic modulators for voltage sensors, and in electro-optic light gate arrays for optical memories.

(12) *Synthetic diamond:* Strontium titanate and synthetic rutile (TiO_2) have emerged as a synthetic substitute for natural industrial diamond for high-tech uses.

(13) *Adhesive*: Adhesive is an organic or inorganic substance capable of bonding together other substances by surface attachment. Non-toxicity, resistance to acids and salty seawater and abilities to opacify and scatter ultraviolet light are the main criteria for adding TiO_2 as an ingredient of adhesives.

2. Titanium metal: Titanium is an emerging new-generation metal. For the purpose of producing titanium metal, the $TiCl_4$ produced by chlorination of rutile in the Kroll or chloride process, is treated with red-hot magnesium metal under an inert gas blanket (the inert gas is necessary because liquid titanium tends to absorb oxygen and nitrogen very rapidly). The resultant products are commercially pure spongy titanium metal and $MgCl_2$. The $MgCl_2$ is drained out and electrolyzed to recover both chlorine and magnesium for re-use. The titanium sponge mixed with titanium scrap is melted into a primary ingot in water-cooled copper crucibles. If titanium alloys are to be made, then the alloying elements are added at this stage. The primary ingot is re-melted in electric arc furnace to get the final ingot, which is suitable for forging, rolling, drawing, etc. to make the desired products.

Titanium is a silver white coloured strong and light metal having the strength to weight ratio at ordinary temperature exceeding that of both aluminium and steel. It possesses excellent corrosion resistance in atmosphere and salt water, high melting and boiling points (1690^0C and 3535^0C, respectively), poor conductor of electricity (3.1% of standard copper, i.e., International Annealed Copper Standard or IACS) and paramagnetic metal. It burns at 538^0C. By virtue of these properties, titanium is used either as such or in alloy form in aircraft and shipping industries for making many critical components, in racing cars, in orthopaedic appliances, in fast-burning rocket fuel, in titanium carbide (TiC) cutting tools, in permanent magnets etc.

3. Welding: According to the definition of the American Welding Society, “Welding is a metal-joining process wherein coalescence is produced by heating to suitable temperature with or without pressure and with or without the use of filler metal”. The mechanism of welding is based on electron emission. In this, the electron discharge takes place in the form of an arc. When electricity is passed though two electrodes (cathode and anode) in contact with each other, and then the contact is broken by moving them a little away, the resistance and consequently the potential, increases so much that the tips of the electrodes begin to glow. The temperature at the tips increases rapidly, and electron emission takes place. The high energy electrons associated with the temperature ionizes the air in the gap between the electrodes. This ionized air becomes an electrical conductor and current flows from one electrode to the other. This is the mechanism of arc discharge. The temperature of the arc may be of the order of thousands of degrees (20000-50000^{0}C). If the broken pieces of a metal are placed in the arc, then they will fuse and join together, and this process is known as welding. The most common type of welding is arc welding. In this, electrodes (more commonly consumable) made of rods of covered metal are used. The covering serves various electrical and metallurgical purposes. Electrically, the covering insulates the rod from accidental contact with adjacent material and also stabilizes the arc; its metallurgical function is to provide gas- and slag-forming ingredients to protect the weld from the air, and it may also supply de-oxidizers or alloying material resulting in sound welds.

Rutile is used as one of the coating materials for stabilizing the arc by preventing its tendency to sputter and flicker caused by momentary excesses and shortfalls in charge. By virtue of its high dielectric constant and ability to store electrical charge, rutile can momentarily store the excess charge and release the same to make up momentary shortfalls, thus stabilizing the arc.

Rutile should be of very high purity. Iron oxide is the most objectionable deleterious constituent because it counters the efficiency of rutile as an insulating material. The Indian industries specify a minimum of 96% TiO_2 and a maximum of 1.0% Fe_2O_3. but for high performance applications still purer grade containing 98% (min) TiO_2 and 0.1% (max) Fe_2O_3 is preferred.

4. Gem: Gem includes both precious and semiprecious stones. The criteria that make a gem are:

(1) *Rarity*: By the law of demand-supply, the scarcer a commodity is, the higher is its value.
(2) *Durability*: The combination of hardness, toughness and acid-resistance makes a stone durable.
(3) *Colour and optical properties*: Colour, lustre and optical dispersion are the most important parameter of beauty.
(4) *Clarity*: Small bubbles, cracks and other flaws reduce the clarity of a gem, and consequently, its value.
(5) *Cut*: Natural gems are mined as rough stones. They need to be cut into well defined faces and the faces are polished to produce their characteristic sheens and optical effects. The cutting requires a very high degree of skill – particularly when the individual pieces are small. Minimum loss of stone is to be ensured during cutting.
(6) *Specific gravity:* The value/volume ratio depends on this parameter.
(7) *Caratage:The* larger a gem is, the rarer and, hence, more valuable it is. So the individual weight of a piece is important for determining its value.
(8) *Certification*: For a common retail buyer, the physical and optical properties of gems carry little sense, and he is most concerned, besides size, with the colour and sheen as judged with naked eyes. But both these characteristics can be replicated by unscrupulous people. So for him certification by some trusted authority or agency assumes importance.

(9) *Aggressive marketing*: Demand of gems being elastic, almost any gemstone can be sold irrespective of colour and cost, provided the basic criterion of rarity is met.

(10) *Therapeutic value*: Gems are traditionally believed to possess some indirect beneficial effects on body and mind if worn on the body. This branch of therapy known as gemmotherapy works on the hypothesis that different gems, when worn by a man on his body, react differently to different kinds of cosmic rays having different effects on the health of his mind and body. Besides, some gems have been found to produce beneficial effects on human skin.

(11) *Beliefs and superstitions:* Gems, many people believe, bring luck or misery to lives.

(12) *Stability of value*: Economic phenomena like inflation, stagflation, recession and even political instability which exercise adverse impact on other manufacturing and processing sectors, do not affect adversely the demand of gems, particularly the high-value ones.

Generally, the gemstones with hardness of at least 8 are regarded as precious stones. Therefore, strictly speaking, rutile does not qualify to be a precious stone because its hardness is 6.0-6.5 on Mohs scale. But it is otherwise durable by virtue of its massive form and resistance to acids. Its high refractive index, 2.616-2.903 (cf., diamond – 2.42), double refraction giving it a phenomenally high dispersion with an effect of changing colours and its heaviness (specific gravity varying up to 5.2) also go in favour. So, large-sized (5 cm size has been collected) primary crystals of rutile with rich green colour and showing a high degree of dispersion that are scarcely encountered, have been marketed as semiprecious stones.

SUBSTITUTION

1. Synthetic rutile: Titanium dioxide manufactured from ilmenite (containing 52.6% TiO_2 and 47.4% FeO) is called *synthetic rutile* and is used as titanium dioxide pigment and for making titanium metal. It is a popular substitute of natural rutile and is used widely nowadays. The reason for this substitution is that, in comparison to the natural rutile, ilmenite is abundantly available in many beach sands. For example in the beach sands of Florida, USA the ilmentite content is 1.6% (40% of the total heavy minerals) in comparison to only 0.3% rutile and in the beach sands of Kerala, India, the ilmenite content 50-70% is compared to 1-4% rutile. Due to this scarcity, natural rutile is very costly.

Since the difference between ilmenite and rutile is mainly in the percentage of iron oxide, the processes for manufacturing of TiO_2 pigment and titanium metal from ilmenite are the same as those from natural rutile, i.e., sulphate and chloride processes. The only difference is that in case of ilmenite more of the reagent, i.e., sulphuric acid or chlorine, have to be used. In the sulphate process, therefore, more waste acid has to be discharged causing environmental problem. As much as 4 tons of $Fe(SO_4)_2$ for every ton of TiO_2 recovered will be generated as solid waste which will have to be disposed. By comparison, in the chloride process, since the waste chlorine is recovered and recycled and generation of the solid waste comprising $FeCl_2$ is only 1.2 tons per ton of TiO_2, environmental problems are negligible. The sulphate process is therefore not suitable and has been discarded in many countries, and the chloride process is popular in most of the countries for making synthetic rutile from ilmenite.

Since the titanium is regarded as the metal of the future with its demand in aircraft and aerospace industries increasing day by day, all out efforts are underway to reduce its cost of production. Consequently, use of costly natural rutile has practically been discarded and only synthetic rutile is used.

2. Anatase: Anatase can be used interchangeably with rutile depending on availability and cost. Till 1940, anatase was used in USA for crystallizing and precipitating titanium hydrate in the manufacture of TiO_2-pigment. However, it being less stable than rutile, the bright white colour of this pigment used to fade over a period of time. Moreover, its opacity and the resulting covering power was less than that of rutile. So it gave way to rutile in 1942 in the countries where rutile is available. However, where anatase is available and rutile is not, the former can be used as a substitute, albeit inferior, of rutile in the manufacture of the pigment.

Chapter 39

SALTPETRES

Saltpetre (also called *nitre*) is a naturally occurring nitrate. The name has come from medieval Latin “sal petrae” meaning "stone salt". There are three types of saltpetre, namely,

1 Ordinary saltpetre, or potassium nitrate (KNO_3) and generally referred to as ‘saltpetre’ without any prefix;
2 Chile saltpetre or cubic nitre or soda nitre or *nitratine* or sodium nitrate ($NaNO_3$);
3 Lime saltpetre or wall saltpetre or calcium nitrate [$Ca(NO_3)_2$] or Norgessalpetre (*Norwegian saltpetre*) or kalksalpetre

These three saltpetres generally occur as efflorescence caused by the oxidation of nitrogenous matter in the presence of the potassium, sodium or calcium. It is believed that nitric acid formed in the atmosphere after thunderstorms was responsible for deposition of these nitrates on the surface. However, lime saltpetre is very rare in nature. *Nitrocalcite* is a form of calcium nitrate which occurs in nature. It occasionally forms an efflorescence where manure contacts concrete or limestone in a dry environment, as in stables or caverns.

ORDINARY SALTPETRE

History

A variety of gunpowder based on potassium saltpetre, according to a recent research in Munich University (Germany), was in use in Persia during the 6th century. According to the report, it was gifted to Sharva Varman, the Maukhari ruler of Kanauj, India by the Persian ruler Khusrau II in lieu of the secret of a game called *Chaturanga* (an old version of chess played in India during that time).

Prior to the large-scale industrial fixation of nitrogen through the *Haber process*, a major source of potassium nitrate was the deposits crystallizing from cave walls or the drainings of decomposing organic material. Dung-heaps were a particularly common source. Ammonia from the decomposition of urea and other nitrogenous materials would undergo bacterial oxidation to produce nitrate.

Since the late and early modern era through the 19th century, it was widely recovered by crystallization from urine. Potassium saltpetre was originally a sought after material both as a fertilizer and for gunpowder. But in the first use, its importance declined after its sodium counterpart started dominating the market. It has now come to be recognized as an indispensable ingredient for making gunpowder.

In India, potassium saltpetre, which was regularly gathered from sandy areas of Bengal and Bihar, was an important item of export from Bengal up to mid-nineteenth century. It had a huge market in Europe. Consequently, there was intense competition among the Dutch, the English and the French companies who tried to secure as much saltpetre as possible. According to some old records, the total annual export of saltpetre during the 1730s varied between 1,000 and 2,000 tons. Later on, during the period 1791-1805, its average annual export from India peaked at over 80,000 tons. It fell to about 21,000 tons and then to less than 20,000 tons by the end of the 19th century. Thereafter it kept fluctuating between a low of 1,700 tons and a high of 22,000 tons. Production of saltpetre in India was mainly from the North Bihar region, and also for a brief period, from the tea gardens of Assam.

Presently, in some parts of India like Punjab and Haryana, potassium saltpetre is deposited as surface encrustations every year after the rainy season when the atmosphere dries up. The deposition is believed to be by the action of some bacteria which facilitate fixation of the atmospheric nitrogen and oxygen and their reaction with the potassium present in the soil. Every year during summer, these encrustations are “harvested”. After rains, they again start depositing. Thus it is one of the two examples of “renewable” mineral resource (the other one is groundwater).

Critera of Use

(a) Potassium nitrate contains 13% K and 44% N.
(b) It is difficult to dissolve in water, but it does go into solution slowly over a period of time releasing a little potassium and relatively more amount of nitrogen.
(c) It easily releases one atom of oxygen and it does so with such rapidity that if there is any combustible material on fire, it will cause violent deflagration.
(d) By virtue of its ability to release oxygen, it is a strong oxidizing agent.
(e) It is soft (hardness 2 on Mohs scale) and it crumbles into powder easily.

Uses

The principal uses of potassium saltpetre are:

1 Gunpowder (propellant)
2 Manufacture of nitric acid
3 Glass
4 Fertilizer

These uses are discussed as follows.

1. Gun powder (propellant): *Propellant* is the general name for gun powders. In common types of propellant or gunpowder, 75% of potassium nitrate is nixed with 15% powdered charcoal (substantially carbon) and 10% sulphur. Gunpowder is an explosive with relatively low detonation velocity and requiring ignition. The reaction products of the mixture are mostly gases occupying a much larger volume. In a confined space, the gases generate enormous pressure forcing the projectile out of the barrel.

The sulphur and charcoal are ground together dry so that the thixotropic (thixotropy is the property of pseudoplastic fluids showing time-dependent change in viscosity) sulphur thoroughly coats the active surface of the charcoal. Then the nitrate is added, and the mix is wet ground until homogenized. The dried mix is formed into grains of the desired size, and the powder is ready for filling of cartridges, fireworks, blasting fuses etc.

Potassium nitrate acts as an oxidiser, rapidly releasing oxygen to burn the carbon and sulphur to their respective oxides, and the process generates heat causing ignition. It provides that oxygen by virtue of its ability to release oxygen easily. Once the charcoal is ignited, it rapidly and violently catches fire and burns the non-inflammable sulphur for rapid generation of the gases, which, in a confined space, generates great explosive force. Gunpowder is used in firecrackers, cannons, rifle cartridges, rockets, etc.

2. Nitric acid: One of the most useful applications of potassium nitrate is in the production of nitric acid. Concentrated sulphuric acid is added to an aqueous solution of potassium nitrate, yielding nitric acid and potassium hydrogen sulphate (or potassium bisulphate) which are separated through fractional distillation.

3. Glass: Physically, common standard glass is an amorphous, hard, brittle and transparent substance and chemically, it is a mixture of the silicates of sodium, calcium and magnesium. The composition of typical ordinary glass is [$18Na_2O.2MgO.8CaO.72SiO_2$]. Essentially, the process of manufacture of glass consists in melting a mixture of 47% silica sand, 14% soda (Na_2CO_3), 12% dolomite ($CaCO_3.MgCO_3$), 3.5% limestone ($CaCO_3$), 2.5% carbon (coke) and the balance broken waste glass (called *cullet*) at 1400-1500^0 C, and then cooling it first to a thick viscous liquid at 800-900^0 C and then rapidly quenching this thick liquid to a solid glass product. A little of sodium sulphate (Na_2SO_4) and feldspar may be added to the charge for process control and for adjusting the composition of the final glass. But among the various types of glass, there are two potash-rich types:

- *Jena glass*: This is a potash-lime glass. It is hard and used in chemical laboratory ware.
- *Lead crystal or flint or cut glass*: It is a lead-potash glass. It is lustrous with high refractive index. Due to its lustre, brilliance and sparkle this glass is used for ornamental purpose and for making superior tableware. In old times, due to its high refractive index, it was used for making some kind of lenses also.

Potassium nitrate and carbonate are added to the raw material mix for making of these types of glass (see also the chapter on silicon for details).

4. Fertilizer: Nitrogen, phosphorus and potassium (commonly referred to as N-P-K) along with calcium are essential for plant growth. These four principal elements are so interrelated that deficiency of even one of them in the soil affects the ability of a plant to assimilate the others. This saltpetre is not popular in this application because it is not readily soluble in water (water-solubility is the most important criterion for conventional fertilizers). Nevertheless, it was and is used as a component in some fertilizers as a source of both potassium and nitrogen, mainly where potash, the main potassium fertlizer is not easily available or is costly. When used by itself as a fertiliser, potassium saltpetre has an NPK rating of 13-0-44 (indicating 13%, 0% and 44% of nitrogen, phosphorus, and potassium, by mass, respectively). Sometimes, a mixture containing two-thirds Chile saltpetre and one-third potassium saltpetre is used to serve the dual purpose of supplying nitrogen and potassium to the soil while, at the same time, the problem of difficult water-solubility of the latter is partially addressed.

In an Israeli technology called *fertigation*, the insoluble potassium nitrate can be used as an effective fertilizer. In fertigation, fertilizer and irrigation are combined. Fine powders of KNO_3 are mixed with water and sprayed on the leaves (folial spray). The nitrogen and the potassium are readily absorbed by the leaves and transported to all parts of the plant especially the growing sites like new leaves, young fruits, shoots and root tips. The technology has been applied successfully for inducing unseasonal flowering in mango trees in Philippines.

The softness of saltpetre facilitates grinding of it to a fine powder easily, and thus it can be made into a fine spray.

5. Other uses:

(a) Beverage and ice-cream: As a cooling agent.
(b) Smoke bombs: In these, its mixture with sugar produces a smoke cloud of 600 times their own volume. The ratio for *smoke bombs* using sucrose or powdered sugar ($C_{12}H_{22}O_{11}$) and potassium nitrate is 2:3. It can be used as is, or carefully melted together using a hot plate.
(c) *Food preservation*: In this, potassium nitrate has been a common ingredient of salted meat. Its derivative potassium nitrite inhibits the growth of the botulism-causing bacterium *Clostridium botulinum* and fixes the colour of the meat. It is also used in curing of meat.
(d) Tree-stump removing: It forms a major ingredient in the chemicals for accelerating the natural decomposition of stumps.
(e) Toothpaste: It has been used in the manufacture of some toothpastes for sensitive teeth although its efficacy to help dental hypersensitivity has not been conclusively proved.
(f) Matches: In the past it was used for burning fuse technologies including *slow matches*.

Waste Utilization

Wastes from purification of crude saltpetre can be used for recovering potash. Crude saltpetre (KNO_3) contains NaCl, KCl, K_2SO_4, $CaSO_4$, and $MgSO_4$ as impurities. After KNO_3 is recovered from crude saltpetre, all these impurities and a little KNO_3 go into the waste. The Central Salt and Marine Chemicals Research Institute (CSMCRI), India conducted experiments in 1964-65 with a sample containing 53.1% NaCl, 31.6% KCl, 8.7% K_2SO_4, 0.8% $CaSO_4$, 1.1% $MgSO_4$, 1.4% KNO_3, 1.3% insolubles and 2% moisture. This material was boiled at 112^0C with a saturated NaCl-KCl solution. The KCl of the waste material went in solution and rapidly filtered in vacuum while the other constituents were left in the residue. On cooling crystals of pure KCl were obtained. The mother liquor was recycled for a repeat of the experiment. Since now the material has a higher concentration of K_2SO_4, crystals of this salt along with that of the unrecovered KCl were obtained at the end of the second experiment.

Substitution

1. Synthetic potassium saltpetre:

(a) Historically, nitre-beds were prepared by mixing manure with either mortar or wood ashes, common earth and organic materials such as straw to give porosity to a compost pile typically 1.5 metres high by 2 metres wide by 5 metres long. The heap was usually under a cover from the rain, kept moist with urine, turned often to accelerate the decomposition and leached with water after approximately one year. The liquid containing various nitrates was then converted with wood ashes to potassium nitrates, crystallized and refined for use in gunpowder.

(b) In another practice also in vogue in olden times, urine was collected and used in the manufacture of gunpowder. Stale urine was filtered through a barrel full of straw and allowed to continue to sour for a year or more. After this period of time, water was used to wash the resulting chemical salts from the straw. This slurry was filtered through wood ashes and allowed to dry in the sun. Saltpetre crystals were then collected and added to brimstone (impure ore of sulphur) and charcoal to create black powder.

(c) The Central Salt and Marine Chemicals Research institute (CSMCRI), India has developed a process to prepare high purity potassium nitrate (99.5% purity) with 90-92% yield utilizing potassium sulphate, limestone and nitric acid as raw materials.

2. Guano: Guano is a kind of excreta of birds which are found in coastal areas, sea islands and caves. The composition of a typical fresh guano was analyzed to be 7.3% nitrogen, 1.5% phosphorus, 60% moisture and 31.2% other substances. Potassium nitrate could be harvested from accumulations of bat guano in caves. This was the traditional method used in Laos for the manufacture of gunpowder for *Bang Fai rockets*. Peruvian guano is extensively used as an organic fertilizer, as a source of nitrogen.

3. Sodium saltpetre: Today, most potassium nitrate is made from natural sodium nitrate ($NaNO_3$, nitratine) mined in the Chilean deserts. The sodium nitrate is purified and then reacted in solution with potassium chloride (KCl, sylvite), from which the less-soluble potassium nitrate is precipitated out.

CHILE SALTPETRE

History

The world's largest natural deposits of *caliche* (an impure mixture of several chemical compounds including sodium saltpetre) were in the Atacama desert of Chile, and many deposits were mined for over a century, until the 1940s. The former Chilean saltpetre mining areas of Humberstone and Santa Laura have been declared by the Unesco as World Heritage sites in 2005. Chile still has the largest reserves of caliche, with active mines in such locations as Pedro de Valdivia, Maria Elena and Pampa Blanca. Sodium nitrate, potassium nitrate, sodium sulphate and iodine are all obtained by the processing of caliche.

Sodium nitrate (or soda nitre, $NaNO_3$), is commonly called Chile saltpetre after its mineral deposits in northern Chile, the principal source. Enormous deposits of this kind of saltpetre are found in the desert region near the boundary of Chile and Peru. These deposits can be 3 kilometres wide, 300 kilometres long, and up to 2 metres thick. The dry climate of the area had permitted the accumulation and preservation of huge quantities of high-quality sodium saltpetre along with guano (the composition of a typical fresh guano was analyzed to be 7.3% nitrogen, 1.5% phosphorus, 60% moisture and 31.2% other substances) deposits over thousands of years.

The discovery during the 1840s of their use as fertilizer and as a key ingredient in explosives made the area strategically valuable. Initially, guano was in the limelight. The USA passed a law (Guano Islands Act) in 1856 enabling its citizens to take possession of unoccupied islands containing guano. World powers started directly or indirectly vying for control of the area's resources. Peru later nationalized guano exploitation during the 1870s. Spain had seized Peruvian territory, but was repulsed by Peru and Chile fighting as allies during the *Chincha Islands War.*

Later on, Bolivia, Chile and Peru had suddenly found themselves sitting on the largest reserves of a resource (sodium saltpetre) that the world needed for economic and military expansion. The *War of the Pacific*, sometimes called the *Saltpetre War* in reference to its original cause, was fought between Chile and the joint forces of Bolivia and Peru, from 1879 to 1884. Chile gained substantial mineral-rich territory in the conflict, annexing both the Peruvian province of Tarapaca and the Bolivian province of Litoral, leaving Bolivia as a landlocked country.

Criteria of Use

Chile saltpetre is a white substance having specific gravity 2.26. It is also found in the form of colourless trigonal crystals. It melts at 307^0C. But the most important properties determining its use are as follows:

(1) It is soft with hardness 1.5-2.0 on Mohs scale (slightly softer than ordinary saltpetre), and can easily become powdery.

(2) It decomposes at 380^0C releasing the NO_3 radical.

(3) It is an oxidizing agent capable of releasing one oxygen atom, but with much less ease and rapidity than potassium saltpetre.

(4) It is soft and, contrary to potassium saltpetre, it is easily and highly soluble in water, its solubility being 87.4 gm per 100 ml of water at 25^0C.

(5) It is mildly poisonous for human beings. If consumed or exposed to in large quantities, it may cause abdominal pain, respiratory problem or irritation of eyes and skin. It is also associated with the formation of an alleged carcinogen.

Uses

The principal uses are:

1 Fertilizer
2 Agriculture
3 Preservation and curing of food
4 Human health
5 Glass
6 Enamel
7 Nitric acid

1. Fertilizer: Sodium saltpetre is an important source of nitrogen (one of the essential four elements — N, P. K, Ca — necessary for survival and growth of plants) and this is its most important use. Nitrogen in the form of ammonia is used by plants and microbes as a building block for the synthesis of amino-acids and other nitrogenous compounds. Wherever intensive agriculture was practiced, there arises a demand for nitrogen compounds to supplement the natural supply in the soil. Chile saltpetre being plentiful was and is being imported by many countries for this purpose. Sometimes, a mixture containing two thirds Chile saltpetre and one third potassium saltpetre is used to serve the duel purpose of supplying nitrogen and potassium to the soil while, at the same time, the problem of difficult water-solubility of the latter is partially addressed.

2. Agriculture: Chile saltpetre is used for top-dressing of soil for providing the Na-ions to sugar beets and fruits during early winter as a prevention against damage due to frost. Additionally, it supplies the nitrogen also.

2. Preservation and curing of food: In addition to retarding spoilage, some preservatives have an aesthetic role — that is, they improve the appearance of the product. An example of one such preservative is sodium nitrate (or its nitrite form). It is used in the curing of meats to prevent the development of botulism-causing bacterium *Clostridium botulinum* and fixes the colour of the meat. It is irreplaceable in the prevention of *botulinum* poisoning. Its poisonous nature is the criterion.

It is also used in curing of ham and is added to sugar in the curing mixture. It improves the flavour and texture of the meat, which most consumers prefer to the plain salt-cured product. But due to its harmful effect on human beings when used in large quantities, its usage is carefully regulated in the production of cured products and its concentration in finished products is limited to 200 ppm in USA.

3. Human health: It is found naturally in leafy green vegetables. It has possible health benefits for increasing oxygen to blood by virtue of its capability to easily release one oxygen atom.

4. Glass: Physically, common standard glass is an amorphous, hard, brittle and transparent substance, and chemically, it is a mixture of the silicates of sodium, calcium and magnesium. The composition of typical ordinary glass is [$18Na_2O.2MgO.8CaO.72SiO_2$]. Essentially, the process of manufacture of glass consists in melting a mixture of 47% silica sand, 14% soda (Na_2CO_3), 12% dolomite ($CaCO_3.MgCO_3$), 3.5% limestone ($CaCO_3$), 2.5% carbon (coke) and the balance broken waste glass (called cullet) at 1400-1500^0 C, and then cooling it first to a thick viscous liquid at 800-900^0 C and then rapidly quenching this thick liquid to a solid glass product. A little of sodium saltpetre may be added to the charge as a supplement to the soda and for supplying oxygen for the reactions. Its ability to decompose into sodium and nitrate molecules at a low temperature of 380^0C is the criterion.

5. Enamel: Chemically, enamel is a complex mixture of silicates, borates and fluorides of some metals like sodium, potassium, aluminium, etc. It is a glaze coating on metallic surfaces so as to give protection to the latter against high temperature and corrosion. It is prepared by mixing borax ($Na_2B_4O_7.10H_2O$), quartz, feldspar, fluorspar, soda (Na_2CO_3), sodium nitrate, oxides of cobalt, manganese and nickel and an opacifier substance (e.g., tin oxide, titanium silicate, antimony trioxide). This mixture is ground, melted and quenched in water to yield a glassy mass. To this glass are added clay and more quartz powder and the mixture is finely ground to powder and made into a slurry with water. This is called *"enamel slip"*. Metallic objects are dipped in it and fired to about 900^0 C. Two to three of such enamel coats are usually applied. Sodium saltpetre is sometimes added as a supplementary source of sodium. Its ability to decompose into sodium and nitrate molecules at a low temperature of 380^0C is the criterion.

6. Nitric acid: One of the most useful applications of sodium nitrate is in the production of nitric acid. Concentrated sulphuric acid is added to an aqueous solution of sodium nitrate, yielding nitric acid and sodium hydrogen sulphate (or sodium bisulphate) which are separated through fractional distillation.

7. Other uses::

(a) Dynamite: Various nitrate-based derivatives like nitroglycerine or glycerol tri-nitrate, nitrocellulose, nitroglycol, ammonium nitrate, etc. form the ingredients of different kinds of dynamite with different shattering power suited to different applications. Sodium saltpetre is used either as one of the components or for making those other compounds.

(b) Rocket propellant: Sodium nitrate has been used as an ingredient, as a provider of oxygen. But it is not as popular as its potassium counterpart because compared to the latter, it releases oxygen slowly generating much less violent force of explosion.

(c) Charcoal briquetting: Due to its softness and high solubility in water, it can be made into a soft paste for binding charcoal briquettes. In addition, its ability to release oxygen improves the burnability of the charcoal.

(d) Steel heat treatment: Chile saltpetre is used as a component in the molten salt mixture.

Substitution

1. Ammonia: With increasing understanding of the importance of fixed nitrogen to growing plants, ammonia (NH_3) released during manufacture of coke from coal started being recovered for use as a nitrogenous fertilizer (ammonium sulphate). This ammonia was found to be very cheap as otherwise it used to be wasted. Consequently, the value of sodium saltpetre declined dramatically in the first decades of the twentieth century.

2. Organic manure: After generation of biogas, the residue that is left in biogas plants, is a nitrogenous manure. The advantage of this manure vis-à-vis coal-based fertilizer is that its production is very cheap and environment-friendly, and also it is porous with high capacity to hold water. Such manure is even otherwise made extensively by leaving cow dung in the open and allowing it to dry.

3. Chemical fertilizers: Nowadays various nitrogen-rich fertilizers are manufactured chemically. Some of these fertilizers combine nitrogn with phosphorus making them more effective plant nitrients (see also the chapter on phosphorus). These are as follows.

(a) *Ammonium nitrate*: Now ammonia is manufactured by Haber-Bosch process using hydrogen gas, atmospheric nitrogen and heat energy. This industrially fixed ammonia is used for production of ammonium nitrate a chemical fertilizer of today.

(b) *Mono-ammonium phosphate(MAP)*: It is a rich source of phosphorus and supplies both phosphorus and nitrogen to the soil. It contains about 55% P_2O_5 and 11-12% N.

(c) *Di-ammonium phosphate(DAP)*: It also supplies both phosphorus and nitrogen—but more of the latter compared to MAP — to the soil. It contains about 46% P_2O_5 and 18% N.

(d) *Ammonium phosphate sulphate (APS)*: Its basic composition is 60% ammonium sulphate and 40% ammonium phosphate. This mixture contains 20% P_2O_5 and 16% N.

(e) *Nitro-phosphates(NP)*: The term nitro-phosphate covers a range of fertilizers containing P and N obtained by treating rock phosphate (34% P_2O_5 and 1.5:1 CaO/P_2O_5) with nitric acid (53-60% concentration) and ammonia. A typical nitro-phosphate contains 20% of each N and P_2O_5.

(f) *Urea ammonium phosphate (UAP)*: This group of fertilizers are manufactured by using urea, ammonia and phosphoric acid. First, phosphoric acid is neutralized by ammonia to form ammonium phosphate to which more ammonia and urea are added to augment the nitrogen content. A typical UAP contains 24-28% of each N and P_2O_5.

Though these provide relatively more nitrogen in a soluble form, they are costly — usually beyond the reach of ordinary farmers of the developing countries.

4. Biofertilizer: Next to photosynthesis, the most important biological process taking place on the earth is *nitrogen fixation*. The atmosphere contains 79% nitrogen, but not in the form that plants can make use of it. It has been estimated that 100-200 million tons of nitrogen are turned over on the earth each year biologically. In this process, atmospheric nitrogen is converted into ammonia which is rapidly assimilated by plants and converted into organic nitrogen compounds by the metabolic processes of the cell. In biofertilizers, some nitrogen-fixing micro-organisms are made use of. Such micro-organisms belong to two groups — free living bacteria and blue green algae. Examples of the former are *Azolla*, *Azolobacter* and *Azospirillum* while those of the latter are *Rhizobium* and *Anabaena*. All these micro-organisms live in the soil, but all of them are not suitable for all types of plants. The right micro-organism is selected and taken out for making plant-specific inoculum. Once the soil is enriched through inoculation with the right strain of biofertilizer, the plants can themselves fix atmospheric nitrogen to fulfil their requirements.

5. Synthetic Sodium nitrate: Sodium nitrate is also synthesized industrially by neutralizing nitric acid with soda ash ($NaNO_3$)

6. Guano: Guano is a kind of excreta of birds which are found in coastal areas, sea islands and caves. The composition of a typical fresh guano was analyzed to be 7.3%

nitrogen, 1.5% phosphorus, 60% moisture and 31.2% other substances. Peruvian guano is extensively used as an organic fertilizer — as a source of nitrogen.

LIME SALTPETRE

Lime saltpetre [Ca(NO3)2] is very rare in nature. Some efflorescence deposits of a form of calcium nitrate called Nitrocalcite is occasionally found.

Criteria of Use

$Ca(NO_3)_2$ is a white coloured *salt*. It is commonly found as a monohydrate, with the formula $Ca(NO_3)_2.H_2O$. It is deliquescent, readily absorbing moisture from the air, and with excess water it forms a soluble salt.

Uses

1. Fertilizer: Nitrogen, phosphorus and potassium (commonly referred to as N-P-K) along with calcium are essential for plant growth. These four principal elements are so interrelated that deficiency of even one of them in the soil affects the ability of a plant to assimilate the others. Calcium nitrate, being a water-soluble salt, is easily assimilated by the roots of plants for getting both calcium and nitrogen. There are two fertilizer grade formulations of calcium nitrate commonly marketed:

(a) With some ammonium nitrate and water incorporated in the molecular structure as $5Ca(NO_3)_2.NH_4NO_3.10H_2O$. Its N-P-K-Ca content is 15.5-0-0-19;
(b) Without ammoniun nitrate in the molecular structure as $Ca(NO_3)_2.3H_2O$. Its N-P-K-Ca content is 12.8-0-0-18.3.

Calcium nitrate fertilizer is popular in the *greenhouse* and *hydroponics* (a technique of growing plants without soil, in water containing dissolved nutrients).

2. Explosive: It is used as a secondary nitrate in emulsion explosives containing ammonium nitrate solution as the primary nitrate (an emulsion is a dispersion of liquid in another immiscible liquid). Calcium nitrate improves the quality parameters of the emulsion in the following ways:

(a) It extends the shelf life of the emulsion
(b) It increases the solubility of the ammonium nitrate
(c) It increases the total energy content of the emulsion.

3. Other uses:

(a) Deliquescent reagent

(b) Pyrotechnics
(c) Incandescent mantle
(d) Matches
(e) Radio tubes (as a deliquescent)
(f) Corrosive inhibitor in diesel fuels

Substitution

Calcium nitrate being rare in nature, is widely used as a manufactured commodity. It was the first nitrogen fertilizer compound to be manufactured and its production commenced at Notodden, Norway in 1905. Most of the world's calcium nitrate is now made in Porsgrunn. Hydrated calcium nitrate is prepared by neutralizing nitric acid with calcium carbonate. The anhydrous substance, a white deliquescent compound very soluble in water, is obtained from the hydrate by controlled heating (it decomposes on strong heating into calcium oxide, nitrogen dioxide, and oxygen).

Chapter 40

SILICON AND ITS MINERALS

The nonmetallic element silicon is the most widely distributed substance in the earth's crust next only to water, and so is its compound silica (SiO_2) whose incidence is 12 percent. Silica may be either reactive or nonreactive (free silica). The former occurs in the form of silicates which are ingredients in a number of minerals and rocks. It is the free silica occurring in various forms that is the concern in this chapter, because some of its forms, each named differently, are of economic importance either as a source of silicon or as silica as such.

TYPES OF SILICA

The common name for silica is quartz. Mineralogically, quartz is classified into two broad divisions based on degree of crystallization. These are: (a) Phenocrystalline (large crystal embedded in a fine grained mass) and (b) Cryptocrystalline (intrinsically crystalline but apparently massive). This classification, however, has no economic significance. There are some commonly encountered terms used to indicate different types of naturally occurring silica, each of which is important from the economic point of view. These can be grouped as follows.

1 Quartz

- (a) Crystal quartz
- (b) Amethyst
- (c) Citrine
- (d) Tiger-eye
- (e) Smoky quartz
- (f) Rose quartz
- (g) Chalcedony
- (h) Flint (including its impure variety called chert)
- (i) Onyx
- (j) Agate Jasper
- (k) Blood stone
- (l) Star stone

   (m) Plasma
   (n) Aventurine

2 Opal
3 Sand

   (a) Silica (or glass) sand
   (b) Building and stowing sand
   (c) Moulding (or foundry) sand

4 Quartzite

   (a) Fragmented pieces
   (b) Massive blocks

There are many other terms used for different variations, but they are either extremely rare or not of any economic significance. This classification is based on a combination of factors like degree of crystallization, morphology, mode of occurrence, colour, lustre and industrial usage. Of these, crystal quartz, amethyst, citrine, Tiger Eye, smoky quartz, rose quartz, bloodstone, star stone and aventurine are phenocrystalline while flint, onyx, agate, jasper and plasma are cryptocrystalline. But chemically, the basic and predominant composition of all is SiO_2 . The last one namely quartzite in massive block form is not used as a source of silica or silicon, but as a building stone and is covered under the section "Industrial Rocks" in this book. The distinguishing features amongst the broad types are as follows.

1 Quartz: Silica is in the form of single mineral pieces – crystalline or cryptocrystalline. It may be colourless (as in the case of crystal quartz) or of different colours and shades depending on inclusions present. The small fragments and powders of crystal quartz retrieved from mining rejects, constitute what is called fusing grade quartz or "*lasca*". By fusing lasca, a product called "*fused quartz*" can be obtained.
2 Opal: In addition to SiO_2, it also contains 3-9% water and small amounts of some impurities like ferric oxide, alumina, magnesia and alkalis. Its general composition is $SiO_2.nH_2O$. In contrast to quartz, opal is amorphous (i.e., colloidal).
3 Sand: According to the definition of the American Society of Testing Materials (ASTM), sand is naturally occurring unconsolidated or poorly consolidated rock particles ranging in size from 0.074 mm to 4.75 mm, and gravel is similar rock ranging in size from 4.75mm to 76.2 mm. But according to many sedimentary petrologists, sand is an unconsolidated granular material coarser than 1/16th of a millimetre and finer than 2 mm (cf. granular gravels are of 2-4 mm size and gravels more than 4 mm). Silica sands are such materials resulting from natural disintegration of siliceous rocks. Sand ground to particles to less than 45 microns (may even be as fine as 0.5 micron) size is called "*silica flour*".

4 Quartzite: Silica is in the form of very fine grains constituting a massive compact rock. It is a metamorphic rock, and due to metamorphism, the silica is in the form of stable 'cristobalite' which forms at 1470^0 C.

Besides these natural sources of silica, certain industrial wastes made up of high-purity silica are also of economic significance. This variety of silica is called "*silica fume*" or "*micro-silica*" or "*fluffy silica*" or simply "*silica dust*". It is the waste material generated as smoke or fume from ferrosilicon, semiconductor and other industries. It is amorphous, lightweight, nanometre-sized, fluffy and free-flowing silica powder having specific surface area of the order of 22000 m^2/kg. It is non-injurious to marine, animal and plant kingdom and is non-toxic.

HISTORY

Flint was the oldest mineral used for some economic purpose, its usage dating back to the times when the evolution of man was still in the Homo erectus stage. Axes fashioned out of flint as early as 700000 years ago have been discovered in Tanzania. Much later, during the Paleolithic Period (10,000-50,000 years ago), use of axes, arrow-heads and other implements made out of the hard sharp-edged pieces of flint became common for hunting animals, cutting and tearing hides etc.—the main economic activities of the prehistoric men then. Early man also used pointed flints to scratch pictures on cave walls. Certainly, during those times, flint used to be picked up from the ground or dug out from the outcrops. But long after man gained knowledge of copper (12000 BC) or even after the advent of Copper age (6000 BC) and of Bronze age (3000 BC) in some parts of the world, it seemed that flint still played an important role in human life in certain other parts. This is apparent from the discovery of an old 9-metre deep shaft dating back to 2500 BC. in Norfolk, UK. The shaft was sunk cutting though chalk, up to a flint deposit suggesting that the miner was not interested in chalk, but only in flint.

Next to flint it was probably building sand that was mixed with lime and used extensively for construction of buildings. Glass came much later. It was accidentally made in Syria in 368 BC by a group of sailors who was cooking food using soda ash on the sands of a river bank. After putting out the fire they found that a new material had formed as a result of the combination of soda ash and sand below the fire. They probably did not immediately know what this new material was good for. But today we know that it was a kind of crude glass. But there are historical records pointing to use of some kind of glass in the form of bangles in India before the beginning of the Mourya period (321 BC). But the real impetus for modern glass began in the 2nd century BC in Egypt where Alexandrian craftsmen used glass for making various decorative designs. The art of glass-blowing and moulding into different shapes was known to the Romans in the 1st century AD. The Romans also introduced the technique of making coloured glass. During the 9th and 10th centuries, stained glass art (an intricate art form created by fusing together pieces of coloured glass) flourished in the Roman empire of Europe. By 13th century, Venice became the most important centre of glass-making, and from here the art spread to England, Bohemia etc. with developments of more and more improved varieties.

Use of certain varieties of quartz and opal as gemstones was known to the women and the artisans of the old civilizations of Mohenjodaro and Harappa during the 3rd millennium BC.

Those artisans excelled in cutting, polishing, boring and fashioning beads of such gemstones into beautiful necklaces and girdles. In recent times this market of quartz and opal gemstones started being rediscovered since around 1975, and such gems are again gaining popularity.

The high-tech applications of quartz have been developed only in the 20th century. Since 1921, its suitability in electronics has become known, and silicone has been invented only recently.

RECOVERY OF SILICON

Elemental silicon is produced either by what is known as carbothermic process or by electrolytic process.

(a) *Carbothermic process*: In this process, quartz is reduced by carbon at 1700^0 C. The carbon provides heat and it also serves as the reductant. The silica should be more than 98% pure. This process is relatively cheap and is widely practiced. The silicon produced is of 98% purity and suitable for metallurgical purpose.

(b) *Electrolytic process*: This process is carried out in an electric arc furnace (EAF). Molten calcium chloride ($CaCl_2$) is used as the electrolyte and the furnace as the anode. As regards the cathode, earlier, quartz was used, but now it is replaced by its powders which have been briquetted and then sintered. Electric current is passed to the silica through tungsten wire. Silica itself is an insulator. But at the point of its contact with the tip of the tungsten, it breaks up into molten silicon and oxygen. The silicon, being an electrical conductor (albeit weak), conducts electricity to its boundary with the surrounding solid silica which melts at the zone of contact. This way the process of decomposition of silica to silicon propagates throughout the entire charge of silica. Quartz is not very amenable to this propagation as it is not porous so as to allow the initial free spreading of the molten silicon. That is why nowadays porous lumps of sintered silica powder are used into the pores of which molten silicon can enter creating more points of contact with solid silica. The silicon recovered by electrolytic process is purer than that by carbothermic process.

CRITERIA OF USE

1. Physical criteria: Both quartz and opal are hard and tough minerals. Hardness of quartz is 7 in Mohs scale and that of opal is 5.5-6.5. Quartz being practically devoid of cleavage and opal being amorphous, both are resistant to breakage. Crystals of quartz are highly elastic. Although due to these properties, crushing and grinding of quartz is costly, the naturally ground sand is available in plenty. Quartzite, being fine-grained and compact, is available in hard and lumpy form. Powders of quartz or sand bond well with clay, lime and cement. Specific gravity of quartz is about 2.65.

2. Colour and optical properties: Pure quartz (crystal quartz or rock crystal) is transparent with vitreous lustre, while chalcedony is white and translucent with soft waxy lustre. Other varieties of quartz have varying colours and shades due to inclusion of foreign matter that entered into them at the time of crystallization. Some typical colours are:

(a) Amethyst (“Jamunia” in Hindi): Clear purple to violet believed to be due to presence of manganese inclusion.
(b) Citrine (“Sunyla” in Hindi): Yellow; due to this colour it resembles yellow topaz and hence also called “false topaz”.
(c) Smoky quartz (“Dhunyla” Hindi): grayish to brownish black believed to be due to inclusion of organic matter.
(d) Rose quartz (“Roji” in Hindi): Pink believed to be due to inclusion of titanium.
(e) Tiger-eye (“Chitti” in Hindi): Earlier called Cat’s-eye, but now, to avoid confusion with the highly priced variety of chrysoberyl by the same name, it is called Tiger-eye; it shows different colours when seen from different angles (opalescence) due to the effect of asbestos fibers included in it.
(f) Onyx (“Sulemani” in Hindi): Layers of white alternating with those of black, red etc; sometimes spots of white in black.
(g) Agate : May be red coloured (“Emni” in Hindi) or white with red bands of varying designs like dendrites and irregular patches (“Hakeek” in Hindi); the designs are due to presence of impurities like manganese oxide.
(h) Blood stone (“Pitounia” in Hindi): Red spots on green.
(i) Star stone or Star quartz (“Sange Sitara” in Hindi): Whitish or variously coloured star-like radiation supposed to be due to presence of submicroscopic needles of some mineral as inclusions arranged in a unique manner.
(j) Plasma: Red
(k) Aventurine: Green.
(l) Opal: It shows a rich play of different colours like white, yellow red, brown, blue, green etc.; the dark colours are due to foreign inclusions, and the play of colours is produced by subtle variations in refractive index of different layers within combined with microscopic cracks in the layers.

These colours and visual effects make some of the pieces of quartz and opal very attractive. The refractive index of quartz is low, 1.55, and that of opal is still lower, 1.45, (cf. glass 1.54), and consequently these minerals lack brilliance of lustre.

3. Thermal properties: The low-temperature quartz is called ‘alpha-quartz’. It transforms into ‘beta-quartz’ on being heated to 573^0C which, in its turn, takes the form of ‘tridymite’ above 870^0 C. On further heating to 1470^0 C, this tridymite passes over into the stable form called ‘cristobalite’. All these transformations are accompanied by changes in crystal structure and some optical properties, but the stability of cristobalite makes it strongly resistant to thermal shocks. Of the different varieties of quartz, flint transforms to cristobalite more readily than others. Pure quartz melts at 1700^0 C, but the melting point varies with degree and nature of impurity. Loose silica sand melts at a lower temperature of 1580^0 C. Elemental silicon melts at 1414^0 C and boils at 2900^0 C.

4. Electrical properties- Silica is an electrical insulator with low dielectric constant of 4-12 indicating weak electrical conductivity (cf., value for air, one of the poor conductors of electricity, is 1). However, when in pure crystal form, it shows piezoelectric properties. The elemental silicon is a semiconductor.

i. *Semiconductivity*: Semiconductors are materials with resistivity intermediate between metals (resistivity < 10^4 ohms/cm) and insulators (resistivity >10^3 ohms/cm). Their atoms are generally tetravalent. They contain only a small number of loosely bonded electrons at room temperature, and hence their conductivity is very poor (of the order of 100,000 times less than that of conductor metals). However, their low electrical conductivity can be substantially improved by bombarding them and incorporating within them ions of some foreign substance of a different valency – either lower (say trivalent) or higher (say pentavalent), which act as points of disturbance releasing charge carriers (negative charge by free excess electrons or positive charge by what are called *holes* formed due to vacancies created by deficiency of electrons). This process is called '*doping*'. Boron (trivalent) is such a dope for silicon, and one part in ten thousand of boron can increase the conductivity of silicon one million times. Another characteristic of semiconductors in general is that their properties can be controlled by supplying some external energy (e.g., optical energy, thermal energy). When optical energy excites this semiconductivity, the substance is called '*photovoltaic*'. Elemental silicon is photovoltaic and is capable of acting as a very good semiconductor.

ii. *Piezoelectricity*: Piezoelectric crystals can change alternating mechanical strains into electrical impulses and vice versa. This property is also called '*electrostriction*'. Such a crystal must not have a centre of symmetry. When pressure is applied, its ions are displaced resulting in polarization of the crystal and flow of electric current when circuit is complete. In other words, mechanical force is converted into electrical energy, and if the force is alternate (e.g., sound vibrations) causing alternating contraction and expansion, then the electric current becomes oscillatory. Conversely, if oscillatory current is applied to the crystal, it will set up a cycle of alternate expansion and contraction i.e. vibration. Quartz has the highest known efficiency of transfer of energy back and forth between strain and motion. This efficiency is expressed by *'Q' factor* which is defined as the ratio of energy stored to energy dissipated. The higher the Q, the lower will be the energy losses. The Q of quartz is very high – hundred times higher than that of the best resonant electrical wire circuits. This is also related to the high elasticity of quartz crystals.

5. Chemical affinity: Silica can react with other elements and radicals to form inorganic and organic chemical compounds. Quartz and borax together dissolves slowly to a clear glass. Quartz is not affected by hydrochloric acid and caustic soda or potash affects it only weakly. It is soluble in boiling soda (Na_2O_3). Silicon has strong affinity for oxygen.

5. Alloyability: Silicon is one of a few nonmetals that can form alloys with different metals.

6. Therapeutic value: Certain varieties of gems are believed to possess some indirect beneficial effects on body and mind if worn on the body. This branch of therapy known as gemmotherapy works on the hypothesis that different gems, when worn by a man on his body, react differently to different kinds of cosmic rays having different effects on the health of his mind and body. It is a scientific fact that mesons produce cosmic rays which come from outside the earth in varied intensities every minute, and day and night about 600 rays pass through our body. Gemmotherapists believe that each kind of cosmic ray has some specific effect on human health, and these effects are modified by different gems which preferentially absorb or transmit specific rays.

7. Psychological criteria:

(a) *Aggressive marketing*: Almost any gemstone can be sold irrespective of colour and cost, provided the basic criterion of rarity is met. Economically, demand of any gem is, by and large, elastic, i.e., they are luxury items, and not essential in our lives. Consequently, gems do not follow the conventional law of demand and supply according to which, demand generates first and supply follows. On the other hand, in case of gems, supply comes first and demand generates later in response to that. Emeralds and its sister gems are no exception.

(b) *Beliefs and superstitions:* Gems, many people believe, bring luck or misery to lives.

8. Pozzolanic property: True "*pozzolana*" is a fine, sandy volcanic ash and "*pozzolan*" is an acidic alumino-siliceous material (also see the chapter on pozzolanic clay). It reacts with calcium hydroxide in presence of water to form calcium aluminium hydrate compounds (C-S-H) which is a compact substance with low porosity and having cement-like properties at room temperature. Further, due to the acidic nature of pozzolan, the C-S-H produced from it is resistant to corrosion by sulphates and it is also resistant to water leakage and spalling due to low porosity. The industrial waste micro-silica (or silica fume or fluffy silica or silica dust) has good pozzolanic properties.

USES AND SPECIFICATIONS

Quartz, along with its derivatives, is a wonder mineral having a very diverse field of application ranging from everyday materials to high-tech ones. The important industrial uses of silicon and its minerals and forms are:

1. Microprocessor chip (elemental silicon)
2. Solar or photovoltaic cell (elemental silicon)
3. Alloys (elemental silicon)
4. High-frequency oscillator (crystal quartz)
5. Quartz clock (crystal quartz)
6. Gas lighter (crystal quartz)
7. Glass (silica sand)
8. Ceramics and glaze (quartz and silica sand)
9. Enamel (quartz)
10. Laser material (quartz)
11. Quartz bulb (quartz)
12. Silane (elemental silicon)
13. Silicon carbide (quartz and silica sand)
14. Silicon nitride (elemental silicon and silica sand)
15. Sodium silicates (quartz and silica sand)
16. Potassium silicate (quartz and silica sand)
17. Silica gel (quartz and silica sand)

18. Aero gel (quartz and silica sand)
19. Silicone (elemental silicon)
20. Refractories (quartzite and fused quartz)
21. Cement manufacturing (sand)
22. Construction aggregates (building sand)
23. Flux (quartzite)
24. Oil well (quartz, microsilica)
25. Foundry (quartz, quartzite, moulding sand, silica flour)
26. Gemstones (quartz and opal)
27. Traction sand (sand)
28. Water filtration (sand)
29. Adhesive
30. Gallium thermometer
31. Synthetic marble (silica flour and onyx flour)

All these uses as well some other minor uses are discussed as follows.

1. Microprocessor chip: For this application, a perfectly pure semiconductor material is required before doping it with some predetermined impurity in a controlled manner. Any crystal defects like grain boundaries and dislocations may absorb or obstruct the current carriers of the doping impurity. In semicrystalline silicon consisting of smaller crystals or grains, such defects are common. Therefore single crystals of elemental silicon doped with boron is the most preferred material because it is relatively easy to produce a single crystal of silicon with a high degree of purity (99.9999% or six '9' grade). This is done by either *Czochalski* method or *float zone refining* method.

Czochralski method is based on surface tension. Silicon is melted in a crucible. A seed crystal is attached to one end of a rotating rod which is first lowered till it just touches the surface of the melt, and then is withdrawn slowly at a rate varying from 0.1-10.0 cm per hour. The molten material gets attached to the rotating seed due to surface tension, is gradually pulled up by the seed out of the hot crucible, cools down and solidifies. This process continues till the entire molten material gets pulled up and becomes a solid single crystal taking on the pattern of the seed. The sizes of the crystals grown by this method depend on the amount of molten material available in the crucible. In float zone refining, a seed crystal is attached to one end of a silicon rod is lowered through an electromagnetic coil, which first heats and melts contact zone of the rod with the seed ; single crystal forms at that zone and it moves upward as the rod continues to be lowered. After the rod is withdrawn, it cools and solidifies into a large single crystal rod. In the float zone method, unlike in the Czochralski method, there is no crucible required and hence no chance of any contamination from crucible. In either of the methods, the intrinsic impurities of the original silicon rod migrate towards one end and that end is later cut off.

The most important application of silicon semiconductor is for making diodes, triodes (or transistors) and microprocessors making integrated circuit chips (IC chips), which are widely used in all chip-based technologies computers and other electronic equipments. In a silicon microprocessor, the basic component are, (i) an ultra-thin doped and polished miniature silicon wafer (the source of the electric charge); (ii) an insulator substance (SiO_2) between the circuit lines, and (iii) metal to collect the electric charge and transmit the current. To begin with, a very thin wafer is diamond sawn from a pure single crystal silicon rod. On this wafer, a layer of SiO_2 is grown by exposing it to extreme heat and gas in vacuum. On the wafer, a pre-designed electronic circuit in the form of a stencil called *mask* (made by chromium deposited on ultra-pure glass plate) is superimposed and the SiO_2 layer exposed along the circuit lines is etched away by a process called *photolithography* (using ultraviolet light and a solvent). This leaves a circuit pattern of silicon with ridges of SiO_2 in between which act as insulators. Atoms of a metal (aluminium, copper or gold) are deposited on the silicon circuit for collecting and transmitting the electric charge. On a single wafer, hundreds of such microprocessors are created to make an IC chip.

2. Solar or photovoltaic cell: In this application, both the photovoltaic and the semiconductor properties of silicon are made use of. A pure ultra-thin wafer (180-350 micrometre thick) cut from a high-purity (99.9999% or six '9' grade) single crystal of silicon rod and then doped with boron converts photons of solar light into electricity with a high degree of efficiency. The reasons for requirement of such high purity single crystals are the same as in case of microprocessor and the methods of producing them are explained above. However in cells for ordinary purpose, less pure quartz can suffice. An anti-reflector silicon nitride (Si_3N_4) coating of few hundred nanometre thickness is vapour deposited on the front surface facing the sun, and on the back surface silver paste in a grid pattern connected to a metal conductor serves to transmit the current generated. Several such solar cells interconnected by metal ribbons constitute a solar panel.

For making low-power solar cells used in watches, calculators and the like, amorphous silicon (one micrometre thick) deposited on a plate of glass or plastic or metal is good enough.

3. Alloys: Alloys of silicon with metals are nowadays made in the EAF without extracting silicon separately. In the furnace charge itself, metal oxide powders are added to the quartz powder and then the process of electrolysis is continued in the same manner as in the case of making elemental silicon.

(a) *Ferrosilicon*: Amongst the silicon alloys, ferrosilicon (FeSi) is somewhat special inasmuch as it is not only an end product like other alloys, but is an agent for effecting de-oxidation in steel melting shop. As an alloying additive to low-carbon iron, silicon – being an extremely weak electrical conductor, increases its resistivity, and thus minimizes eddy current losses and increases magnetic permeability. Sheets of ferrosilicon with some insulating material (often iron oxide) between them are laminated to produce transformer cores. The insulation reduces eddy current losses further. Standard ferrosilicon contains 5% (max) Si, 95% (min) Fe and practically nil carbon (carbon tends to increase conductivity and offset the benefit due to silicon).

A special type of ferrosilicon containing 84-86% Fe and 14-16% Si in powder form is used in the heavy medium mix for separation of diamond from kimberlite. The ferrosilicon helps in maintaining the specific gravity of the medium at a level of 2.7- 3.0, i.e., just above that of kimberlite (2.6) and below that of diamond (3.5), without increasing the bulk, and it is also easily retrievable by magnetic separation due to its high magnetic permeability.

Another special kind of ferrosilicon containing as high as 70-75% Si is referred to in the industry as *"elemental silicon"*. It is used in inoculation for iron foundry and as a trimming addition in steel.

Ferrosilicon is manufactured in EAF in the same manner as in case of recovery of silicon. Oxide of iron is mixed with the sinters of quartz powder and electrolyzed. As iron oxide is highly resistant to electric current, the process is extremely power intensive, the requirement of power being 8500-9500 kwh per tonne of ferrosilicon produced.

According to the user industries, quartz suitable for ferrosilicon production should have more than 98% SiO_2, less than 0.4% Al_2O_3 and not more than 0.2% each of Fe_2O_3, CaO and MgO. No phosphorous or arsenic should be present in quartz. The melting point of Al_2O_3 being very high, its presence aggravates the difficulty in melting of the charge in the electric furnace and increases power consumption. CaO and MgO have a tendency to react with silica to form silicates, and so their higher contents will consume part of the silica. Iron oxide is electrically insulator, its presence in quartz (which is also an insulator) will increase the difficulties of electrolysis further.

(*b*) *Silicomanganese:* Silicomanganese is a very recent product developed on commercial scale for the first time in India during the late 1980s. Its development was prompted by the progressive deterioration every year of the quality of manganese ore produced in India, the percentage of manganese decreasing from 47-48 to 44-46 and that of silica increasing from 5-5.5 to 7-8. The Silicomanganese technology was developed as a substitute of ferromanganese, out of the sheer necessity to adjust to the changed resource availability of low-manganese high-silica ore. Its composition is 50-74% Mn, 14-28% Si, 2.5% (max) C, 0.3% (max) P and 0.05% (max) S. Silicomanganese also acts as a de-oxidizer and de-sulphurizer in steel melting shop, and in addition, it helps form manganese- and silicon-bearing alloys of steel. On an average, its consumption is of the order of 10 kg per tonne of steel produced. Sometimes, it may be used only for de-oxidation and de-sulphurization purpose, and then its consumption is 5-6 kg per tonne of steel produced. A typical type of steel containing both silicon and manganese is Ferro-silico-calcium-manganese (Fe-Si-Ca-Mn) alloy containing 15% Mn and varying percentages of Si.

(c) Spiegeleise:- It is sometimes referred to as "*silicospiegeleisen*". Its development was also prompted by the progressive deterioration every year of the quality of manganese ore produced in India. The Spiegeleisen technology was developed as a substitute of ferromanganese, out of the sheer necessity to adjust to the changed re source availability of low grade manganese ore containing high iron and high-silica. Composition of a standard product is: Mn 20- 22%; Fe 65%; Si 11 percent.

(d) Other silicon-bearing alloys:

Name of Alloy	Composition	Properties/Uses
Nitralloy steels	0.2-0.5% C; 0.35% Si; 0.65% Mn; 1.6% Cr; 1.1% Al; 0.2% Mo; balance nitrided steel.	Surface-hardened steel which are machinable.
Silicon-chromium-tungsten shock resistant steel.	0.55% C; 1.0% Cr; 2.0% W; 0.6% Si	Chisels; snap and caulking tools; heading and nail dies; engrossing punches.
Electrical steel (also called silicon steel)	Si 0.4-4.5% (preferably 1.2-3.2%)	Soft magnetic material suitable for electrical applications like transformer, electric motors.
Ferro-silico-calcium-barium (Fe-Si-Ca-Ba).	Ca 15%; Ba 15%.	De-oxidizer, de-sulphurizer, inclusion modifier and inoculant for iron & steel industries.
Ferro-silico-zirconium (Fe-Si-Zr)	Zr 20-35 % ; Si 55%	De-oxidizer, de-sulphurizer and inclusion modifier for iron & steel industries.
Ferro-silico-calcium-manganese (Fe-Si-Ca-Mn).	Ca 15%; Mn 15%	De-oxidizer, de-sulphurizer and inclusion modifier for iron and steel industries.
Ferro-silico-rare earth (Fe-Si-RE)	RE 30-35%..	De-oxidizer, de-sulphurizer, inclusion modifier and inoculants for iron & steel industries.
Ferro-silico-magnesium (Fe-Si-Mg)	Mg 5-20%; Ca and Ce if required.	Spherodizing alloy for iron.
Ferro-silico-magnesium-titanium (Fe-Si-Mg-Ti)	As required	Spherodizing alloy for iron to yield compacted graphite.
Ferro-silico-calcium (Fe-Si-Ca)	Ca 30%; Si 60%.	Modification of inclusion for better mechanical properties and avoiding nozzle clogging during continuous casting; . inoculant for iron and steel industries.
Aluminium-magnesium-silicon (Al-Mg-Si)	--	Medium strength semis
Aluminium-cadmium-silicon	Cd in Al-Si matrix	Improved wear resistance and strength; used in highly loaded engine bearings.
Aluminium-zinc-silicon-nickel-magnesium	Si, Ni, Mg added in a matrix of Al-Zn	Used in light alloy crankcases of vehicle engines.
Graphitic aluminium alloy	Up to 16% graphite with or without coating of Ni/Cu ; Al-Si alloys containing 2-24% Si, up to 7.5% Ni, 4% (max) Cu and up to 1% Mg employed as base.	Used in self-lubricating bearings and other antifriction applications.
Titanium aluminium molybdenum tin silicon alloy	Ti 87.5%; Al, Mo and Sn each 4%; Si 0.5%.	High strength alloy, used for highly stressed structural components in aircraft and structural engineering.
Stellite	25-30% Cr; 1% (max) Mo; 2-15% W; 0.25-3.3% C; 3% (max) Ni; 2% (max) Si; 1% (max) Mn; balance Co.	Used in hard facing materials (e.g. armaments, cutting tools).
Aluminium-copper-silicon-magnesium	86.5% Al; 3.0% Cu; 9.5% Si; and 1.0% Mg	Casting alloys used in automotive pistons etc.
Aluminium-silicon	6.3-11.0% of fine Si particles evenly distributed in a matrix of Al with addition of 1.0-3.5% Cu.	High wear resistance, improved castability and corrosion resistance, decreased coefficient of expansion, elevated strength and ductility; used in pistons of automotive engines and bearings; used for hot-dipped coating on iron.

4. High-frequency oscillator: In acoustics, an oscillator device performs the function of transmitting and receiving of the carrier energy – electromagnetic waves in case of radio communication or electrical alternating current in case of loudspeakers, ultrasonic generators and microphones. The sound waves are transferred to the carrier which strikes the oscillator, sets off oscillation of the oscillator device and is transferred back to sound waves due to the oscillations. Prior to 1921, circuit-type oscillators were used in radio and portable telephones. These were vulnerable to external disturbances causing deficiency in the transfer of sound energy to the carrier energy and vice versa. Thus frequent mismatches ("poor modulation" in the jargon of acoustic engineers) between the frequency of the sound energy and that of the carrier energy took place resulting in the frequencies of sound to keep altering continually. This problem made the tuning of receivers and the frequency of sound reception difficult to stabilize.

In 1921, a new type of oscillator device based on the piezoelectric properties of quartz was invented Prof Walter G. Cady of USA. This is also called *piezoelectric resonator*. The high Q value of quartz makes it possible to transfer the energy of sound to the carrier energy through a quartz oscillator in the transmitting device, and then back to sound energy through another oscillator in the receiving device with remarkable efficiency. In a transmitter (e.g., microphone), the oscillating pressure of a sound wave is converted to electric pulse while in a receiver, there is the opposite effect. These devices find wide applications in military for communication by radios and portable telephones, and also in transducers for converting electrical pulses to mechanical vibrations as in loudspeakers and ultrasonic generators.

Perfect flawless and colourless crystals (crystal quartz) are required, because their Q value is the maximum. From such a crystal, circular or rectangular plates of less than 1 mm thickness and 12-18mm diameter or side are cut. Such plates are used in most of the applications, but in a few, however, bars are used.

5. Quartz clock: Quartz clocks were developed and improved during 1920s and 1930s. In this application, both the piezoelectric property of quartz and the semiconductivity of silicon are made use of. The principle in essence consists in a quartz plate being excited by an alternating voltage applied to it. The alternating voltage is produced by a silicon transistor supplied by direct current from a cell. Under the influence of this alternate energy, the piezoelectric quartz plate starts oscillating and keeps doing so until the original source of energy, i.e. the cell is not discharged. The oscillatory movement of the quartz plate, in its turn, generates an output of alternate electric current which is conducted by a conductor metal chemically deposited on the plate. This current either activates a microprocessor to display the time or drives a motor and through a system of gears, moves the hands of the clock. But this time, the frequency of this alternate current output is tuned to that of the oscillation of the quartz plate, and this latter frequency can be changed by changing the dimensions of the plate. In a quartz clock, the thickness and other dimensions of the quartz plate is carefully designed so that the frequency of oscillation matches exactly with some unit of time (one second, half a second, etc).

Thus the function of the quartz plate is not only to generate the oscillatory energy output, but also to modify the frequency of that oscillation as per requirement. The plate of the proper thickness and other dimensions has to be cut from a perfectly pure crystal quartz. For making the silicon chip (transistor) also, very pure crystal quartz is necessary.

6. Gas lighter: The piezoelectric property of quartz is made use of. A little hammer is made by a spring to hit a quartz plate and set it into a high-frequency oscillatory motion. Thousands of volts of electricity is generated. This, in its turn, generates a spark that ignites the gas. Thus the mechanical action of momentarily releasing a spring is ultimately transformed into electrical energy and a spark.

7. Glass:

(a) Definition and types: Physically, common standard glass is an amorphous, hard, brittle and transparent substance and chemically, it is a mixture of the silicates of sodium, calcium and magnesium. The composition of typical ordinary glass is [$18Na_2O.2MgO.8CaO.72SiO_2$]. From the point of view of chemical composition and usage glass may be classified into the following types (see also the chapter on borax).

- Common soda-lime glass: This is the ordinary colourless glass having composition sodium-calcium silicate.
- Jena glass: This is a potash-lime glass. It is hard and used in chemical laboratory ware.
- Lead crystal or flint or cut glass: It is a lead-potash glass. PbO is used as the flux. It is lustrous with high refractive index. Due to its lustre, brilliance and sparkle this glass is used for ornamental purpose and for making superior tableware. In old times, due to its high refractive index, it was used for making some kind of lenses also.
- Borosilicate glass: This glass is made by replacing much of the soda by boric oxide (B_2O_3) and some of the lime by alumina. It is characterized by very low coefficient of thermal expansion (one-third of common soda-lime glass). Consequently, unlike other types of glass, borosilicate glass does not crack under thermal shock, and hence it is used for making special cookware, laser tubes in glow-discharge type etc. This glass is nowadays engineered into hollow micro-balloons for use as fillers (in refractories, concrete, oil well cement, brake linings etc), sealants and coatings due primarily to its heat resistance, inertness and high strength.
- Optical glass: Very pure, colourless and transparent glass made out of pure white silica sand or crystal quartz is used for making high-quality lenses for spectacles, microscopes, telescopes etc.
- Photochromatic or photochromic glass: It is a barium-containing borosilicate glass that has the unique property of temporarily darkening when exposed to sunlight – especially ultraviolet light – and is used in spectacles and other optical lenses. It is made by adding silver chloride an alkali metal (lithium or sodium or potassium) and barium to the raw material mix for borosilicate glass. The $AgCl_2$ and alkali metal can also be replaced by some other substance like Al_2O_3 (introduced through feldspar) and Nb_2O_5. Such glass can also be made by applying some special organic coating to the finished optical glass.
- Optical fiber glass: Optical fiber is a comparatively recent development in communication. In optical fibers, light, instead of electromagnetic energy (as in copper wires) or radio waves or microwaves (as in case of wireless communication systems), is used for carrying information in the form of video, voice or data. Optical fibers use the principle of successive total internal reflection of laser beam within a

hair-thin glass fiber comprising an inner denser core surrounded by a lighter cladding – both highly transparent. Light is carried along the core due to total internal reflection at the contact surface between the core and the cladding, even if the fiber is bent. The glass for this purpose has to be of extraordinarily high purity and such glass is not made from natural silica. Instead a compound of silicon namely silicon chloride is reacted with oxygen to yield pure silica as below:

$$SiCl_4 + O_2 \rightarrow SiO_2 + 4Cl$$

This silica is then processed to make glass of the required grade. Then the question arises of increasing the refractive index of the core glass and/or reducing that of the cladding glass. To increase the refractive index, germanium is added and to reduce, either boron or fluorine is added to the pure silica glass.

- Coloured glass: To make coloured glass, colouring agents are added. The different agents are: cobalt (purple-blue), chromium oxide (green), chromium (yellow), uranium (dichroic canary colour), manganese (violet), ferrous oxide (pale blue to olive green), ferric oxide (yellow), lead (pale yellow), silver oxide (yellow), charcoal (yellow), selenites and selenates (pale pink to pinkish yellow), tellurium (pale pink), nickel (violet colour in lead-potash glass and brown colour in soda-lime glass) and copper (peacock blue to green).
- Glass wool: Glass wool consists of a very thin string of glass arranged into a spongy texture. For manufacturing glass wool, molten glass is first drawn into fibers which are then cemented into a *fiber mat* with the help of some resin binder. The fiber mat is heated to 200^0C to polymerize the resin and make the product a strong and cohesive material called glass wool. It is a light weight, corrosion free, waterproof absorbent material capable of absorbing sound and heat. It finds use in thermal and sound insulation, and in fire resistant applications. Typical composition of this glass is 5% B_2O_3, 16% Na_2O, 8% CaO, 3.5% Al_2O_3, 3% MgO and 64.5% SiO_2.

During the early 1800s, glass used to be manufactured by first blowing a bubble of molten glass and then spinning it. A flat glass with a bump or “crown” left at the centre was produced by this way, and it used to be called “*crown glass*”. By 1825, this process was replaced by what was called “*cylinder process*”. In this process, molten glass was blown into a hollow cylinder, cooled, sliced down on one side and then reheating. The cylinder opened up to form a flat sheet. Now-a-days, glass is subjected to different processes like rolling, pressing, blowing, casting, drawing, spinning, laminating etc to yield different products which can be broadly grouped as :

- Ordinary window or sheet glass: This is made by rolling and pressing semi-molten viscous glass in the form of sheets. This type of glass is used as ordinary window and plate glasses.
- Thick flat panel or float glass: The concept of float glass is comparatively new to India, having entered here in 1990s. Float glass is a type of sheet glass that is exceptionally smooth on both surfaces and free from internal stress. For its manufacturing, molten glass at 1100^0 C is discharged from the furnace onto a bed of

molten tin, where it floats and spreads out freely in the form of a long strip. It is, then cooled either slowly (annealed float glass) or suddenly (heat-strengthened float glass). Molten tin by virtue of its low shrinkage on solidification, higher than glass specific gravity, non-adherence to glass surface, and low coefficient of friction allows the molten glass to spread freely without any resistance and then solidify without any wrinkle. The float technology is suitable for producing thick glasses (above 0.5 mm) in large sizes.

- Thin flat panel glass: For making flat panel display glass of less than 0.5 mm thickness, down-draw or slot-draw technology is employed. In this technology, glass is formed by a slot which determines the thickness of the glass sheets. Sheets as thin as 0.03 mm and with excellent surface qualities have been produced.
- Safety glass: This glass product is used in automobiles. Flat glass is strengthened by means of lamination (inserting a celluloid material layer between two sheets of glass) to make safety glass.
- Container glass: This is produced by blowing or casting molten glass. Bottles, tableware etc. are common examples.
- Architectural glass: Different designs are created by bending and twisting sheet glass in different ways.
- Fiber glass: This is glass formed into fine fibers (thinner than human hair) by drawing molten glass through tiny holes. It is resistant to heat and fire. Fiber glass reinforced plastics (FRP) are extremely strong and light, finding application in furniture, car and boat bodies, rail carriage components and many other objects.
- Hollow glass micro-balloons: These are engineered spheres made out of borosilicate glass. These are very light weight strong materials having application as fillers in refractories, PVC flooring, oil well cement, brake linings, sealants etc. Special concrete made of portland cement, glass micro-balloons, latex, acrylic fortifier and water is strong, lighter than water and highly flexible. Research is underway to make racing canoes out of it.

(b) Manufacturing process: Essentially, the process of manufacture of glass consists in melting a mixture of 47% silica sand,14% soda (Na_2CO_3), 12% dolomite ($CaCO_3.MgCO_3$), 3.5% limestone ($CaCO_3$), 2.5% carbon (coke) and the balance broken waste glass (called cullet) at 1400-1500^0 C, and then cooling it first to a thick viscous liquid at 800-900^0 C. After first neutralizing the original colouring substances present in the charge by adding MnO_2, Sb_2O_3, As, etc. and then forming it into different desired shapes, colours and types, this thick liquid is rapidly quenched so as to prevent devitification to a solid glass product. Slow cooling will result in vitrification (i.e. formation of grains or crystals). The two-stage cooling prevents fractures. The function of carbon is to combine with the excess oxygen and to provide heat while the soda, lime and broken glass act as fluxes lowering the melting point of silica from 1580^0 C to 1400^0 C. However, lime has a tendency to form crystals and addition of magnesia helps prevention of this devitrification. The CO_2 of the carbonates of calcium and magnesium are expelled reducing them to CaO and MgO. The low-melting soda and broken glass become liquid first and silica (quartz) being soluble in boiling soda, dissolves in this liquid to form low-melting sodium silicate which then reacts with the CaO and MgO to form

glass. A little of sodium sulphate (Na_2SO_4) and feldspar may be added to the charge for process control and for adjusting the composition of the final glass.

(c) Specifications: So far as the specification of the silica sand is concerned, silica-content, size and iron-content (in the form Fe_2O_3, very common in silica sand) are the most critical while the somewhat uncommon impurities Al_2O_3, TiO_2 and some coloring constituents like MnO, CuO and Cr_2O_3 are also objectionable if present.

First of all, silica sand is preferred to quartz because the latter has to be crushed and ground to fine grains in order provide larger surface area for reactions to be quick, complete and effective. And this process of crushing and grinding of quartz will be power-intensive and costly due to its hardness. Silica sand, on the other hand, is already in a naturally ground state. However, ultimately it is the economics that will count. For a plant situated far away from a suitable silica sand deposit crushing quartz may be more economical than transporting silica sand. The size specified by the Bureau of Indian Standards (BIS) in 1980 is 125-600 microns. Finer than this size may result in the sand being carried away by the draft in the melting furnace, while coarser sand will provide less surface area for the reactions to take place quickly and economically.

The content of silica (SiO_2) in the sand is obviously important because it is this substance that goes into the production of the silicates constituting glass. According to the Bureau of Indian Standaeds or BIS (1980), a minimum of 97% SiO_2 for dark coloured glass is required, progressively increasing with increase in quality of glass to 99% and above for high quality colourless glass. The highest silica content is of course specified by the makers of optical glass.

The most common and invariably present impurity is Fe_2O_3. this is a colouring substance and during manufacturing of high quality glass, must first have to be neutralized before solidification of the glass (although it may have to be added later on in a calculated amount depending on the colour of glass desired). According to the BIS (1980), a maximum of 0.1% Fe_2O_3 for dark coloured glass is required, progressively decreasing with increase in quality of glass to 0.02% and less for high quality colourless glass. However, some of the manufacturers of cheap dark-coloured glass for bottles, window panes, bangles, etc. prefer to let the iron content in natural sand to be carried to the finished glass, and they accept even as high as 0.5-0.7% Fe_2O_3 content. The lowest Fe_2O_3 content of 0.005-0.008% is of course specified by the makers of optical glass. Fe_2O_3 of natural sand can be reduced to 0.06% by hot acid leaching and further to 0.03% by froth flotation.

Both alumina and titanium dioxide have high melting points and they require more heat to melt and to become fluid. Besides, imperfect melting of the alumina results in higher viscosity of the melt. The BIS (1980) has recommended 1.5% and 0.1% as the maximum limits of Al_2O_3 and TiO_2 respectively in the silica sand. Metallic oxides like MnO, CuO, Cr_2O_3 etc. have colouring effect and hence are considered undesirable.

8. Ceramics and glaze: The word “ceramic” derived from Greek “keramos” originally meant fired and fused common clays. But in modern usage it includes some other inorganic materials mixed with clays in different forms (common clay, china clay, ball clay, etc.) which are fired together and fused, though clay still remains the core component. The original ceramic products (e.g., bricks, potteries) made only of clay were hard and resistant to heat and chemicals, but at the same time porous and brittle. To make new products which are not only hard and resistant to heat and chemicals but also nonporous and strong, additional materials are added. Silica is one such material – in the form of either quartz or silica sand. Consequently, today, the product range has gone much beyond bricks and potteries and include stoneware crockery, vitreous tiles, sanitary ware and porcelain (in a broad sense refractories and advanced ceramics are also sometimes included, but these are not always clay-based and hence considered here separately). On fusion, silica is converted to glass which fills up the pores and adds strength to the product.

The principle of the manufacturing process, in essence, consists in mixing quartz or silica sand, one or more types of clay, feldspar and some flux (soda) with 30-40% water. This mixture is ground, thoroughly agitated, filter pressed, moulded into the required shape, dried and then fired to a temperature ranging from 1200-1500^{0}C depending on the product hardness required. Different ceramic products can be prepared by varying the types of clay and their proportion in the mixture. If the product is to be a glazed one, then it is glazed before firing.

The purpose of glazing is to provide a uniform firmly adhering coating on the surface of the ceramic body concealing defects such as pinholes, bubbles, etc. Glaze may be "*raw glaze*" or "*fritted glaze*". Raw glaze consists of insoluble material applied as such (soluble components crystallize in the mixture and cause blemishes on the treated surface), while fritted glaze is heated beforehand to cause chemical change in the components. Glaze should not only melt but also spread uniformly. The glaze is made of the same ingredients but with predominance of quartz and feldspar. The ingredients are mixed, finely ground and mixed with water, and this mixture is the glaze. The moulded raw body of the product is dipped into the glaze and then fired to a higher temperature of about 1400^0 C. Colours and decorative designing, if required, are painted after glazing and before firing.

A special type of ceramic product used for making "*water filter candles*" contains micro-pores to arrest passage of particles suspended in water. To make these, some finely ground organic substance (wood powder) is added to the raw material mix. On firing, the organic matter burns out leaving the candle porous.

As regards the specification of quartz or silica sand for making ceramics, silica should be high – at least 97%, but preferably above 99 percent. Iron oxide is the most deleterious constituent as it is a colouring substance and it will tend to form coloured dots on the body of the product. The maximum limit of 0.1% is generally specified. Alumina is also not desirable, because, although it goes into the mix through feldspar, its presence in the quartz makes it difficult to control the overall composition of the mix. So far as the specifications of quartz for glazing are concerned, the chemical specifications are the same as in case of ceramics, but since quartz is a predominant raw material, its thermal stability and resistance to cracking on heating is more important. Amongst the different varieties of quartz, flint readily transforms into the stable form cristobalite, and hence flint is preferable.

9. Enamel: Chemically, enamel is a complex mixture of silicates, borates and fluorides of some metals like sodium, potassium, etc. It is a glaze coating on metallic surfaces so as to give protection to the latter against high temperature and corrosion. It is prepared by mixing borax ($Na_2B_4O_7.10H_2O$), quartz, feldspar, fluorspar, soda (Na_2CO_3), sodium nitrate, oxides of cobalt, manganese and nickel and an opacifier substance (e.g., tin oxide, titanium silicate, antimony trioxide). In this mixture, borax (34%), quartz (20%) and feldspar (28%) are the dominant components. This mixture is ground, melted and quenched in water to yield a glassy mass. To this glass are added clay and more quartz powder and the mixture is finely ground to powder and made into a slurry with water. This is called *"enamel slip"*. Metallic objects are dipped in it and fired to about 900^0 C. Two to three of such enamel coats are usually applied. Colour effects can be produced by addition of colouring oxides of metals (e.g., iron, chromium, cobalt, uranium etc.) to the melt before it is quenched.

As regards the specification of quartz, silica should be high, and iron oxide is the most deleterious constituent as it is a colouring substance. Enamel coating used to be very common in earlier times, but now-a-days various superior alloys like stainless steel etc. have made it obsolescent.

10. Laser material: The medium for transforming ordinary light to laser (see also chapter on ruby) can be a solid crystal (e.g., ruby) or a gas or vapour like argon. In the latter type of medium, laser can be yielded by glow discharge or arc discharge. In the glow discharge lasers, the operating current is a few milli-amperes and the heating is not severe. Hence, a tube made of borosilicate glass can be used. But, in case of arc discharge laser, the current is in the range of 20-50 amperes, and the tube is required to withstand severe thermal shock and conduct the heat rapidly to the coolant water encircling it. Although a bad conductor of heat, fused quartz is the most successful material for the tube for this purpose. Its high melting point and ability to withstand thermal shock serves it well.

11. Quartz bulb: An ordinary electric bulb consists of a tungsten metal filament through which current is passed raising the temperature of the conductor and causing it to glow and emit light. The wire in the form of a coil is welded to thicker support wires and encased in a glass bulb, the inside of which is either vacuum or filled with some inert gas to prevent oxidation during glowing. But in halogen bulbs, tungsten iodide filament is used instead of tungsten metal. The iodide can withstand much higher intensity of heat than tungsten metal, and give out brighter light. However, the iodide vapour tends to corrode the glass, and hence, the filament is encased in an inner quartz bulb (prepared from molten quartz without addition of fluxes or other materials) within the glass bulb.

12. Silane: Silane is silicon tetrahydride (SiH_4). It is gaseous even at very low temperature (it melts at (-) 185^0 C and boils at (-) 112^0 C), and it breaks up into silicon and hydrogen at 420^0 C. This characteristic has made it useful: (i) as a silicon coupling agent to bind glass fibers with polymer matrices in fiber-reinforced plastics, (ii) for vapour depositing silicon on silicon wafers, and (iii) for sealing leaks with silicon.

Silane is prepared by first treating powdered silicon with hydrochloric acid at 300^0 C to obtain trichlorosilane, which is then boiled on a resinous bed (catalyst) to yield silane and silicon tetrachloride.

$$Si + 3HCl \rightarrow HSiCl_3 + H_2$$
$$HSiCl_3 \rightarrow SiH_4 + 3SiCl_4$$

13. Silicon carbide: Silicon carbide (SiC) was made prepared in laboratory in 1892, and later, commercialized. It is one of the hardest materials known, its hardness being in the region of 9-10 on the Mohs scale. There are several processes for manufacturing SiC as follows.

(a) High temperature chemical reaction: This is the most commonly practised process. Sand or quartz and petroleum coke are reacted in a resistance furnace (plasma-arc furnace or arc induction furnace) under cover of CO or some inert gas. The SiC is then ground to powders of 10-100 micron size. The quartz or sand should be very pure containing more than 99% SiO_2. The most objectionable impurities are Fe_2O_3, Al_2O_3, lime, magnesia and phosphorus. The oxides – particularly lime and magnesia, tend to form silicates and (if phosphorus is present) phosphates.
(b) Sol-gel process: In this process very fine powders of silicon and a carbide are mixed together as a colloidal mixture or gel. The carbide dissociates releasing carbon which combines with silicon to form ultra-pure and ultra-fine silicon carbide.
(c) Gas-phase process: In this process silane, (SiH_4) and methane (CH_4) gases are reacted in a radio frequency plasma reactor at a temperature of 2000^0 C to produce silicon carbide and hydrogen. For this purpose silane which is an unstable compound, is prepared from elemental silicon in two steps:

$$Si + 3HCl \rightarrow HSiCl_3 + H_2$$
$$4HSiCl_3 + \text{catalyst} \rightarrow SiH_4 + 3SiCl_4$$

Silicon carbide powder is used:

(a) as such as an abrasive (sold under the trade name *carborandum*), one of the applications being to coat mild-steel wires used for cutting medium-sized to very large-sized blocks of granite.
(b) after fabrication by sintering or hot-pressing, as high-performance advanced structural ceramics for use in heat exchangers, cutting tools, electronic devices etc.
(c) in the form of whiskers for reinforcing ceramics and metal-matrix composites (MMC)
(d) as oxidation- and wear-resistant coating by chemical-vapour-deposition (SiC readily oxidizes to form a thin surface layer of silicon oxide which inhibits further oxidation)
(e) as refractories and crucibles

14. Silicon nitride: Silicon nitride (Si_3N_4) is an advanced ceramic material and is looked upon by automotive industry as a rising star. It is synthesized by one of the following three high temperature chemical reaction processes.

(a) Elemental silicon powder is reacted with nitrogen
(b) High-purity silica sand or quartz is reacted with carbon and nitrogen
(c) Triclorosilane ($HSiCl_3$) is reacted with a gas containing nitrogen or nitrogen compound.

By the above processes, powders of Si_3N_4 are produced. With some variation in the process, whiskers can also be produced. The Si_3N_4 powders are then fabricated into dense products by sintering or hot-pressing.

The fabricated ceramic products can be machined after softening by laser heating to 1000^0 C and then cutting with the help of boron nitride tool. Silicon nitride ceramics have potentialities for use in automobile engine parts and in tool bits. It may also be applied on metals as oxidation- and wear-resistant coating by chemical-vapour-deposition (Si_3N_4 readily oxidizes to form a thin surface layer of silicon oxide which inhibits further oxidation). In 2000, a new process has been developed in China to form a refractory ceramic adhesive interlayer which forms a joint that is strong and stable at high temperature. The process consists in heating a slurry based on Si_3N_4, SiO_2, Y_2O_3 and Al_2O_3.

15. Sodium silicates: Sodium silicate is a family name and it includes sodium metasilicate (Na_2SiO_3), sodium ortho-silicate (Na_4SiO_4), sodium pyro-silicate ($Na_6Si_2O_7$) etc. They are also called "*water glass*" or "*liquid glass*". These are white, water soluble alkaline solids. They are prepared by fusing silica sand or quartz powder (20-100 mesh) containing 99% SiO_2, with soda (Na_2CO_3) at 1200^0C to 1400^0C. Al_2O_3, Fe_2O_3, CaO & MgO are undesirable as they tend to combine with silica and sodium forming water-insoluble salts. The ratio of the sodium carbonate to silica can be varied to obtain different varieties of sodium silicate. The uses of sodium silicate are as follows.

(a) *Soaps, detergents and cleaning compounds*: These contain three basic components – surfactants, chelating agents and builders. *Surfactant* is the acronym of "surface active agent", and it removes dirt from a soiled surface attracting the dirt particle to its surface by ion exchange. A *chelating agent* surround and hold the unwanted ions of calcium and magnesium – the water-hardening substances, thus softening the water. A builder (i) helps softening of water by deactivating calcium and magnesium ions either by sequestration (i.e., holding them in solution) or by precipitation (i.e., removing them as insoluble materials); (ii) helps removal of acidic fatty and oily soils by increasing alkalinity of the cleaning compound; and (iii) emulsifies oily and greasy soil by breaking them up into fine globules and also keeps the globules under suspension by preventing them to settle on the cleaned surface. Sodium silicate acts as a builder and soaps, detergents and other cleaning compounds generally contain 5-10% of it.

(b) *Sealant*: Sodium silicate together with magnesium silicate forms a thick paste when dissolved in water. This paste, on being heated, becomes hard and glasslike due to the water being driven off. It can be applied (i) to repair cracks in exhaust systems of automobiles, (ii) to seal holes in radiators of automobiles by pouring it into them and allowing it to circulate, (iii) to paints to seal porous surfaces of asbestos and other fibrous materials, (iv) to concrete or cement plaster surfaces to reduce porosity.

(c) *Cement, stucco and concrete*: These materials are sometimes treated with a solution of sodium silicate at the curing stage. It reacts with excess CaOH to strengthen the bond between these materials and the surface.

(d) *Binder*: Sodium silicate is a useful binder of vermiculite and perlite and thus bonded aggregates can be made into high temperature insulation boards and pipes. For making strong cores in foundry, moulding sand is mixed with sodium silicate solution, moulded in required shapes, and then treated with CO_2 forming soda (Na_2CO_3) and colloidal silica which forms a strong and uniformly spread bond.

(e) *Adhesive*: It is used for this purpose in paper and board industry.

(f) *Timber treatment*: Pressure treating wood with sodium silicate serves to fill up the pores and to provide a protective cover against insects and fire.

(g) *Egg preservation*: It was an old use. Eggs used to be covered with sodium silicate to protect against bacteria. This way eggs were known to remain fresh for up to 9 months.

(h) *Fire protection*: Sodium silicate — whether in liquid or in solid form – is endothermic due to presence of the liquid water in the water glass and of the hydrate in the solids. A thin waterproofed sheet of it can be used in plastic fire-stop devices.

16. Potassium silicate: Potassium metasilicate (K_2SiO_3) is the common type and generally referred to simply as potassium carbonate. It is prepared by fusing silica sand or quartz powder (20-100 mesh) containing 99% SiO_2, with potassium carbonate (K_2CO_3)at 1200^0C to 1400^0C. It is a transparent and corrosion resistant. Since potassium carbonate is costlier than soda, potassium silicate is also relatively costly and hence its usage is limited. It is applied as a covering on welding rod, on cathode ray tube of black and white television, on inorganic paints etc. to protect them against corrosion.

17. Silica gel: "Gel" is apparently a misleading suffix because silica gel is solid and in granular form (the real gel of silica is what is called "*silica-sol*"). Silica gel is prepared from silicic acid and the process is reversible. On reaction with acid, sodium silicate yields silicic acid releasing hydrogen. Depending on the type of the sodium silicate -- meta, ortho, pyro etc.—the product may be meta-silicic acid (H_2SiO_3), ortho-silicic acid (H_4SiO_4), pyro-silicic acid ($H_6Si_2O_7$) etc. On heating and roasting the silicic acid, the water molecules are driven off and a glassy mass of highly porous silica are left. This mass is broken into porous grains to obtain the product silica gel. Due to high porosity, silica gel is strongly hygroscopic i.e. it can easily absorb water and on heating, can easily gives off water. Its porosity expressed in terms of surface area per unit mass is 800 m^2/gm. This property makes it one of the most popular desiccant. For commercial use, the grains are doped with some moisture indicator substance like cobalt chloride (deep blue when dry and pink when moist), phenolphthalein (turns yellow when moist) etc. It was extensively used during World War I (1914-18) as an absorbent of gases and vapours in gas masks, and during World War II (1940-44) for keeping penicillin dry.

18. Silica aerogel and aero-sil: Silica aerogel or (simply) aerogel is the lowest-density solid known so far, its density being 1.9 mg/cm^3 i.e. 1/530th that of water. This low density gives it a very large surface area per unit mass making it a highly efficient adsorbent and catalyst, and making it useful (i) for cleaning spills and (ii) for desiccation.

It has the unique ability to absorb infrared (the heat-producing component of sunlight) while letting the remaining sunlight to pass through, and also, in general, to absorb heat from any source. This makes it useful: (i) as a construction material for trapping heat for solar heating purpose, and (ii) for application on human hands to protect them from the heat of blow torch even at point blank range.

To prepare aerogel, first a neutralized solution of tetra-methyl ortho-silicate [$Si(OCH_2CH_3)_4$] is dissolved in water. Colloidal silica known as *silica-sol* separates out.

$$Si(OCH_2CH_3)_4 + 2H_2O = SiO_2 + 4HOCH_2CH_3 \text{ (liquid)}$$

This silica-sol is sprayed into fine spherical droplets. Finally, the droplets are dried in a stream of hot air to yield aerogel.

Sometimes, nano-sized particles are vibro-fluidized to increase their fluffiness, reduce the density and thus increase the surface area. The product thus prepared is called "*aero-sil*".

19. Silicon:e Silicones (or organosiloxanes) are synthetic inorganic polymers in which atoms of silicon and oxygen form the central chain (cf. carbon in organic polymers). Silicones may be classified into:

(a) Silicone oils: These oils are non-toxic, non-volatile, water-repellent, electrically, insulating substances, and are soluble in hydrocarbons and ether. They emulsify easily with suitable alkaline agents. Their main uses are as waterproof coatings on textiles, leather garments and footwear, as waterproof polishes and in high temperature greases and lubricants. A common example of its use as a lubricant is for coating the needles of insulin injection syringes.
(b) Resins: These are electrically insulating with high dielectric strength. Its solution can be sprayed or brushed on electric equipments as an insulating coating. Some components of electric equipments can be moulded using a mixture of silicone resin and fiber glass.
(c) Elastomer or silicone rubber: This is a waterproof and strongly insulating rubbery solid . It can retain the insulating property over a wide range of temperature from (-) 50 to 250^0 C or even wider. This is used for sealing of aircrafts and of electric equipments, in gaskets of hydraulic systems, in fire-resistant insulation covering on electric cables, etc. It can be used in breast implants. In optical fiber cable, silicone rubber is used as a waterproof jacket which encase the inner core and the cladding.

By mixing silicone with boric acid a product called "*silly-putty*" can be made. It has some unique properties. It can stretch without breaking, but can be snapped off cleanly; it bounces higher than a rubber ball, with rebound of 80%; if it is hit with a hammer, it keeps its shape, but under light even pressure, it flattens easily; it has lower dielectric constant than quartz, i.e., 2-4 indicating weak electrical conductivity (cf., value for air, one of the poor conductors of electricity, is 1). First made in 1943, it finds application in toy industry, as a grip strengthener and as an art medium.

20. Refractories: Refractory materials are defined as those resistant to heat and having a melting temperature of not less than 1580^0 C. The function of refractory lining on a furnace wall is not only to withstand high temperature, but also to withstand temperature fluctuation, and to resist penetration, abrasion, and erosion by hot gases and molten materials in the furnace, and over and above, it should not chemically react with those materials. Life of refractory lining is increasingly becoming a critical parameter in the productivity of a furnace and economics of a plant, because each time the lining fails and needs replacement, the furnace has to be shut down. The high melting point (1700^0 C) of quartz makes it suitable for use as an acid refractory and it is used for this purpose in two forms:

(a) Lumpy quartzite: Quartzite should be high in silica content – at least 95% (preferably 98%) and the lumpy form is specified because the crushing cost is relatively low. The lumps are crushed, the grains formed into bricks, and finally fired to about 1500^0 C. At this temperature, the quartz grains fuse together to yield a solid compact refractory brick. Quartzite refractory bricks are mainly used in coke ovens, because the affinity of oxygen to silicon is much stronger than to carbon and hence silica does not react with carbon. They are also used in blast furnace stoves. Further, the quartz grains in quartzite being very closely bonded, such bricks are very compact and resistant to penetration to liquid and gaseous materials in the oven.

(b) Fused quartz: Very pure quartz (99.9% SiO_2) is fused and then either shaped into blocks for refractory lining or crushed to (-) 45 micron sized powders to be used as such for repairing of refractory linings. Such refractories are of very high quality, being very solid and compact with high thermal stability.

Quartzite being of metamorphic origin, consists of silica grains cemented with cristobalite and tridymite which are stable phases of silica, and no further deformation takes place during firing of the bricks. Fused quartz also reaches these stable phases during fusing itself and no further deformation takes place during its exposure to the conditions in the furnace.

Refractoriness is lowered by the presence of fluxes such as CaO, MgO and alkalis which form low-melting brittle glass with silica, and hence these are considered highly deleterious.

Fe_2O_3 melts at a relatively lower temperature and is readily reduced by carbon of the coke oven, and therefore, Fe_2O_3 is also a highly deleterious constituent in quartz, its maximum permissible limit being 1% (preferably 0.75%). If, in addition to Fe_2O_3 , TiO_2 is also present then at the high temperature in furnaces where the refractory products are used, they form low-melting iron-titanate glass causing blisters in the refractory bricks and consequent increase in porosity. The industries specify the maximum limit for TiO_2 at 0.2 per cent.

For a different reason, Al_2O_3 is extremely undesirable, and quartz and quartzite containing more than 0.01% and 0.75% respectively of Al_2O_3 is not preferred by the industry, though there have been instances when up to 1.5% Al_2O_3 has been accepted by some Indian industries. Although melting point of alumina is higher than that of silica, upon fusion, it forms silicates (kyanite, andalusite or sillimanite) with increase in specific gravity (from 2.7 of silica to 3.2-3.7 of the silicates) and then mullite at temperatures $1200\text{-}1600^0$ C, with disturbance of the eutectics and resultant deformation of texture and weakening of the refractory.

The other specifications include a minimum Pyrometric Cone Equivalent or PCE as 32, and 0.2 (max) creep when tested for 5-50 hours at 1500^0C under pressure (creep is a time-dependent deformation as a result of constant stress conditions over a long period of time).

21. Cement manufacturing: In the cement industry building sand is used as an additive to make up for silica deficiency in the raw material mix. The specifications are not rigid, nor are they very important because it all depend on the composition of the other raw materials. Only magnesia is considered undesirable in cement (because it being hygroscopic absorbs water during plastering and gives it off later causing vesicles) and hence, in the raw materials also. The Indian industries generally use sand containing 65-98% SiO_2 and 1-1.5% MgO.

22. Construction aggregates:

(a) *Cement mortar*: Only cement, if mixed with water, forms a colloidal solution jellifying quickly to a solid compact mass, and is difficult to apply for plastering. Hence it is mixed with both sand and water to form a paste. In this use of sand, porosity is the key, because; (i) cement particles fill up the intergranular pores of the sand, (ii) the large surface area available in the pores facilitate thorough bonding of the cement with the sand, and (iii) during drying of the plaster the water comes off through the pores without causing any damage to the plaster. The specifications of the sand are also linked to porosity and the important parameters are (i) size of grains, (ii) distribution of size, (iii) shape of grains and (iv) clay content. Medium and even-sized round grained sand free from clay is ideally suited. Too fine grain size means less porosity, and large sized grits are not amenable to formation of a paste with water. In case of uneven grain-size distribution, the finer grains fill up the pores between coarser ones. Angular grains interlock with each other leaving less pores in between. Clay fills up and blocks the pores and should be less than two percent. River sand with its naturally sorted rounded grains is the most preferred building sand.

(b) *Sand-lime bricks*: Also called "*calcium silicate* bricks", these are used particularly where clay bricks are scarce or where consistently high-strength bricks are required. Sand-lime bricks are compact with water absorption less than 7.15% by weight after 24 hours. Here, calcium hydroxide [$Ca(OH)_2$], instead of cement, is mixed with sand and water to form a paste which is then pressed into solid, perforated or hollow bricks and hardened under high-pressure steam whereby calcium hydroxide and silica combine to yield calcium hydrosilicate, and strongly bonded bricks become ready. These are ordinarily off-white in colour, but pigments can be added to make coloured bricks. The key criterion is porosity of the sand as in the case of cement mortar (see above) and the specifications are the same.

(c) *Asbestos cement*: Silica powder containing (+) 97.5% SiO_2, 0.8% R_2O_3 & 1.5% CaO are used as constituents in the manufacture of asbestos cement sheet and pipes. Asbestos fibers become interlocked around a sand-cement paste. The criteria are the same as in case of cement mortar (see above).

(d) *Cement concrete*: Addition of up to 7.5% of microsilica (industrial waste) to plain concrete improves mechanical properties and strength/weight ratio of the concrete such high-strength concrete (HSC) has 2-4 times higher compressive strength than ordinary concrete. But if the microsilica is above 10%, then the concrete becomes harsh, dry and difficult to work. The Indian industries specify microsilica with minimum of 88% SiO_2, maximum 1.5% Na_2O, maximum 3% each of moisture and LOI, and about 22000 m^2/kg specific surface area.

(e) *Concrete hollow blocks*: For speedy construction, solid or hollow concrete blocks are used in place of traditional clay-bricks. An aggregate made of sand, clay, fly ash and gravel ranging in size from 300 microns to 12.5 mm is mixed with cement water, pressed and sun- or steam-dried. Ratio of cement to aggregate is maintained at 1:6.

23. Flux:

(a) *Iron metallurgy*: The problem of large slag volume in blast furnace is multiplied if alumina is high and is not completely melted, thus resulting in higher viscosity. To counter this higher viscosity, silica in the form of quartzite lumps is added resulting in increased slag volume. Nevertheless, a little alumina (that does not require too much heat for melting) is desirable, because this fully melted alumina will then serve to increase the fluidity of the slag. Some alumina and silica are also desirable for achieving an optimum level of slag volume so as to facilitate absorption of the sulphur, if any. So, to sum up, ideally both alumina and silica should be low, but not too low; and there should be an optimum Al_2O_3/SiO_2 ratio in the ore, and some silica is added to adjust this ratio – particularly if the iron ore is high-alumina as in India. Lumpy quartzite is preferred because it is hard and does not break into powder under the stress of fall through the height in a large blast furnace during charging. The size of the lumps should be 10-80 mm. High silica content of at least 94% and low alumina of maximum 1% is preferred by the Indian iron industries. The BIS (1993) has recommended 96-98% SiO_2 , the balance being alumina. Iron oxide is not at all objectionable in the quartzite for use in iron metallurgy, and so banded hematite quartzite (BHJ) can also be used. For BHJ, the BIS (1993) has recommended 48-50% SiO_2, 50-52% Fe_2O_3 and maximum 1% Al_2O_3.

(b) *Welding electrode coating*: According to the definition of the American Welding Society, "Welding is a metal-joining process wherein coalescence is produced by heating to suitable temperature with or without pressure and with or without the use of filler metal". The most common type of welding is arc welding. The mechanism of arc welding is based on electron emission. In this, the electron discharge takes place in the form of an arc. When electricity is passed though two electrodes (cathode and anode) in contact with each other, and then the contact is broken by moving them a little away, the resistance and consequently the potential, increases so much that the tips of the electrodes begin to glow. The temperature at the tips increases rapidly, and electron emission takes place. The high energy electrons associated with the temperature ionizes the air in the gap between the electrodes. This ionized air becomes an electrical conductor and current flows from one electrode to the other. This is the mechanism of arc discharge. The temperature of the arc may be of the order of thousands of degrees (20000-50000^0 C). If the broken pieces of a metal are placed in the arc, then they will fuse and will be welded together. In this, electrodes made of rods of covered metal are used. The covering serves both electrical and metallurgical purposes. Electrically, the covering insulates the rod from accidental contact with adjacent material; metallurgically, the covering may provide gas- and slag-forming ingredients to protect the weld from the air, and it may also supply de-oxidizers or alloying material resulting in sound welds. In one of the types of covered electrodes, the covering material consists of iron or hematite powder to increase the rate of deposition of weld metal. The role of silica is to balance the slag composition and fluidity in the same way as in iron metallurgy (see above) except that the silica is in the form quartz powder or sand.

24. Oil wells:

(a) *Proppant*: If there are fracture zones in the rocks of a petroleum or natural gas reservoir, then the rocks tend to cave in and block the wells adversely affecting the recovery. Proppants are materials which are used for filling up the fracture cavities to prevent closure of the wells, but without reducing the permeability of the reservoir

rock, so that flow of oil or gas can be sustained. Silica sand is used in wells up to 3000 m deep (beyond this depth calcined and sintered bauxite is used as silica sand is not strong enough to be suitable). For this purpose, haphazardly sized angular grains are specified. The angularity helps the grains to interlock with each other and provide a strong support for the cavities, while the haphazard sizes leave some pores and channels so as to make the fillings permeable for the oil and gas to flow.

(b) *Oil well cement*: The industrial waste micro-silica having good pozzolanic properties, reacts with calcium hydroxide in presence of water to form calcium silico-aluminium hydrate compounds (C-S-H) which is a compact substance with low porosity and having cement-like properties at room temperature. Further, due to the acidic nature of pozzolan, the C-S-H produced from it is resistant to corrosion by sulphates and it is also resistant to water leakage and spalling due to low porosity. Taking advantage of these characteristics, microsilica is mixed with ordinary portland cement to produce what is called "*portland cement-pozzolan*" for use underwater in oil wells as well as offshore oil wells.

25. Foundry: The whole system of mould-making, melting of metals, casting of the melt in mould, solidifying the cast metal to produce an object in the form of the mould, and final dressing and finishing of the object is called foundry. Moulds may be of two types:

- Those made of some metal (e.g., zinc) in which case the mould is called "*die*" and it is permanent; the casting operation is called "*die casting*".
- Those made of sand which are called "*sand mould*" or simply "*mould*", and they are generally of the "use-and-throw" kind; the casting operation is called "*sand casting*".

A sand mould (hereinafter referred to as mould) for solid cast is made with moist sand bonded by clay or resin or bentonite rammed into the desired pattern by hand or machine, and is suited to casting of metals or alloys which melt at temperatures less than the sand (pure silica melts at 1700^0 C). To make a hollow cast, a core also made of sand but bonded with linseed oil, is prepared within the mould by forming it into the required shape and then baking (to impart strength). Some moulds (called "*shell moulds*") meant for mass production of small objects, are partially fused to increase strength and durability. The following conditions should be fulfilled in a good mould:

i. The inner surface of the walls of the mould and outer surface of core should be smooth so as to minimize the need for dressing and finishing of the cast.
ii. The walls of the mould should be slightly porous and permeable so as to allow the gases released during casting to escape, but not permeable enough to allow metal penetration. The core of the mould, in contrast, should be impermeable so as to prevent metal penetration (the question of gases escaping through the core does not arise as it is inside the mould).
iii. It should be strongly bonded.
iv. The sand should not melt and react with the casting metal at the operational temperature of casting.
v. The sand should bond well with clay.

Silica in the form of a special type of sand called "*moulding sand*" is used for making sand moulds. This sand is, in a large measure, self bonding containing some clay, unlike river sand which is clay-free due to natural sorting under the action of flowing water. Good moulding sand is generally found in lacustrine, beach and dune sand deposits.

The size, distribution of sizes and shape of the silica grains are the important in as much as these determine the smoothness and the degree of permeability of the mould. Finer and more rounded the grains are, smoother will be the surface, but too fine a size will reduce the permeability of the surface. The permeability of the surface will also reduce if the range of sizes is very wide, because in that case the fine grains will fill up the intergranular spaces. Therefore, sand containing optimum sized rounded (or at the most sub-angular) grains with narrow range of size distribution is suited to the main mould, and that containing very fine grains suit the core of the mould. For the mould, the BIS (1974) has classified natural moulding sand into 6 relatively narrow size fractions, the minimum being 75 micron (minimum 70% retention on the sieve) and maximum being 3.35mm (minimum 98% passing through the sieve). For the core, BIS (1974) has recommended *silica flour* produced by grinding quartz or quartzite or silica sand to less than 75 micron size.

Silica content in the moulding sand or the silica flour will determine its melting temperature. Pure silica melts at 1700^0 C and more the impurities, lower will be the melting point. The BIS (1965) recommended a minimum grade of 95% SiO_2 for the lowest grade and minimum 98% for the highest grade. Along with the highest grade moulding sand for the main mould, will go silica flour containing 98% or more SiO_2 for the core (BIS, 1975) enabling the mould to take casting metals at almost 1700^0 C temperature.

The clay content should not be too low as it will not then form a strong bond for the sand grains, nor it should be too high because then the fine clay will fill up the pores and reduce permeability. The BIS (1965) had specified 5-20% clay content. However, this is not very critical, because some extra clay can always be added to low-clay sands and high-clay sands can easily be blended with low-clay ones.

Amongst the deleterious constituents, gravels and mica are highly objectionable because they do not bond with the rest of the sand and will tend to peel off.

26. Gemstones:

(a) *Ornaments*: Hardness of the silica minerals is lower (7 in Mohs scale) than the high-end gemstones like diamond, beryl, etc. Besides, the refractive index of quartz is low – 1.55 and that of opal is still lower – 1.45 (cf. glass --1.54) and they lack in the brilliance or sparkle. But some of the varieties of quartz and opal have attractive colours, clarity and visual effects making them useful as low-end gems, and ornaments, decorative showpieces and innovative artifacts are made out of them. Examples of silica gems are crystal quartz, amethyst, citrine, smoky quartz, rose quartz, tiger eye, onyx, agate, blood stone, star stone, plasma, aventurine and opal.

(b) *Gemmotherapy*: A sizable section of population – elite and common — believe in an unconventional system of healing known as Gemmotherapy, according to which the above silica gems, when worn on the body as a ring or a locket or in any other form, have beneficial effect on persons suffering from psychological and some physiological problems. Clarity and caratage (generally 2-7 carats) of these gems are very important criteria in this use.

27. Traction sand: Composite loose aggregate of sand and microsilica is applied on railway tracks as lining. As a train passes over it, it is compacted under its weight. The air molecules entrapped between the particles are first compressed and then pushed out. This produces a lift and on the locomotive wheels and a frictionless cushion below them. The train can glide upon it.

28. Water filtration: Sand and gravel are usually used as filter media for filtration of water. The sand serves the purpose of arresting the passage of fine particles suspended in water. Shape and degree of uniformity of size (rather than actual size) of the grains and clay-contents are the most important criteria for selection of the sand. In effect, the sand bed should be just sufficiently porous. Medium-and even-sized round grained sand free from clay is ideally suited. Too fine grain size means less porosity. In case of wide variation in grain-size distribution, the finer grains fill up the pores between coarser ones. Angular grains interlock with each other making the bed compact. Clay fills up and blocks the pores and should be less than 5 % (BIS specification, 1977).

29. Adhesive: Adhesive is an organic or inorganic substance capable of bonding together other substances by surface attachment. Silica flour (size 0.5-9.0 microns) can be used as an adhesive (e.g., in toothpaste). The important criteria are: (i) small particle size and large surface area, (ii) low oil absorption, (iii) chemical inertness to common acids and alkalis, (iv) easy dispersion, (v) resistance to heat, and (vi) low refractive index (permitting usage in transparent systems).

30. Gallium thermometer- The unique combination of low melting point and high boiling point make gallium indispensable in high temperature thermometers and temperatures in the range of 500 - 1200^{o}C have been measured with such thermometers (mercury is not suitable as this range of temperature is well above its boiling point of 357^{o}C). One of the problems with gallium is its extremely corrosive nature. For this reason, such thermometers are made of fused quartz tubes.

31. Synthetic marble: Synthetic marble is a strong, homogeneous, dense, translucent product which can be cast into different shapes and sizes. It finds use in bathrooms and as structural components. It is made by casting and heat-curing (in presence of a catalyst) a finely ground mixture of alumina and resin matrix with some filler material. The filler constitutes 50-85% of the weight of the mixture and includes calcite, silica, oxides of antimony and titanium and talc. The refractive index of the mixture vis-à-vis the resin matrix is so manipulated as to give an illusion of depth. Silica used is in the form of silica flour, onyx flour, glass flour, glass frit. The role of silica is to impart strength and its refractive index is also a criterion.

32. Other uses:

(a) *Filler*: Rubber (silica aerogel added to reinforce the resilience, strength, grip and wear resistance); fertilizer (to balance composition); insecticide (silica aerogel added as a carrier); talcum powder (microsilica added to prevent caking); synthetic marble (silica flour used to adjust refractive index of the product and plasticity of the mould).

(b) *Stowing*: Building (river) sand mixed with water to form a slurry, is pumped into worked out underground galleries; after draining out the water, solid sand is left in place to support the roofs and prevent them from caving.

(c) *Silicothermic process*: Strong affinity for oxygen makes silicon useful as a reducing agent, and the process in which it plays that role is called "*silicothermic process*". This process is employed in manufacture of medium carbon ferromanganese, extraction of manganese metal etc.

(d) *Coal washery*: Just as ferrosilicon is used for adjusting the density of the medium in concentration of diamond by heavy media separation process (see Ferrosilicon), silica sand is used as one of the ingredients in case of coal. Sand with a constant density of more than 2.64 is used. Grains must be sub-angular to round. Clay content is limited to 0.5%, and no organic matter is tolerated. Particle size ranges from 30-100 mesh.

(e) *Sand blasting*: Sand is fired under pressure against the material to be polished — usually in the presence of water — to dislodge and suppress the dust. For this purpose the chemical composition of the sand is not important, but absence of clay and other clogging materials, is very important. Sand, as per the definition of the American Society of Testing Materials (ASTM), consists of particles ranging in size from 0.074 mm to 4.75 mm.

(f) *Sand and silicon carbide paper/cloth*: Silica sand papers/cloths are used for polishing wood, and silicon carbide papers/cloths for hard surfaces. For making these, hot sands of quartz (flint) containing high silica (99%) and low iron or ground silicon carbide are sprayed or gravity-dropped on sheets of paper/cloth coated with heated glue (shellac, gelatin etc.).

(g) *Plant micronutrient* : Silica of the soil, which is converted by acids to a form that can be assimilated by plants, is responsible for the strength of the wheat and corn blades, of the wood and of the nuts.

(h) *Silicon monoxide coating*: SiO is sometimes used as a final protective coating at thickness around 100 mm on metallic surfaces.

(i) *Paint industry*: Coloured quartz in powdered form is used.

(j) *Grinding mills*: Flint pebbles of size varying from 6-15 cm. are used.

SUBSTITUTION

1. Crystal quartz: Perfectly pure crystals of quartz for use in various high-tech applications like microprocessor chips, photovoltaic cell, high frequency oscillators etc. are very rare in nature and their finding is also unpredictable. So, nowadays, cultured (synthetic) quartz crystals are made by hydrothermal method. The small fragments and powders of crystal quartz retrieved from mining rejects, which constitute the fusing grade quartz or "*lasca*", serves as a nutrient in quartz crystal synthesis. Lasca is melted in large pressure-vessels known as autoclaves. Varying temperatures are maintained in different parts of this fused silica. A seed crystal is dipped in the cooler zone, and the fused lasca of that zone deposits on this seed. The process continues as the hotter zones progressively become cooler. For a sufficiently large crystal for industrial usage to grow, the process may take up to 60 days.

2. Microprocessor chips:

(a) Gallium arsenide: It is a powerful semiconductor material and is used in transistors, IC chips etc, particularly suitable in high frequency telecommunications and high speed computers (super computers). Gallium arsenide has several advantages over silicon: (i) it is more radiation-resistant than silicon chips, and hence is considered suitable for use in satellites, (ii) it can move electrons six times faster than silicon does, and consequently processing speed of chips made of it is enormous, (iii) it can absorb sunlight faster than silicon does, and is more suitable in solar photovoltaic cells, and (iv) it can combine both light and electronic data processing on a single chip. However, the major impediments for wide use of gallium arsenide are its cost and the extreme difficulty in making a perfect crystal. It is said than very small vibration or even gravity has a negative effect on it. The best crystals of gallium arsenide have been made in outer space, of course, at a huge cost.

(b) Carbon nano-tubes: The trend in microprocessor chip industry today, is towards more and more miniaturization and higher and higher speed. In early 2005, some scientists of USA and Australia have reported a breakthrough in research in the field of nano-technology by creating industry-ready sheets of a new material made from carbon nano-tubes having solar cell capabilities. Nano-tubes are rolled up sheets of electrically conductive carbon atoms and are more than a thousand times thinner than human hair. The invention has heralded a new era of ultra-miniature electronics with potentiality to replace silicon transistors (see also the chapter on graphite).

3. Glass:

(a) Chalcogenic and magnetic glass: There are certain amorphous and transparent materials which are not silica-based but called glass because physically they resemble glass. Chalcogenic glass and magnetic glass are two such materials. The former is a selenide containing thallium, arsenic, tellurium and antimony and is characterized by photoconductive and semiconductor properties. The latter is a metallic glass characterized by high electrical resistivity and high magnetic permeability, and is used in magnetic cores of transformers.

(d) Plexiglas: It is a hard, insoluble, highly transparent and completely non-toxic organic glass. Plexiglas is prepared by polymerizing a mixture of acetone, hydrocyanic acid, sulphuric acid and alcohol. Compared to inorganic glass, Plexiglas is half as light and is much more easily workable into various shapes and products by drilling, punching, sawing, casting, polishing, etc. It allows ultraviolet light and X-rays to pass, but not heat. It is resistant to temperatures up to 100^0 C. It finds wide application ranging from objects like goggles, models, fluorescent tubes, musical instruments, measuring instruments, ornaments, toys, etc. to materials for aircrafts, motors, buildings, and artificial organs and limbs.

(e) Perfect glass: “Perfect glass” has been experimentally prepared in the University of Wales, USA by a process known as amorphization. In this process, pressure is applied to zeolite crystals under normal temperature. The zeolite crystals collapse slowly and transform into glass without melting. This glass is harder, but lighter and chemically more durable than ordinary glass.

4. Construction aggregates: In a few states in India (e.g., Andhra Pradesh, Kerala), there is a shortage of river sand in a number of places, and also there is a growing concern for ecological damages to many rivers due to indiscriminate sand mining. Now granite sand is emerging as a viable alternative.

5. Oil spillage recovery: In recovery of oil from oil spillage in water/sea, microsilica can substitute silica aerogel.

6. Laser material: In spite of some favourable factors, the poor thermal conductivity of fused quartz causes repeated failure and limited life span of arc discharge laser tubes. Graphite has been tried with some success in lasers with operating current less than 20 amperes. However, though it has solved the problem of thermal conductivity, graphite is prone to sputtering and dust formation.

Chapter 41

STAUROLITE

The most striking characteristic of staurolite is its twinned crystal form that is in the shape of a cross. In fact, its name is derived from the Greek words “stauros” meaning cross and “lithos” meaning stone. It is a complex mineral having chemical formula $[(Fe,Mg,Mn,Zn)_2Al_9(Si,Al)_4O_{22}(OH)_2]$. Staurolite is a regional metamorphic mineral of intermediate to high grade. It occurs in schist, phyllite and gneiss with almandine garnet, micas, kyanite and other metamorphic minerals. Bruce Foote was the first to identify occurrence of staurolite in the mica schist rocks of Nellore area of Andhra Pradesh, India in 1880 and he recognized its potential as an abrasive material. In 1945-1946, some samples of staurolite collected from Hassan district, Karnataka, India were tested. Since then, its occurrences have been found in Singbhum district of Jharkhand state and in Hyderabad district of Andhra Pradesh, — all in mica schist, and during a brief period of 1969-1981, small quantities ranging from one ton to 43 tons have been produced, but investigation for its usability as an industrial abrasive was not pursued with. Elsewhere, its occurrences are known in Switzerland and USA.

USES AND CRITERIA

It is an opaque mineral with colour varying from reddish brown to black. Its hardness on Mohs scale is 7.0-7.5, i.e., it is harder than quartz (Mohs hardness 7). These properties as well as the unique cross-shaped crystalline form traditionally qualified it as a semiprecious gemstone and it has been a stone-collectors’ delight.

However, since 1997, it is being regarded as an industrially useful mineral and is now being recovered as a byproduct from a titanium mineral mine in Western Australia. Its principal and emerging application is in *sand blasting* (also called *abrasive blasting*) as a substitute of quartz and garnet which have been the traditional materials in this application. Sand blasting is a technique routinely employed by industries, shipping companies and navies while polishing before painting for corrosion control. In this technique sand is fired under pressure against the material to be polished—usually in the presence of water—to dislodge and suppress the dust. For this purpose the chemical composition of the sand is not important, but absence of clay and other clogging materials, is very important. Sand, as per the definition of the American Society of Testing Materials (ASTM), consists of particles ranging in size from 0.074 mm to 4.75 mm. Traditionally, silica sand and garnet have been the preferred materials of the user industries. However, of late, the health authorities in USA are increasingly putting pressure to phase out these materials because of their tendency to generate finer particles during blasting and the potential hazards associated with handling of their dust. It is in this backdrop that staurolite, being a harder and safer-to-handle material which also is effective as an abrasive due to its sub-conchoidal fracture, is emerging as a substitute. Staurolite is safer because it tends to generate less ultra-fine dust during blasting than silica sand and garnet.

Chapter 42

SULPHUR AND ITS MINERALS

Sulphur is one of the *chalcogenides*, or "ore-formers." Its oxides form acidic solutions in water. It is the 15th element in order of abundance in the lithosphere, the incidence being 520 ppm. Since the average SO_4-content per litre of seawater is approximately 2.65gm, the seas probably contain most of the crust's sulphur as sulphate. There is a number of allotropic forms in which sulphur can exist; rhombic, monoclinic, plastic, amorphous and colloidal. From the industrial point of view, sulphur is one of the essential minerals.

ECONOMIC MINERALS OF SULPHUR

Although sulphur is combined in many minerals as sulphide and sulphate, it is not commercially recovered from all of them. The economically important sources are:

1 Native sulphur
2 Pyrites (Fe_2S)
3 Galena (PbS)
4 Zinc blende or sphalerite (ZnS)
5 Chalcopyrite ($Cu_2S.Fe_2S_3$)
6 Gypsum ($CaSO_4.2H_2O$)
7 Petroleum and natural gas
8 High-sulphur coal

Of these, native sulphur and pyrite are valued primarily for their content of sulphur while from the others, sulphur is generally recovered as a by-product.

1. Native sulphur: Most of the sulphur used in the industries is derived from the native mineral, which is found in many places, but usually in volcanic regions. It is always impure, being mixed with gypsum, aragonite, clay, or other matter, in the interstices of which the sulphur is deposited. This impure ore of sulphur is called *brimstone*. The formation of sulphur beds may have occurred by one of the three processes: (i) reaction of hydrogen sulphide (H_2S) with sulphur dioxide (SO_2) or with oxygen (both H_2S and SO_2 are gases that come out with volcanic lava) aided by the bacterium *Rhodospirillum rubrum* which obtains energy by oxidizing H_2S to elemental sulphur; (ii) decomposition of metallic sulphides through the agency of heat; (ii) reduction of sulphates, especially of calcium sulphate.

While some volcanic deposits of elementary sulphur exist in the Andes mountain region of South America, Japan and Sicily, they are not mined extensively because of difficult access. Most of the sources of elemental sulphur are biogenic. Deposits of gypsum and anhydrite are processed by anaerobic bacteria, especially where hydrocarbons are available as food for the bacteria, which reduce the sulphate to sulphur with the emission of CO_2 and H_2S. The CO_2 reacts with the calcium present to make the mineral calcite, and limestone. The H_2S may escape, or, if trapped, may be oxidized to elemental sulphur either by oxygen-containing surface waters that have percolated into the area or by biological action. In this way, some stratified deposits were formed in which sulphur is disseminated within a matrix of limestone and gypsum or anhydrite, sometimes in considerable masses of nearly pure sulphur, but usually in fine seams or grains. Such deposits are mined in south-central Sicily. Deep-seated (more than 300 m depth) domes have also been formed in this way in Texas-Louisiana region which contain economic amounts of sulphur.

So far as India is concerned, there is only one known occurrence in Puga valley, Ladakh (Jammu and Kashmir state) where 40% grade sulphur occurs in a narrow bed. The narrowness of the bed and the remoteness of location are the main deterrent against its commercial extraction. However, some quantities of sulphur is recovered as by-product from fertilizer plants and oil refineries.

2. Pyrites: Pyrites (FeS_2) theoretically contains 53.4% S and 46.6% Fe. It is a very common mineral, often well-crystallized. A unique variety in the form of flat radial crystal discs found near Sparta, Illinois, USA is called *Sparta dollar*. The sulphur in bituminous coal is often in the form of pyrite. It is light-brass coloured. It often occurs in flakes associated with placer gold, and is called *fool's gold*. Marcasite—a polymorph of pyrites—has the same composition, but a different crystal structure. It is whiter, and has different crystal habits. Sulphur is not recovered as such from pyrites, but when roasted, SO_2 and further downstream products are produced.

Pyrite is the most common of the sulphide minerals. It is usually found associated with other sulphides or oxides in quartz veins, in sedimentary rocks and in metamorphic rocks as well as in coal beds, and as a replacement mineral in fossil. In India, there is a pyrites mine in Amjhor, Bihar where it occurs as bed associated with carbonaceous shale.

HISTORY

Sulphur has been known since antiquity. It is described in the Bible. Sulphur has been used by the Greeks and Romans as a fumigant and disinfectant. The name comes from its Latin namesake. In the ancient times, it was considered as the embodiment of fire, and related to lightning. In Christian mythology, it is referred to as the *Fuel of Hell*. The name pyrite is from the Greek word *pura* meaning "fire". This is likely due to the sparks that result when pyrite is struck against steel. This capacity made it popular for use in early firearms such as the wheel-lock (an obsolete gunlock using flint and a revolving wheel). Its allotropic form marcasite owes its name to the Arabic word for pyrite. In earlier times, native Americans used to carve and polish pyrite for use in mirrors.

Until the first quarter of the 19th century, Sicilian native sulphur mined by costly underground methods with low recovery, dominated the market. When this became costly by the middle of the 19th century, pyrites assumed importance as source of sulphur. Then, in the early 20th century, Herman Frasch developed the technique of solution mining of the deep-seated sulphur domes of USA producing almost pure sulphur at a very low cost. This resulted in switching the consumer preference again to sulphur and also ended the Sicilian dominance.

In the world, USA and Canada are the leading countries accounting for around 38% of the total production of native sulphur followed by Russia, Japan and others. So far as pyrites is concerned, China is the leading producer accounting for over 70% of the world production (in terms of sulphur content). The world production of sulphur which was about 2.75 million tons in 1939, increased to about 5 million tons in 1949, to 5.7 million tons in 1953 and by the turn of the century in 2000, it has risen to 53.6 million tons. In contrast, the world production of pyrites which had been increasing from 7.25 million tons in 1948 to about 13.18 million tons in 1953 has declined to 10.5 million tons in 2000 (this figure is approximate on the basis of an assumed global average grade of 40% S).

In India, small amounts of sulphur were produced in the past from hot springs. Significant quantities were also produced from the waste gas obtained from coal-gas industry. During 1949 alone, the total production from this source was over 90,000 tons. Now, only by-product sulphur is being recovered from fertilizer and petroleum refineries since 1970, but evidence of old working were seen in Amjhor area, Bihar. As per old records, total production of pyrites from these unorganized mines till 1950 was about 1,050 tons. Its production in an organized manner here started in 1951, when a company named *Pyrites Phosphates and Chemicals Limited (PPCL)* was set up under the public sector. The history of the growth of productions of both sulphur and pyrites is:

Year	By-product sulphur	Pyrites
1951	Nil	538 tons
1952	Nil	2,203 tons
1959	Nil	15 tons
1960	Nil	Nil
1968	Nil	13,914 tons
1970	840 tons	25,643 tons
1975	6,200 tons	50,633 tons
1980	5,144 tons	82,905 tons
1990	10,315 tons	94,073 tons
Year ending March, 2001	62,047 tons	Nil
Year ending March, 2005	113,904 tons	Nil

Since 1999, the pyrite mining has remained suspended in India. Indian pyrites is, however, low grade with an average sulphur content of 22% compared to some Spanish deposits that contain as high as 48% S (cf., theoretical content is 53.6%).

PROCESSING

1. Native sulphur: There are various methods of processing crude sulphur as follows.

(a) *Gill process*: Sulphur is separated from the minerals in its ores by heating at 115-120^{0}C, when the liquid sulphur drains from the ore mass. Normally, part of the sulphur in the ore is burned and the heat used to melt the remaining sulphur so that it leaches from the hot mass. This extraction procedure is widely used in Sicily. The mineral is generally refined in a very simple manner, the process being carried on in kilns called *calcerone*. As usually constructed, these are shallow pits, about 30 feet in diameter, with walls about 10 feet high, made tight with mortar. The ore is arranged in the *calcerone* so as to leave a few vertical draught holes from top to bottom of the heap, which is fired by dropping burning brush or straw into these openings. The sulphur, constituting 25-40% of the ore, burns freely, and when the heap is well on fire, the draught holes are closed, the *calcerone* is covered with spent ore and is left for several days. The heat given out by the burning of part of the sulphur is sufficient to melt the remainder from the gangue, and it collects in a pool near a tap-hole, made in the wall at the lowest point. At intervals of a few hours, the melted sulphur is drawn off into moulds. If the temperature rises above 180^{0}C., there is a large formation of plastic sulphur, which will not flow from the tap-hole. The time necessary to burn out a *calcerone* varies from 35 to 80 days, according to its size, the weather, and the nature of the impurities (e.g. gypsum retards the process owing to the water it contains). Usually from a quarter to a third of the sulphur is lost as sulphur dioxide during the burning. As this causes much damage to vegetation in the vicinity, the burning of *calcerone* is prohibited during the spring and summer months.

(b) *Steam/hot air extraction*: Sulphur can be separated by heating with hot air or with steam under pressure or with superheated steam. But this is not practised because of the high cost of fuel.

(c) *Solvent extraction*: Sulphur may be separated by a solvent, such as carbon disulphide (CS_2), which may be recovered afterwards, but this necessitates an expensive plant. So, treatment with a solution of calcium chloride ($CaCl_2$) was tried and it proved successful for some ores. The ore is placed in an iron basket or crate and suspended in a boiling solution of calcium chloride, which boils at 125^0 C. Since sulphur fuses at 115–120^0 C, it melts and flows away from the rock matrix. Passing through the basket meshes, it falls to the bottom of the tank, and is drawn off and cast in moulds. After the sulphur is melted out, the basket of hot rocks is lowered into a tank of water. They heat the water which then removes the calcium chloride from the rocks. This warm water is then used to replace that lost by evaporation from the boiling calcium chloride solution. This process causes no loss of sulphur as sulphur dioxide, and no nuisance is created, while a fairly pure product is obtained. The calcium chloride used is a waste product of the ammonia soda industry and hence comes cheap.

(d) *In situ refining (Frasch process)*: In this process, sulphur is extracted from ore bodies by pumping superheated water underground to melt the sulphur which is then forced to the surface. The sulphur in subsurface salt domes in Texas-Louisiana, USA are at depths of over 300 m, beyond the reach of normal mining techniques. Herman Frasch, in 1904, devised a method for reaching the sulphur. Three concentric pipes were lowered in the casing of a well (only an 8" diameter hole was required). Superheated water, at 160°-170°C was forced down the outer annulus. The sulphur at the bottom of the hole melted at 110°C. Hot compressed air was then blown down through the innermost tube, which made a froth of the molten sulphur, which rose automatically through the third annulus. This sulphur is 97-99.5% pure. Once on the surface, the liquid sulphur may require filtration in order to free it from organic impurities and to obtain a uniformly pure sulphur. This is generally done by passing it through a mixture of sulphuric acid and diatomaceous earth. Finally, it is led into large ponds to solidify. This sulphur is over 99.5% pure.

2. Pyrites: Iron pyrites (FeS_2), when heated in a closed retort, yields one atom of sulphur per molecule of sulphide; and has been used as a source of sulphur, but the process is not now employed. It is nowadays used as a substitute of sulphur in some of the latter's applications.

3. Metallic sulphides: Chalcopyrite, galena and zinc-blende or sphalerite are the most common metallic sulphides which are widely used as sources of sulphur or its products (sulphides of nickel, mercury, etc. have also been used). Chalcopyrite ($Cu_2S.Fe_2S_3$) theoretically contains 35% S, galena (PbS) 13.4% S and zinc blende or sphalerite (ZnS) 33% S. During processing of all these sulphides for extraction of their metal values, sulphur in the form of SO_2 is generated as wastes and is a source of pollution (the sulphur gets concentrated after flotation, and during subsequent roasting of the concentrates, this gas is emitted). In many countries, the environmental regulations are so stringent and so costly to comply, that they tend to serve as an economically viable option to trap this SO_2 and convert it to sulphuric acid (H_2SO_4). However, for this, there has to be a ready consuming market of H_2SO_4 near the smelter requiring minimal transportation and storage cost. In industrialized countries, where the level of H_2SO_4 consumption is already very high, and there is no consuming market near copper smelters, possibility of surplus supply situation of H_2SO_4 is a matter of concern, because the environmental regulations create problems for its disposal also.

4. Gypsum: The SO_3-content in gypsum ($CaSO_4.2H_2O$) is taken advantage of for manufacturing sulphuric acid from it. In USA, sulphur was extracted in the past from gypsum when there was a shortage of supply of native sulphur. In South Africa, there is a plant for extraction of sulphur from by-product gypsum.

5. Petroleum and natural gas: A great deal of sulphur comes from the refining of crude oil and natural gas. They contain significant amounts of sulphur in the form of different compounds. In petroleum it occurs in the form of organic compounds like thiophen, thioethers, mercaptan, etc. and in natural gas in the form of H_2S. All these compounds are considered deleterious and must be removed before the refined products are sold, or the gas supplied to the pipeline. The sulphur derivatives are removed by various oxidizing agents such as copper oxide, bleaching powder, sodium hypochlorite, potassium permanganate, etc. The sulphur so recovered is a useful by-product from petroleum refineries.

6. Sulphur-containing wastes: Such wastes include:

(a) Calcium sulphide waste of the Leblanc soda process,
(b) Residues from the purification of illuminating gas by means of moist iron oxide. In this process the reaction that takes place is:

$$Fe_2O_3.3H_2O + 3H_2S = 2FeS + S + 6H_2O.$$

On exposure to the air, this moist ferrous sulphide is oxidized thus:

$$2FeS + 3H_2O + 3O = Fe_2O_3.3H_2O + 2S.$$

Hence the iron oxide is restored and may be recycled.

From the processing of these wastes, a crude impure product of sulphur is obtained, which, although, is good enough for a large number of manufacturing operations requires purification for some purposes. This is generally done by distillation in a cast-iron retort (*Dejardin's apparatus*). The crude sulphur is first melted in a vessel, heated by the waste heat of the fire, fed into the retort, and then heated directly by fire. The vapours pass into a receiving chamber, which is usually made of brick. If the temperature of the chamber is not allowed to rise above 110° C, the vapours condense at once to fine colloidal powders, which are called *flowers of sulphur*. If the temperature rises much above 110° C, then the vapours condense as a liquid, which is drawn off into moulds and the cast sulphur is called *roll sulphur*. This roll sulphur, when ground, yields a product called *flours of sulphur*, the powder size of which is slightly coarser than the flowers.

7. High-sulphur coal- Sulphur is found in coal in three forms – pyrites, sulphate and organic sulphur. Sulphur content is believed to be high in coals deposited at shallow depths in neutral to weakly alkaline environment. Of the three forms of sulphur, organic sulphur poses problems for utilization particularly when its content exceeds 2 percent. The pyrite and sulphate can be reduced by nascent hydrogen such as through treatment of finely crushed coal in acid solution containing granulated zinc and chromium powder. Experiments on removal of pyritic sulphur and sulphate sulphur through bacterial leaching by means of *Thiobacillus ferro-oxidants* and certain micro-organisms present in coal, have been reported to be successful. Possibility of recovering some sulphur as byproduct can also not be ruled out.

CRITERIA OF USE

1 *Physical properties:* Sulphur is a yellow-coloured soft (hardness 1.5-2.5 on Mohs scale) and brittle mineral. Specific gravity of solid sulphur varies from 1.98-2.04. On melting, the liquid sulphur becomes slightly lighter having specific gravity 1.81.

2 *Thermal properties:* Melting point of pure sulphur varies from 110-120^{0}C depending on the allotropic form. Molten sulphur is straw-yellow coloured. It is a very poor conductor of heat.

3 *Electrical conductivity:* Its electrical resistivity is very high at about 2 x 10^{23} micro-ohm-cm, and it is the best electrical insulating material known.

4 *Chemical characteristics:* It is insoluble in water and dissolves easily in carbon disulphide and carbon tetrachloride, and less readily, in chloroform, benzol, turpentine and other oils. Sulphur burns readily in air forming sulphur dioxide (SO_2). It reacts with hydrogen to form H_2S and with caustic alkali solutions to form sulphides and thiosulphates. It remains unaffected by acids.

5 *Flower of sulphur:* It is the sublimed colloidal powdery substance from purification by distillation. It contains a little oxygen, and some sulphuric acid created by slow oxidation, but these are the only impurities. Its colloidal form makes the powder very active.

6 *Toxicity:* Sulphur, and most of its compounds are non-toxic and completely safe. The notable exceptions to this rule are H_2S, SO_2 and CS_2. Although sulphuric acid is very deleterious to tissue, but it is not a poison, and dilution eliminates any hazard.

7 *Pyrites:* Pyrites (FeS_2) has a slightly uneven and conchoidal fracture, hardness of 6–6.5 on Mohs scale, and specific gravity of 4.95–5.10. It is brittle, i.e., it breaks or powders easily. Its lustre is metallic and colour pale-to-normal brass-yellow and due to these it has earned the nickname *fool's gold* because many miners used to mistake it for real gold.

8 *Marcasite:* Though an allotropic form pyrites having the same composition, marcasite has a tendency to crumble easily.

USES AND SPECIFICATIONS

The principal uses of sulphur are:

A. Sulphur:

1. Vulcanization of rubber
2. Soil-conditioning
3. Human health
4. Pyrotechnic mixture (gunpowder and matches)
5. Insecticide and germicide
6. Preparation of sulphur dioxide
7. Manufacture of sulphuric acid
8. Preparation of hydrogen sulphide gas
9. Preparation of organic chemicals
10. Magnesium casting

B. Pyrites:

1. Manufacture of sulphuric acid
2. Soil conditioning
3. Gem

These uses are discussed as follows.

A. Sulphur

1. Vulcanization of rubber: Although a substance obtained from the latex of the tree *Hevea brasiliensis*, was in use as solid playing balls, clothing etc. by the South American natives during the ancient times, it was not until 1770 that its potentiality as an industrial material was recognized when Joseph Priestley named the substance "rubber" from its ability to rub out pencil marks.

The tree grows wild in South America. Natural rubber is nothing but a processed product of the natural gum which is present as tiny droplets in the juice (not the sap) called *latex* that comes from just under the bark of the tree. It consists of long chains of interconnected isoprene molecules containing C, CH, CH_2 and CH_3. The normally entangled chains can straighten up when stretched, giving rubber its most important characteristic—elasticity. The latex is coagulated with formic acid, and the liquid pressed out between rollers, forming sheets. Later on, it was found that if it was dissolved in turpentine, fabrics and leather boots could be impregnated with the solution and made waterproof, and by 1830 it was widely used. Seeds of *Hevea brasiliensis* were smuggled out of Brazil in 1876 by Sir Henry Wickham, and was used to establish plantations in southeast Asia, which has now become the most important source of the natural rubber. Rubber is elastic, water repellent and a good electrical insulator. However, it becomes brittle at low temperatures and sticky at high temperatures, has little mechanical durability and oxidizes rapidly.

After intensive experimentation to overcome these shortcomings, Charles Goodyear found in 1839 that if rubber was cooked with sulphur at 120-160°C for a sufficient time, it became practically a new substance. It was elastic over a wide range of temperature, becoming neither brittle nor sticky, mechanically more durable, and quite impermeable. This process is called *vulcanization* (named after Vulcan, the Roman god of fire) and the rubber product *vulcanized rubber*. A method of *cold vulcanization* was developed by Alexander Parkes in 1846, in which rubber was treated with a bath of sulphur-containing vapours. If about 5% sulphur is used, the rubber is soft and flexible. When 32% sulphur is used, the product, called *ebonite* or *hard rubber*, is an excellent, durable thermosetting plastic, once popular as a structural material in all kinds of electrical apparatus. It has now been replaced by cheaper plastics.

Most of the vulcanized rubber produced nowadays is used for making pneumatic tyres and tubes (invented in 1877 and improved in 1910). The mix for making a tyre includes, besides rubber and sulphur, accelerators (CaO, MgO, organic compounds), softeners (stearic acid, paraffin, petroleum jelly), reinforcing agents (carbon black, zinc oxide), and antioxidants. The green tyre is assembled with all its fabric, cord, and wire reinforcement, and put into the vulcanizing mould. Heat and pressure then make the finished tyre.

Although, now techniques of vulcanization with peroxides, with gamma radiation and with some organic compounds have been developed, sulphur remains the main plank in this application.

2. Soil-conditioning: Sulphur is an essential element in plants, and is present in some amino-acids. During the 1990s, sulphur deficiency in Indian soils was estimated by various agencies to occur in over 130 districts. As per the norm of the Indian Council of Agricultural Research (ICAR), a soil is considered deficient in sulphur if it tests less than 10 mg S per kilogramme of soil extractable with 0.15% solution of $CaCl_2$. Powdered sulphur is directly applied to such sulphur-deficient soils. Softness and brittleness of sulphur enable it to be powdered easily, and by virtue of its acidic nature, it neutralizes the adverse effect on plants, of soda or *black alkali* (Na_2CO_3) which is either originally present in the soil or is introduced through the irrigation water. Sulphur is essential for the growth of oil-seed crops. However, sulphur being insoluble in water is not directly assimilated by the plants; it is converted to soluble sulphate in the soil and then it becomes useful.

3. Human health: Sulphur is one of the five essential elements in human bodies (the other four are oxygen, hydrogen, nitrogen and cabon), and methyl sulphonyl methane or MSM constitutes 85% of the natural sulphur content of human bodies. MSM is a naturally occurring organic form of dietary sulphur. Unlike other forms of sulphur, it is odourless and does not produce intestinal gas or body odour. The body uses sulphur in many processes including collagen synthesis, cell oxygenation, carbohydrate metabolism and the maintenance of balance between acidity and alkalinity; sulphur also contributes to the flexibility and elasticity of the tissues and to permeability of the cell walls. The sulphur consumed for all these purposes must be replenished. MSM naturally occurs in raw foods such as fruit and vegetable, meat, milk, white of egg and seafood. However, much of the MSM content in food is lost during cooking.

4. Pyrotechnic mixture: Sulphur is an important fuel in pyrotechnic mixtures, because it is cheap and stable. It is an ingredient in match heads, the most common pyrotechnical device. Also, the compound phosphorus sesqui-sulphide (P_4S_3) is a component of the mixture forming the heads of strike-anywhere matches.

Further, it is used as an ingredient of gunpowder — a common propellant used in firecrackers, for firing cannons and rifles, etc. Gunpowder is an explosive with relatively low detonation velocity and requiring ignition. It is a special mixture of 75% potassium nitrate, 15% charcoal, and 10% sulphur, the reaction products of which are mostly gases occupying a much larger volume. In a confined space, the gases generate enormous pressure forcing the projectile out of the barrel. While the role of the potassium nitrate is to release the oxygen necessary for ignition and that of the charcoal is to catch fire and provide heat, the sulphur being non-inflammable does not catch fire, it only burns and generates the gases.

The sulphur and charcoal are ground together dry so that the thixotropic (thixotropy is the property of pseudoplastic fluids showing time-dependent change in viscosity) sulphur thoroughly coats the active surface of the charcoal. Then the nitrate is added, and the mix is wet ground until homogenized. The dried mix is formed into grains of the desired size, and the powder is ready for filling of cartridges, fireworks, blasting fuses etc. Potassium nitrate acts as the oxidizing agent providing oxygen for igniting the charcoal which then burns the non-inflammable sulphur for rapid generation of the gases.

5. Insecticide and germicide: The chemically active *flower of sulphur* is used as an insecticidal dust. Its proneness to slow oxidation producing SO_2 is the criterion. This poisonous gas SO_2 is the active substance in this application. It is an effective germicide or combating *Phylloxera* – a disease of the grape.

6. Sulphur dioxide: Sulphur dioxide is the chemical compound with the formula SO_2. This important gas is the main product from the combustion of sulfur compounds and is of significant environmental concern because in the presence of NO_2, it forms H_2SO_4 and causes acid rain. It is a colourless non-inflammable gas having specific gravity 2.55, melting at (-) 72.4^0C, boiling at (-) 10^0C and having high water-solubility (940 gm/litre at 25 °C). SO_2 is produced by various industrial processes as follows.

(a) Sulphur dioxide can be produced by burning sulphur:

$$S + O_2 \rightarrow SO_2 \text{ (contact process)}$$

(b) The combustion of hydrogen sulphide (or organo-sulphur compounds) can yield sulphur dioxide:

$$2H_2S + 3O_2 \rightarrow 2H_2O + 2SO_2$$

(c) The roasting of sulphide ores such as iron pyrites, sphalerite (zinc-blende) and cinnabar (mercury sulphide) also emits SO_2:

$$4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2$$
$$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$$
$$HgS + O_2 \rightarrow Hg + SO_2$$

(d) When anhydrous $CaSO_4$ is heated with coke and sand in the manufacture of $CaSiO_3$, sulphur dioxide is a by-product.

$$2CaSO_4 + 2SiO_2 + C \rightarrow 2CaSiO_3 + 2SO_2 + CO_2$$

(e) Action of hot concentrated sulphuric acid on copper turnings will produce sulphur dioxide.

$$Cu + 2H_2SO_4 \rightarrow CuSO_4 + SO_2 + 2H_2O$$

Sulphur dioxide is used for various industrial purposes as follows.

(a) *Preservative*: It is used as a preservative in alcoholic drinks, or dried apricots and other dried fruits due to its antimicrobial properties. The preservative is used to maintain the appearance of the fruit rather than to prevent rotting. This can give fruit a distinctive chemical taste.
(b) *Reductant*: Sulphur dioxide is also a good reductant. In the presence of water, sulphur dioxide is able to decolourize substances that can be reduced by it; thus making it a useful reducing bleach for papers, wool, silk, straw and delicate fabric. However, this bleaching effect normally does not last very long. Oxygen in the atmosphere re-oxidizes the reduced dyes, restoring the colour.
(c) *Sulphuric acid*: Sulphur dioxide is also used to make sulphuric acid. It is first converted to sulphur trioxide (SO_3), and then to sulphuric acid.
(d) *Poison*: Sulphur dioxide gas was in the past used as an execution poison in France. Sulphur dioxide blocks nerve signals from the pulmonary stretch receptors.
(e) *Refrigerant*: Prior to the development of *freon*, sulphur dioxide was used as a refrigerant in home refrigerators. It is easy to liquefy at room temperature by simple compression. The liquid boils at (-) 10°C under one atmosphere pressure, with a latent heat of 172.3 Btu/lb. SO_2 melts at (-) 75.2°C and its specific heat is 1.256. However, due to its irritating nature, it lost its popularity and was substituted by

chlorine-containing freon (chlorofluorocarbons or CFC) which were non-toxic and non-inflammable. But even freon are now banned in many countries because it is one of the five *green house gases* or *GHG* (the other four are CO_2, methane, NO_2 and water vapour) and it is largely responsible for the *ozone hole*.

(f) *Wine-making*: Sulphur dioxide is a very important element in wine-making, and is designated as parts per million in wines. It acts as an antibiotic and antioxidant agent, protecting wine against bacteria and oxidizing agencies, and it also helps to keep volatile acids at desirable levels. The upper limit of SO_2 allowed in wine is 350ppm. At up to 50 ppm concentrations in wines, SO_2 is remains undetected, but at over 50ppm, it becomes discernible in smell and taste.

(g) *Winery sanitation*: A mixture of SO_2, water, and citric acid is commonly used to clean hoses, tanks, and other equipment in a winery to keep them clean and free of bacteria.

(h) *Sugar refining*: For this purpose, concentrated $Ca(OH)_2$ is poured into boiling cane juice and SO_2 is passed through it. The phosphates and organic acid combine with CaO and SO_2 to form $CaCO_3$, $CaSO_4$, calcium phosphates and some organic compounds. When the juice is cooled, all these compounds settle down trapping with it all the impurities in suspension in the juice. The clear juice is decanted out. $CaSO_4$ is precipitated along with impurities which adhere to it.

(i) *Sulphurous acid*: SO_2 is dissolved in water to form sulphurous acid (H_2SO_3). This is a reasonably strong acid. It is the basis for bisulphite and sulphite salts. Sodium bisulphite ($NaHSO_3$) is used to prevent unwanted bacterial action in wine-making while calcium bisulphite [$Ca(HSO_3)_2$] is used to dissolve lignin of wood pulp to release cellulose fibers for making paper.

7. Sulphuric acid: SO_2 can be further oxidized by oxygen to SO_3. At low temperatures, the reaction is extremely slow, but the yield is good. At high temperatures, the reaction is faster but the yield is very poor. To overcome this problem, some catalyst is used. Nitrogen oxide is a suitable catalyst, but the reaction must be carried out in the gaseous phase, which necessitates large space for the reactions to take place and consequently large lead-lined chambers were earlier used. Because of this it was earlier known as *chamber process*. Later, it was found that platinum was a good catalyst and it required much smaller space. This is called the *contact process*, by which most of the SO_3 is produced today.

SO_3 dissolves readily in water to form cent per cent concentrated sulphuric acid (H_2SO_4) having density 1.838 gm/cc. Excess SO_3 makes *fuming sulphuric acid* or *oleum*, which contains the molecule $H_2S_3O_7$ (pyro-sulphuric acid). All these reactions between SO_3 and water are exothermic. Sulphuric acid is the second largest tonnage of industrial chemical produced after ammonia. Once consumption of sulphuric acid used to be regarded as the indicator of commercial prosperity of a country.

Sulphuric acid boils at 330°C, which is higher than the boiling points of most acids. Its important industrial uses are as follows.

(a) Any acid including nitric and hydrochloric acids can be prepared by simply treating its salt with sulphuric acid and then distilling.

(b) Manufacture of phosphoric acid fertilizer from phosphate rock (see the chapter on phosphorus).

(c) Other uses include pharmaceuticals, plastics, alums, paints and pigments, refining of petroleum and coal tar, fixation of ammonia, bleaching and dying, manufacture of sulphates, galvanizing, tinning, enamelling of iron and steel, refining of copper and other nonferrous metals, storage batteries, etc.

8. Photographic hypo: Reaction between SO_3 and NaOH yields sodium thiosulphate (NaS_2O_3). This salt was once believed to be a *hyposulphate* (S_2O_4) and so, it came to be called "hypo" in photography. It dissolves silver halides, so it can be used to remove unexposed silver halide from a developed photographic image.

9. Hydrogen sulphide: Hydrogen sulphide or hydro-sulphuric acid (H_2S) is a gas at room temperature, melting at (-) 82.9°C and boiling at (-) 61.8°C. It is very poisonous (more poisonous than HCN), but fresh air will overcome small concentrations. It has a strong, characteristic rotten-egg odour which disappears at higher concentrations. It can be prepared by the following processes:

(a) It is prepared for laboratory use by the action of hydrochloric acid on ferrous sulphate:

$$FeS + 2HCl \rightarrow H_2S + FeCl_2$$

(b) For production of smaller quantities, a mixture of sulphur, asbestos and paraffin is heated. The asbestos catalyzes the reduction of the sulphur with hydrogen from the paraffin.

(c) It is made by heating an 8%-solution of thionacetamide to 80°C:

$$[CH_3(CSH){=}NH] + 2H_2O \rightarrow [CH_3COOH] + NH_3 + H_2S.$$

Hydrogen sulphide is used in laboratory analysis to precipitate the insoluble sulphides of Ag, Hg and Pb.

10. Organic chemicals:

(a) *Carbon disulphide*: Carbon disulphide (CS_2) is the analogue of carbon dioxide. It is a volatile clear liquid of density 1.26 melting at (-) 111.5°C and boiling at 46.3°C. Like hydrogen sulphide, it has a distinctive odour, but is not poisonous. Sulphur dissolves readily in CS_2, and can be crystallized from the solution. It is prepared by passing sulphur vapour over red-hot coke. It is an industrial solvent used in manufacture of viscose rayon.

(b) *Sulphydryl or mercaptan*: These are the names given to the radical (SH). It appears in many organic compounds, like its more familiar oxygen analogue (OH). Methyl mercaptan (CH_3SH) is a gas added to *natural gas* to give it an odour so that leaks will be noticed before an explosive mixture occurs.

11. Magnesium casting: Due to the strong chemical affinity of magnesium, particularly in molten state, special care is taken during casting of its alloys, to protect it against oxygen.

Otherwise, magnesium will catch fire and pose hazards of explosion. Sulphur is widely used for insulating the molten magnesium from the atmosphere. Its powder is poured into the foundry to react with the air producing a white smoke of SO_2. Non-inflammable nature of sulphur combined with its affinity for oxygen is the main criterion.

12. Adhesive: An adhesive is an inorganic or organic substance capable of bonding other substances together by surface attachment. A hot melt of adhesive based on liquid sulphur called *sulphur cement* is used in acid tank construction where high resistance to acids is required. Resistance of sulphur to acids is the main criterion. Besides, its adhesion to metals is good.

13. Other uses:

(a) Enamels
(b) Ultramarine

B. Pyrites

1. Sulphur dioxide and Sulphuric acid: In nature, when pyrites is exposed to the environment during mining and excavation, it reacts with oxygen and water to form sulphuric acid, resulting in acid mine drainage. This drainage results from the action of *Thiobacillus* bacteria, which generate their energy by using oxygen to oxidize ferrous iron of the pyrites to ferric iron. The ferric iron in turn reacts with pyrites to produce ferrous iron and sulphuric acid. The ferrous iron is then available for oxidation by the bacteria; this cycle can continue until the pyrite is exhausted. But as long as native sulphur was available in plenty, pyrites was never considered as an economic commodity for manufacturing sulphuric acid, more so because of the frequently encountered association of arseno-pyrites, the arsenic of which is a poisonous substance.

During World War II, the demand for sulphur kept increasing while the quantity of native sulphur mined in North America kept decreasing. Soon the native sulphur mines started being depleted one by one. It was in this context that pyrite was first regarded as an alternative source of sulphur.

In India, The average grade of the run-of-mine pyrites is 22 % S. It is first crushed to (-) 300 mm size. At this size it is possible to wash the impurities away and sort the pieces into two grades — 12% and 26% S. Sorting is done with the help of laser sensors (these sense the pyrite pieces on the basis of their lustre) and compressed air blast. Both the grades are separately roasted.

Roasting of pyrites results in generation of SO_2 which are made dust-free with the help of electrostatic precipitator (ESP). The SO_2 can be either used directly (see serial number 6 above) or further oxidized to SO_3. At low temperatures, the oxidation process is extremely slow, but the yield is good. At high temperatures, the reaction is faster but the yield is very poor. To overcome this problem, some catalyst is used. While platinum is the preferred catalyst when native sulphur is the raw material, vanadium pentoxide (V_2O_5) is used nowadays as the catalyst when pyrites is the raw material, because it is not affected by the arsenic impurities frequently found associated with it. SO_3 is dissolved in water to yield sulphuric acid in the same way as in the case when sulphur is the raw material.

Although, pyrites is not the material of choice in countries where native sulphur is available in adequate quantities, it is still the raw material where sulphur is scarce as in India.

2. Soil-conditioning: In India, ground pyrite is a cheap and popular material for direct application to sulphur-deficient alkaline soil as substitute of sulphur. Like sulphur, it is also applied especially to soils on which oil-seed crops grow. Here, a part of the run-of-mine pyrites (average grade 22%) which is crushed to (-) 300 mm size (see sulphuric acid above) is further ground to (-) 6 mm size and sold for this purpose. Generally the hardness of pure pyrites (6.0-6.5 on Mohs scale) makes grinding costly, but in India, where low-grade pyritiferous shale is mined, this problem is not present.

3. Gem: Pyrites by virtue of its metallic lustre, brass-yellow gold-like colour, hardness (around 5 on Mohs scale) and cubic crystalline form is used in costume jewelry such as necklaces and bracelets. But it is not a valued gem because of its brittleness and tendency to oxidize on exposure to air. In this usage, marcasite is not at all suitable though the two are similar, because marcasite has a tendency to crumble into powder. Ironically, however, the trade name for pyrites gem is *marcasite*, which creates confusion amongst lay buyers. The term marcasite as a jewelry trade name is applied to small polished and faceted pyrites stones that are inlaid in sterling silver.

3. Other uses:

(a) *Radio detector*: Pyrites can show negative resistance and have experimentally been used in oscillator circuits as radio detectors.
(b) *Copperas or melanterite*: Copperas is a pale green hydrated ferrous sulphate ($FeSO_4.7H_2O$) obtained by decomposition of pyrites and is used in dyeing, in the manufacturing of ink, as a wood preservative and as a disinfectant.

Chapter 43

TALC-STEATITE-SOAPSTONE

Talc, steatite and soapstone are the names used in trade circle for variations in geological mode of occurrence and in purity, of the same mineral the original name of which is talc (the word has been adopted in English from the Arabic name “talq”). It is a isomorph of pyrophyllite (i.e. they share the same monoclinic structure but have different chemistries). The physical properties of the two minerals as well as their uses bear many similarities. Pure talc is a hydrated silicate of magnesium ($3MgO.4SiO_2.H_2O$) theoretically containing 63.5% SiO_2, 31.7% MgO and 4.8% H_2O and is characterized by extreme softness (cf., composition of pyrophyllite is $Al_2O_3.4SiO_2.H_2O$). It is generally found in nature in massive form. The nomenclature steatite is now generally restricted to the massive compact crypto-crystalline variety of high grade talc, while the name soapstone refers to the massive impure talcose rock generally containing 50-80% talc mixed with chlorite, amphibole, pyroxene, mica, pyrite, quartz, calcite, dolomite etc. Talc may occur in the form of flakes and fibers or blocks. The latter is sometimes referred to as “block talc” or “lava” (general name for any talc or soapstone) or “block steatite talc” (specific name for steatite variety of talc occurring in block form) or “french chalk” (a very soft massive variety of talc).

Talc occurs in chloritic schist, gneiss and dolomite. It is generally derived from either magnesium-bearing sedimentary rocks or ultrabasic igneous rocks, the former type being purer than the latter. It is formed in the former case by metamorphism under conditions of high temperature and/or pressure due to geological disturbance, igneous intrusion, etc. and in the latter case by hydrothermal alteration of non-aluminous magnesium silicates (e.g., asbestos, amphibole, pyroxene, etc.).

HISTORY

Talc was known during the ancient civilizations of Egypt, Assyria, China, Mohenjodaro and Harappa — all belonging to the era before 2800 BC. It was mainly its softness that attracted artisans to carve out of its pieces of jewelry beads, small vessels and art figures, and engrave stamp-seals which were then subjected to heat for ensuring hardness and durability. Its softness and heat-retaining property were known to the native Red Indians of USA 3,000 years ago, who used to cut bowls, cooking stoves, etc. out of it and from whom the early European settlers of 16th century learned its use. During the early eighteenth century, soapstone had already become popular in household fittings and architecture (e.g., kitchen tables, column bases, etc.). Large scale manufacturing industries based on talc began in USA in the 1880s. The world production stood at 5.9 million tons in the year 2000, out of which China accounted for nearly two million tons followed by USA (0.85 million tons). The other important producing countries were India, Finland, France,etc.

As far as India is concerned, the traditional practices of the people of the Mohenjodaro and Harappan periods have continued down the centuries. There is record of 70 tons of talc being exported from India some time around 1880 (i.e., around the same time talc-based manufacturing industry was set up in USA). Post-independence, the production of this mineral has registered a steady increase. From 26,000 tons in 1950, it increased to 92,000 tons in 1960, to 159,000 tons in 1970, to 360,000 tons in 1980. to 406,000 tons in 1990 and to about 596,000 tons in the year ending March 2001. During the year ending March 2006, the production stood at about 684,000 tons.

PROCESSING

Massive talc (including steatite and soapstone) that are mined in the form of blocks for sculpturing purpose has to be used as such and any processing will only destroy its economic value. These blocks are just hand-picked or screened (sometimes after washing) to remove the impure portions and the fines. However, in certain applications talc has to be used in powdered form, and in such cases it has to be subjected to some processing as follows.

(1) *Crushing and grinding*: Primary crushing is generally done in jaw crushers or gyratory crushers and for secondary crushing roll crushers, rotary crushers or disc crushers are deployed. The technique of grinding depends on the fineness of the size to be achieved. For achieving 40-100 mesh (380-150 microns) sizes, hammer mills suffice. But for finer grinding of soft talc to 100-325 mesh (150-45 microns) sizes, roller mills with air separators are used and for that of relatively harder talc, quartzite pebbles may have to be used as the grinding medium.

(2) *Beneficiation*: For removing iron, aluminium, calcium and other gangue materials from impure talc, the latter can be beneficiated. The process involves wet grinding, flotation and drying.

(3) *Micronization*: Micronization is the process for producing micron-sized particles — finer than those that can be produced by conventional grinding techniques. The technology for this purpose was first developed in USA in around 1940 to meet the demands of talc for some special applications, and the special grinding mills employed have come to be known as *micronizers*. The principle involves engaging the grains of talc to intense mutual bombardment within a closed chamber. There are nozzles on the walls of the chamber through which air or steam under high pressure is forced through while the pieces of talc are dropped though a central opening. By this process, particles of size as small as one micron can be produced. Micronized powder of pure white talc goes in Indian trade circle also under the name *french chalk.*

CRITERIA OF USE

In most of the applications of talc, its physical properties are made use of , the chemical nature coming into play only in the few applications involving firing. The important criteria of its industrial uses are as follows.

(1) *Crystal structure*: Crystal of talc may be either platy or fibrous (asbestine). When ground, the crystals break down into plates/flakes or fibers depending on the structure.

(2) *Hardness and surface feel*: Talc is the softest known mineral having hardness of 1 on Mohs scale and its surface is so smooth as to give a soapy and slippery feel. Due to impurities, soapstone is somewhat harder than pure talc, and this increased hardness makes the former preferable to talc in certain applications.

(3) *Colour and optical properties*: In pure state, talc is white to silvery white coloured (sometimes with a greenish tinge). It has a bright pearly lustre and its refractive index 1.54-1.59 (cf., linseed oil 1.48, ordinary glass 1.53, titanium dioxide 2.40, diamond 2.42). It is resistant to ultraviolet rays.

(4) *Density*: For its softness it has a remarkably high density — its bulk density being 2.4 tons/cu.m (cf., the figure is about 3 in case of granite). It is so dense that solid objects cut out of it do not even allow acids to pass through them.

(5) *Mechanical properties*: The thin plates or laminae constituting the talc crystals, although flexible, are not elastic. Consequently, talc possesses good mechanical strength, and for this reason, the structures and articles made up of talc are durable.

(6) *Electrical properties*: It is a poor conductor of electricity having high dielectric strength (dielectric strength is a measure of the electrical insulation, and is the voltage that an insulating material can withstand before break-down).

(7) *Non-plasticity*: Talc is hydrophobic (i.e., averse to water) and hence does not form a plastic mass when mixed with water. This nature is due to the slipperiness of its surface as water tends to slip away instead of adhering to it.

(8) *Chemical characteristics*: Chemically, talc is inert to both acids and alkalis. Its composition is $3MgO.4SiO_2.H_2O$ with 63.5% SiO_2, 31.7% MgO and 4.8% H_2O.

(9) *Oil absorption*: Ground talc has fairly high oil absorption ability — up to 35%. This ability depends on the interfacial tension, shape of particles (fiber or plate) , specific surface (total area of surface of particles per unit mass) and particle size distribution. More interfacial tension means the particles will tend to hold together leaving less space for the oil to occupy and hence oil absorption will be lower. While the interfacial tension is the same for all types of talc particles, it depends on the other three factors. The total surface area provided by the particles is more in case of plates than fibers, and hence both the specific surface and the tension is more in case of plates than in case of fibers. Again, uniform particle size means larger interstitial pore space for oil to occupy than non-uniform particles, and hence in case of the former, oil absorption ability is higher. Summing up, uniformly ground fibrous or asbestine type talc will have higher oil absorption ability than platy type.

(10) *Thermal properties*: In talc are combined the advantages of both metals and water as far as thermal properties are concerned. Like a metal, it gets heated quickly and then,

like water (and unlike a metal), it retains the heat for a long time, slowly radiating it over many hours. This apparently anomalous behaviour is due to a combination of high specific heat and poor thermal conductivity. High specific heat means that for a unit rise in temperature, a mass of talc can absorb a large amount of heat; while poor thermal conductivity means that the absorbed heat does not flow out of it quickly. The thermal conductivity decreases even more when the talc is fired.

(11) *Fired properties*: Talc can withstand temperature of up to 1300^0C. At this temperature the water molecules are completely driven off and in the process part of the silica also breaks off as free silica, converting talc into *clinoenstatite* ($MgSiO_3$ or $MgO.SiO_2$). This clinoenstatite is a hard and practically infusible substance (it does not fuse, but at 1557^0C it disintegrates into forsterite ($2MgO.SiO_2$) and SiO_2). It also possesses high electrical resistivity, tensile strength, compressive strength and impact strength. The low water content of 4.8% ensures low shrinkage on firing.

USES AND SPECIFICATIONS

The principal uses of talc (including steatite and soapstone) are:

1. Paper manufacturing
2. Textile
3. Cosmetics
4. Rubber
5. Refractory
6. Ceramics
7. Paint
8. Insecticide
9. Building and household fittings
10. Crayon
11. Plastics
12. Pharmaceuticals
13. Synthetic marble
14. Sealant
15. Cordierite saggar

These uses are discussed in details as follows.

1. Paper manufacturing: Talc finds use to serve one or more of the following four purposes:

(a) *Filler*: As a filler micronized talc is added for imparting smoothness and opacity to the paper and also for filling up the ultrafine interstitial pores between cellulose fibers of the pulp so as to prevent water from entering into them (hydrophobia of talc helps it in this role as the powders of talc do not adsorb water) and also increase the density of the product. For this usage, talc powder is mixed with china clay before adding. Talc serves to offset the higher cost of ultrafine china clay without affecting the benefits to any great extent. Particle size is the most critical parameter. Micronized talc of less than 2 micron particle size (for ordinary quality paper up to 53 micron size is accepted by the industries) that facilitate a very high degree of dispersion so as to spread uniformly and fill up the ultra-fine pores in the cellulose, is specified. The smoothness of surface, white colour with moderate refractive index, pearly lustre, hydrophobia and inertness to acids are the main criteria for this use of talc. Obviously, grit and calcite which affect smoothness and any constituent soluble in acids, will be highly deleterious. Degrees of brightness and whiteness depend on the quality of the paper. Off-white natural talc is acceptable for roofing and other lower quality paper. However, any extraneous colouring substance (iron, copper, manganese) is objectionable. So far as brightness is concerned, the industry prefers 80-96% value as measured in terms of reflectance from blue light wave length of which is 457 micron (cf. the value of fresh TiO_2, which is the bench mark for brightness, is 97-98). CaO, being strongly hygroscopic, will absorb water and will result in crumbling of talc ingredient of the finished paper on exposure to air. So, it is objectionable.The Bureau of Indian Standards (BIS) in its recommendations of 1978, has set limits for certain critical parameters. Important parameters according to it are: *matter insoluble in HCl acid 95% (min); brightness 80% (min); grit 0.02% (max);* Fe_2O_3 *0.3% (max); Cu and Mn each 0.05% (max); size 75 micron (max).* Additionally, industries specify not more than 4% CaO, but they accept up to 0.03% grit and up to 2% Fe_2O_3 in case of ordinary quality paper.

(b) *Coating*: In this case also talc is mixed with other more expensive whitening substances like china clay in order to reduce the cost. Platy structure of the crystals and brightness are the principal criteria. The plates offer large flat surface areas and facilitate high retention on the coated surface (i.e., the ratio of the talc added during manufacture to the talc which remains in the finished paper). The minute plates of talc stick to the paper along its surface, giving it a smooth bright finish and good printability. The specifications are similar to those in case of filler grade talc.

(c) *Process control*: During the paper-making process, microscopic/colloidal sticky droplets of oily resin get added to the stream. These micro-impurities tend to clog the paper machinery. Talc, having high oil absorption, absorbs the oily droplets that are smaller in size than the talc particles. So far as the bigger sized droplets are concerned, the smooth slippery plates of talc enables its particles to stick to the droplets effectively neutralizing the stickiness of the latter. Additionally, talc, on account of its slippery surface, reduces the friction on paper-manufacturing machinery thus reducing wear.

(d) *Tank lining*: Talc or soapstone is sawn in the form of bricks for lining alkali recovery tanks. In such tanks, the environment is alkaline, and the inertness of talc to alkalis combined with the smooth slippery surface of the bricks are the chief criteria. The talc should be in massive form so as to facilitate cutting bricks out of it.

2 Textile: Talc in micronized form is used as a filler in textile for the purpose of imparting smoothness and opacity to the cloths and also for filling up the ultrafine interstitial pores between cellulose fibers so as to prevent water from entering into them and also increase the density of the product.

Fine particle size will facilitate a very high degree of dispersion so as to spread uniformly and fill up the ultra-fine pores in the cellulose. Softness, smoothness, natural white colour, good hiding power and inertness to acids are the main criteria for this use of talc. Obviously, grit and calcite which affect smoothness and also affect the knives and needles used in textile manufacturing, and any constituent soluble in acids will be highly deleterious. Any extraneous colouring substance (iron, copper, manganese) is objectionable. Moisture, on evaporation, causes shrinkage and cracks, and hence is considered deleterious. The Bureau of Indian Standards (BIS) specifications are similar to those in case of filler grade talc for paper manufacturing. Additionally, industries specify not more than 0.5% moisture.

3 Cosmetics: High-quality talc is used as a base in body and face powders (*talcum powder*), creams, etc. after adding deodorant and perfumes, and also as a polishing agent in toothpastes and powders. Hydrophobia of talc prevents it from adsorbing the sweat and causing stickiness. Natural white colour, softness, smoothness, resistance to ultraviolet light, hydrophobic property and chemical inertness are the principal criteria.

Colour should be very white and hence iron which is a colouring substance is considered deleterious. Grit and calcite affect smoothness. Complete chemical inertness will demand total absence of both acids and alkalis. But a slight alkalinity (pH higher than 7) is not objectionable because bacteria forming in human body sweat and teeth tend to increase the acidity level in them. Lead and arsenic, being highly toxic and poisonous substances, are highly objectionable. Salts (e.g., sulphates) soluble in water should be minimum. These salts go into solution into the water with which talc powder is mixed (as in creams, pastes etc.), and later on, when the water evaporates, the dissolved salts form scum on the surface due to by capillary action.

The Bureau of Indian Standards (BIS) in its recommendations of 1977, has set limits for certain critical parameters. The important parameters according to it are: *matter soluble in water 0.2% (max); Pb 20 ppm (max);* As_2O_3 *2 ppm (max);* Fe_2O_3 *0.3% (max); pH in aqueous solution 9.5 (max); size 90 micron (max).* Industries, however, accept up to 0.75% Fe_2O_3, but specify the maximum limits of 1.5% for CaO (indicator of calcite content), 1.5% for acid insoluble matter and 7.5% for LOI. They do not tolerate any grit.

4. Rubber: The purpose here is to use talc as a dusting agent for lubricating moulds and for preventing surfaces from sticking together during manufacture. Chemical inertness, platy structure and smooth greasy feel are the main criteria. As it is used in the form of dust, fineness of size is obviously important and grit is highly objectionable. The platy structure has a smoothening effect on the surface of rubber tyres.

The Bureau of Indian Standards (BIS) in its recommendations of 1978, has set limits for certain critical parameters for talc for its use as a filler in rubber. The relevant important parameters according to it are: *matter insoluble in HCl acid 95% (min); grit 0.02% (max); size 75 micron (max).*

Besides, talc can also be used as a compounding agent to produce certain types of semi-hard rubber, and for that purpose, the chemical composition of talc becomes relevant.

5 Refractory: Refractory materials are defined as those resistant to heat and having a melting temperature of not less than 1580^0 C. The function of refractory lining on a furnace wall is not only to withstand high temperature, but also to withstand temperature fluctuation, and to resist penetration, abrasion, and erosion by hot gases and molten materials in the furnace, and over and above, it should not chemically react with those materials. Talc as such is not suitable for making refractories, because it can withstand temperature of up to only 1300^0C. Nevertheless, it can be combined with other materials and formed into refractories for use in certain applications as follows.

(a) *Insulation bricks*: A mixture of china clay and talc is used for production of insulation bricks which are not expected to withstand repeated thermal shocks.

(b) *Forsterite refractory bricks*: Forsterite ($2MgO.SiO_2$), a product based on talc, is suited to application as refractory bricks in the roofs of copper-smelting furnaces. Forsterite can be made by heating talc beyond 1557^0C. When talc is heated to 1300^0C the water molecules are completely driven off and in the process part of the silica also breaks off as free silica, converting talc into *clinoenstatite* ($MgSiO_3$ or $MgO.SiO_2$). At 1557^0C, this clinoenstatite disintegrates into forsterite and SiO_2. But made this way, the forsterite contains free silica and is not pure. Besides, the process is energy-intensive. Instead, a less energy-intensive and more efficient process consists in firing a mixture of talc and magnesite to temperatures of $1400\text{-}1500^0$C. They react to form forsterite as follows:

$$3MgO.4SiO_2.H_2O + 5MgCO_3 \rightarrow 4(2MgO.SiO_2) + H_2O + 5CO_2$$

(c) *Steatite bricks*: Crushed steatite pieces are bonded by sodium silicate and moulded into bricks for lining reverberatory furnaces in which crude lead bullion is softened before separation of silver.

(d) *Artificial cordierite*: Artificial cordierite has the composition $Mg_2Al_4Si_5O_{18}$. It has the same characteristics as natural cordierite, which is formed due to contact metamorphism. It crystallizes above 950^0 C and remains stable over a considerable range of temperature i.e., up to 1750^0C. It has low linear expansion, low coefficient of thermal expansion, excellent resistance to thermal shock, high mechanical strength, ability to work in both oxidizing and reducing atmospheres and to withstand rapid temperature changes without breakage. Artificial cordierite can be derived from an admixture clay, grog, bauxite powder and talc. This material has applications in the manufacture of cooking ware, heat radiator parts, stove fronts, burner tips, electrical heater plates, electrical resistor cores and other articles required to undergo repeated and rapid heating and cooling. A comparatively recent development is a material called *"cordierite saggar"*, made from artificial cordierite. Saggars are trays used as kiln furniture and shelves for firing powders or components in porcelain and ceramic manufacturing. Saggars made of artificial cordierite have long lives of 10-15 firing cycles.

In the talc used for making refractories, the most deleterious constituent is $CaCO_3$, which has a strong fluxing effect. Besides, after firing, while the CO_2 escapes leaving holes in the refractory, the CaO remains in the product which, being strongly hygroscopic, increases the chance of crumbling of the product over a period of time.

6. Ceramics: The word "ceramic" derived from Greek "keramos" originally meant fired and fused common clays. The original ceramic products (e.g., bricks, potteries) made only of clay were hard and resistant to heat and chemicals, but at the same time coloured, porous and brittle. Today, the product range has gone much beyond bricks and potteries to include a host of high quality white products which are not only hard and resistant to heat and chemicals but also nonporous and strong materials. In addition, glazed ceramic products are now available. (The purpose of glazing is to provide a uniform firmly adhering coating on the surface of the ceramic body concealing defects such as pinholes, bubbles, etc., and the glaze is made of the same ingredients but with predominance of quartz and feldspar.) For manufacturing them, mixtures of multiple materials in different proportions are used. Talc is one such material. Broadly, the ceramic products based on talc as one of the raw materials can be grouped as follows.

(a) *Wall tiles*: Glazed earthenware wall tiles are used for the surface of walls where cleanliness is an important factor as in hospitals, kitchens, bathrooms, chemical laboratories, etc. To make such tiles, a mixture consisting of ball clay, talc, dolomite, wollastonite and slate pencil powder is wet ground to 120 mesh size, passed through a magnetic separator to remove iron particles, agitated and filter-pressed by which water is driven away and cakes are formed. The cakes are dried, powdered, mixed with some binder and then tile-pressed. The tiles are first biscuit fired (ceramic engineers' term for firing before glazing like baking of biscuits), cooled, glazed on the top surface and glost fired (ceramic engineers' term for post-glazing firing) up to 1050^0C temperature.The criteria of this usage of talc are its poor thermal conductivity, lower fusion temperature (1300^0C) in comparison to ball clay (1600-1750^0C), mechanical strength, low shrinkage on cooling after firing (which in turn minimizes *crazing* i.e., cracking of the glaze), white colour, and inertness to both acids and alkalis. The most deleterious constituent is $CaCO_3$, which although tends to decrease the fusion temperature, has some harmful effects. On firing, while the CO_2 escapes leaving holes in the body, the CaO remains in the product which, being strongly hygroscopic, increases the chance of crumbling of the product over a period of time.

(b) *Potteries*: These include table ware, sanitary ware, porcelain ware, etc. Talc used as an additive to the main ingredients, namely china clay, quartz or silica sand, other types of clay, feldspar and soda as a flux (for manufacturing and glazing processes see the chapter on china clay). The most important criterion for this usage of talc is its smooth slippery surface which prevents the material from sticking to the mould. Other criteria are its lower fusion temperature (1300^0C) in comparison to china clay (1785^0C), mechanical strength, low shrinkage on cooling after firing (which in turn minimizes *crazing* i.e., cracking of the glaze), white colour, and inertness to both acids and alkalis. In case of table ware, talc's combination of poor thermal conductivity and high specific heat resulting in high heat retaining power is of particular advantage for keeping cooked food warm for a long time (see history earlier in this chapter).

White colour and fineness of size are very important. The industries generally specify 80-93% whiteness (cf., fresh TiO_2: 98-100%) and less than 75 micron (200 mesh) size. A little $CaCO_3$ is desirable as it tends to decrease the fusion temperature, too much of it is considered deleterious because of some harmful effects. On firing , while the CO_2 escapes leaving holes in the body, the CaO remains in the product which, being strongly hygroscopic, increases the chance of crumbling of the product over a period of time. Besides, iron oxide, aluminium oxide, tremolite and alkalis are also objectionable. Fe_2O_3 has a colouring effect on the product. Al_2O_3 tends to increase fusion temperature. Tremolite has an abrasive effect on the steel dies used for moulding. Alkalis are deleterious because sodium and potassium in the form of carbonates combine with silica at the firing temperature to form silicates which are water soluble and presence of these silicates in the ceramic product, obviously, will not be desirable. Moreover, alkalis have fluxing property and they get into the raw material mix through the feldspar and soda. So their presence in the talc may create problems of managing the chemistry of the mix. The Bureau of Indian Standards (BIS) in its recommendations of 1982, has set limits for certain critical parameters for talc for its use in pottery manufacturing. The relevant important parameters according to it are: *Al_2O_3 2.5 % (max); Fe_2O_3 1.5 % (max); CaO 3.5% (max) and (Na_2O + K_2O)0.5% (max)*. The industries, however, specify up to 6% CaO and not more than 1% tremolite for use in white ware.

(c) *Electrically insulating porcelain*: This material goes in industry circle also under the name *lava*. It is purely a talc-based product, and the type and quality of talc used for making this product is called *lava grade*. It is actually clinoenstatite ($MgSiO_3$), and not ordinary porcelain (which is based on a raw material mix with china clay as the dominant ingredient). Compared to ordinary porcelain, lava possesses better electrical resistivity and greater tensile, compressive and impact strengths. This product is used for high-frequency insulation of radio, radar, television and other electronic equipments. For manufacturing this lava, the material used is either massive pure block steatite that can be machine-cut into desired shapes and threaded or pure talc in powdered form which is die-pressed in dry or semi-dry state into various intricate shapes. These shapes are fired at 1300^0C allowing a crystalline network of clinoenstatite to form and remain without further transformation. In the case of die-pressing powders of talc, about 10% of china clay (for facilitating mould preparation) and some fluxing material like potash feldspar, barium carbonate, magnesium carbonate (for reducing the firing temperature) is usually mixed (otherwise china clay, having fusion temperature 1785^0C, will increase the fusion temperature of talc). Natural availability in the form of massive blocks, high dielectric strength, high mechanical strength, high specific heat, low shrinkage on cooling after firing and ability to transform to hard and practically infusible clinoenstatite on firing (with the electrical and mechanical properties retained intact) are the main criteria for this application of talc. Due to high specific heat, these products do not become appreciably hot even after being subjected to prolonged heating due to exposure to high voltage.

With regard to specifications, alkalis, both sodium and potassium, are strictly deleterious because their ions are electrically conducting. Al_2O_3 is also considered an objectionable constituent as it tends to increase fusion temperature, and industries specify a maximum limit of 4 per cent.

7. Paint: Talc is not used much as a primary pigment in either oil or water paints. It is not suitable in oil paints owing to its high oil absorption and its poor opacity in oil due to the refractive indices of talc (1.54-1.59) and that of linseed oil (1.48) being close to each other (that of the best pigment i.e., titanium dioxide is 2.40). Regarding water paints, its hydrophobic nature (owing to extreme slipperiness) prevents water from adhering to the surfaces of its particles. It is, however, used as an extender and suspending agent in oil paints. Since the amount of talc used for these purposes is small compared to that of the pigment, its high oil absorption does matter much. In both these applications, iron oxide, volatile matter and moisture are objectionable. Iron oxide has colouring effect. Volatile matter is specified by industries to be below 1% and moisture 4 to 7%, because otherwise painted surfaces may develop cracks due to their escape on drying. The preferred maximum size of powder is 53 micron (300 mesh), but for very high quality paints, industries specify a maximum limit of 2 micron. Water soluble sulphates are considered deleterious because they will adversely affect the durability of coatings. On exposure to water, the sulphates will go into solution and after drying reappear on the surface of the coating as scum. So far as brightness is concerned, the industry prefers 87% value as measured in terms of reflectance from blue light wave, length of which is 457 micron (cf. the value of fresh TiO_2 , which is the bench mark for brightness).

(a) *Extender*: An extender is a slow-drying medium with which a paint is mixed primarily for increasing its volume so as to facilitate its application with a brush. But, at the same time, its colouring property and hiding efficiency must not be compromised, and its viscosity should be maintained at a working level. Refractive index, platy structure, white colour, pearly lustre, durability (due to the combined effect of chemical inertness and mechanical strength), smooth surface, softness and resistance to ultraviolet light are the principal criteria.

The refractive indices of talc and linseed oil being similar, addition of the former does not modify the opacity or hiding power of the composite paint. Due to its platy structure, the powders of talc are made up of micro-flakes with large total surface area enabling the flakes to securely stick to the surface coated and allowing the paint to level out after application. This is called in industrial parlance *flatting effect*. This effect along with smooth surface of the flakes, pearly lustre and their durability, ensures a smooth, even, pleasing and durable finish of the painted surface. Due to its white colour, talc does not affect the colour of the main pigment component of the paint, while its softness facilitates easy brushing without any abrasive effect. Resistance to ultraviolet light is an additional advantage when the painted surface is exposed to sun. Due to these advantages, talc makes a good low-cost substitute of some expensive materials like titanium dioxide and some resins. Industries specify white coloured and platy crystalline type talc.

(b) *Suspending agent*: In this application the fibrous crystalline type of talc (asbestine) in powder form makes a good low-cost substitute of some expensive materials like china clay. Fine-sized fibers of talc trap and hold the primary pigment particles enabling the latter to remain in suspension long enough to facilitate brushing. White colour and close match between the refractive indices of talc and linseed oil ensure that addition of talc does not modify the colouring and hiding properties of the paint. Smooth surface, pearly lustre and durability of talc will ensure a smooth, even, pleasing and durable finish of the painted surface. Its resistance to ultraviolet light is an additional advantage when the painted surface is exposed to sun.

8. Insecticide: It is used as a carrier by virtue of its inertness and high bulk density. For this application, high quality talc is not required, and there is more consideration for low cost. The Bureau of Indian Standards (BIS) in its recommendations of 1978 has set limits for certain critical parameters for talc for its use as a filler in insecticide. The relevant important parameters according to it are: *matter insoluble in HCl acid 95% (min); size 75 micron (max).* Industries prefer a maximum limit of matter insoluble in HCl acid at 97% and, additionally, a moisture content of not more than 7 per cent.

9. Building and household fittings: In roofing products, such as tar, paper, asphalt shingles and roll roofing, talc acts as a fire retardant and it increases weather resistance. Massive steatite cut into panels is used for switch boards and acid-proof table tops in laboratory, laundry and kitchen sinks, in tubs and tanks. Slabs sawn from massive steatite find use for lining stoves, ovens, fire places etc. for their ability to retain heat long after the source of heat is withdrawn. In all these applications, the common criteria are softness and easy workability, chemical inertness, high density, mechanical strength, durability, smooth surface and, above all, aesthetic look. In applications like stoves, ovens, fire places, roofs etc., poor thermal conductivity and high specific heat resulting in high heat retention are additional criteria.

10. Crayon: It is one of the traditional uses of talc. It is used by tailors for marking cloths for alteration purpose and by metal workers for making marks on metals. Lumps of steatite are first sewn into blocks with square or rectangular shaped sides. These blocks are then cut into thin slabs equal in thickness to the desired width of the crayons, and finally, these thin slabs are cut to final size of crayons. White colour, softness, mechanical strength and platy structure are the basic criteria. In addition, poor thermal conductivity facilitates using such crayons for marking on hot metal sheets. Due to the platy structure, when a crayon is rubbed on a surface, the powders produced are made up of microflakes with large total surface area enabling the flakes to securely stick to the fabric and metal surfaces. Consequently, unlike ordinary chalk, the marks made with talc crayons do not go off easily, and those made on metal sheets have the unique characteristic of remaining visible when a cold metal is heated or when a hot metal is cooled.

11. Plastics: Plastics are basically oleo-resinous materials. Talc is used as a filler in polypropylene (PP), high density polyethylene (HDPE), low density polyethylene (LDPE), polyvinyl chloride (PVC), etc. In this application, its properties like high specific heat (ability to take heat without much increase in temperature), high electrical resistance, good mechanical strength, resistance to ultraviolet light, greasiness, platy structure, chemical inertness and high oil absorption are made use of. These improved plastic materials find use in automobile dashboards and bumpers requiring mechanical strength, computer bodies requiring high specific heat and electrical resistance and garden chairs requiring high specific heat and resistance to ultraviolet light. In all these applications, smoothness and greasiness of talc are carried to the product and platy structure gives smooth finish. High oil absorption ensures excellent mixing of talc with the oleo-resinous materials and inertness prevents chemical reaction between them.

For ensuring colour neutrality, talc should be strongly white with a degree of whiteness 92-98% (cf., value for fresh titanium dioxide which is the whitest substance is 98-100%) and the content of Fe_2O_3 should be not more than 0.5 percent. For uniform dispersion within the matrix, industries specify ultra-fine particle size and for high-quality sensitive products the size is as small as one micron.

12. Pharmaceuticals: In the pharmaceutical industry, the main criteria for use of talc are its white colour, mechanical strength, platy structure, low refractive index, chemical inertness and good lubricity (due to smoothness). Its applications are as follows:

(a) It is used as a lubricant to facilitate tablets or capsules to glide along during their manufacture. Talc constitutes only 1-4% of the material.
(b) It is used as a carrier of dusting powders by virtue of the large surface area provided by its plates to which dust particles adhere. Talc constitutes 90-99% of the material. However, it is not suitable for use for dusting surgical gloves because when the gloves are in contact with peritoneal cavities or open wounds, talc causes irritation.
(c) It finds application as a filler in some types of tablets. However, due to slipperiness and hydrophobic nature, particles of talc tend to disintegrate and not hold together often creating problems.
(d) It can be used as a structural strengthening agent in film coating because: (i) its plates facilitate formation of smooth films, and (ii) colours used in the tablets remain unaffected due to the low refractive index of talc.

A very high degree of purity is required and natural talc has to be processed for removing impurities like iron oxide, dolomite and other carbonate materials and carbon.

13. Synthetic marble: Synthetic marble is a strong, homogeneous, dense, translucent product which can be cast into different shapes and sizes. It finds use in bathrooms and as structural components. It is made by casting and heat-curing (in presence of a catalyst) a finely ground mixture of alumina and resin matrix with some filler material. The filler constitutes 50-85% of the weight of the mixture and includes calcite, silica, oxides of antimony and titanium and talc. The refractive index of the mixture vis-à-vis the resin matrix is so manipulated as to give an illusion of depth. Talc used is in the form of powder of size less than 250 micron (60 mesh). The role of talc is to impart strength, density, thermal resistance, chemical inertness (resistance to both acids and alkalis) and smooth finish (by virtue of its platy structure). Its colour and refractive index are also important criteria .

14. Sealant: A sealant is an organic substance soft enough to pour or extrude into an opening in an object, and capable of subsequent hardening to form a permanent bond with the object. Micronized talc is used as a filler in some sealants to perform certain functions as follows:

(a) Talc absorbs the resin binder of the sealants and imparts rheological properties to them, i.e., it prevents them from sticking to the container tubes and facilitates their extrusion into the openings by virtue of its smooth and slippery surfaces of the particles.

(b) Talc serves to reinforce the sealants.

(c) Talc adds to their density by virtue of its high bulk density.

Obviously, the main criteria for this application of talc are high oil absorption, strength , high bulk density and particle size. The degree of oil absorption, in its turn depends on the shape of the particles and uniformity of size. Fibrous or asbestine type of talc ground to uniformly fine particle size has higher ability of oil absorption than its platy counterpart and hence is the most suitable. The fine-sized powder of talc can uniformly disperse throughout the sealant.

15. Cordierite saggars: A comparatively recent development is a material called *"cordierite saggar"*, made from artificial cordierite. Saggars are trays used as kiln furniture and shelves for firing powders or components in porcelain and ceramic manufacturing. Artificial cordierite has the composition $Mg_2Al_4Si_5O_{18}$. It has the same characteristics as natural cordierite, which is formed due to contact metamorphism. It crystallizes above 950^0 C and remains stable over a considerable range of temperature, i.e., up to 1750^0C. It has low linear expansion, low coefficient of thermal expansion, excellent resistance to thermal shock, high mechanical strength, ability to work in both oxidizing and reducing atmospheres and to withstand rapid temperature changes without breakage. Saggars made of artificial cordierite have long lives of 10-15 firing cycles. Artificial cordierite is made from an admixture of fireclay, grog, bauxite powder and talc.

16. Other uses:

(a) *Polishing*: Talc powder is used for polishing delicate wood articles and grains of rice, barley, corns, peanuts, etc.

(b) *Lubricating*: Because of smooth slippery surface, chemical inertness and fineness of size enabling it to uniformly spread or disperse in a medium talc is sometimes used in grease as an additive and also in foundry facing.

(c) *Statues and decorative artifacts*: Pleasing colour, smooth surface, durability (due to the combined effect of chemical inertness and mechanical strength) and above all, softness making it highly amenable to work on, make talc one of the popular materials for statuary and decorative show-pieces. Ancient Egyptians used to cut gem-like pieces out of talc and then engrave on it signets. Massive block steatite is required in this application.

(d) *Curing insulated cables*: For curing, insulated cables are laid inside steam chests. Talc powder serves as a suitable bedding material for laying the cables. Greasy surface and high thermal resistance prevent them from sticking to the surface.

(e) *Gun powder*: Talc powder is added for preventing friction between the particles of gun powder which may produce enough heat to cause accidental explosion. The slipperiness of talc is the main criterion.

Chapter 44

TOURMALINE

The name tourmaline ("Turmali" in Hindi) has been derived from the Singhalese word "*Turmali*". It is widespread in occurrence and is commonly found in pegmatite and granite. Tourmaline is a complex borosilicate of aluminium with uncertain chemical composition. Various general formulae have been suggested. One of them is written as $[(Na, Ca)(Li, Al, Mg, Fe, Mn)_3(Al, Fe)_6B_3Si_6O_{27}(O, OH, F)_4]$ and another as $[4R_6Al_2(SiO_4)_3.R_6Al_2(B_2O_5)_3]$, in which 'R' may be hydrogen, magnesium, iron, calcium or alkali metals. Depending on 'R', tourmaline has been classified into different subspecies known by different names like schorl, rubellite, achroite, Brazilian sapphire, verdellite or Brazilian emerald, indicolite etc. Out of these, the pink to red coloured rubellite containing alkali metals is economically the most significant, and is used both as a gem and for industrial application. Mong Mit in Myanmar was the mining centre for the best crystals of rubellite during the 18th and 19th centuries. But they have become increasingly scarce. In India, there is no reported find of this variety of tourmaline, although other varieties are found in Rajasthan.

CRITERIA OF USE

1 *Colour and refractive index*: Colour is the most important parameter of beauty in case of tourmaline, because it lacks brilliance due to relatively low refractive index (1.62-1.64 compared to 2.42 of diamond). Colour of tourmaline depends on the 'R' in the molecular formula $[4R_6Al_2(SiO_4)_3.R_6Al_2(B_2O_5)_3]$, and it may be colourless (achroite), pink, ruby red, violet red, rose red (rubellite), blue (Brazilian sapphire), indigo blue (indicolite), green (verdellite) or black (schorl).

2 *Polarization of light*: As white light waves propagate through space, the vibrations take place in all possible directions on all possible planes. But due to certain factors, these vibrations are modified so as to take place on a single plane only. This light vibrating on a single plane is called "*polarized* light", and the phenomenon of such modification is called "*polarization*". The polarizing factors are: (i) partial reflection, (ii) double refraction or birefringence, and (iii) absorption. When light is incident on an object, some of its rays are reflected back and some are refracted, and both the reflected and the refracted rays are polarized. When the object is doubly refractive, each of the two refracted rays is polarized. In case of absorption (as in case of a dark coloured object), light rays vibrating in all but one plane are absorbed within the

object and the rays emerging out from it are thus polarized. Polarized light is used for seeing the colour of an object in thin section under microscope, otherwise in unpolarized light it will appear as almost colourless unless the object is very dark coloured. A unique optical property of tourmaline is its ability to polarize light by absorption.

3 *Piezoelectricity*: Piezoelectric crystals can change alternating mechanical strains into electrical impulses and vice versa. This property is also called '*electrostriction*'. Such a crystal must not have a centre of symmetry. When pressure is applied, its ions are displaced resulting in polarization of the crystal and flow of electric current when circuit is complete. In other words, mechanical force is converted into electrical energy, and if the force is alternate causing alternating contraction and expansion, then the electric current becomes oscillatory. Conversely, if oscillatory current is applied to the crystal, it will set up a cycle of alternate expansion and contraction, i.e. vibration. Tourmaline is a piezoelectric material.

4 *Pyroelectricity*: Pyroelectric substances are a kind of semiconductor. Semiconductors are materials with resistivity intermediate between metals (resistivity $< 10^4$ ohms/cm) and insulators (resistivity $>10^3$ ohms/cm). They contain only a small number of loosely bonded electrons at room temperature, and hence their conductivity is very poor (of the order of 100,000 times less than that of conductor metals). However, their low electrical conductivity can be substantially improved by various methods one of which is by supplying thermal energy. This phenomenon of increase in conductivity with increasing temperature is called "*Pyroelectricity*". Tourmaline is a strongly pyroelectric material.

5 *Boron-inertness*: Tourmaline being saturated with boron, does not react with boron.

6 *Durability:* Tourmaline is a hard substance having hardness 7-7.5 on the Mohs scale. Besides, it is practically devoid of any cleavage. This combination of properties gives it resistance to both scratching and breakage. Also, it remains unaffected by acids. All these properties make it durable.

7 *Rarity*: By the law of demand-supply, the scarcer a commodity is , the higher is its value. While certain varieties of tourmaline like the iron-bearing black coloured ordinary tourmaline is a very widespread mineral, the economically significant rubellite is rare.

8 *Clarity*: Small bubbles, cracks and other flaws reduce the clarity of a gem, and consequently, its value. Clear, flawless tourmaline is very rarely found.

9 *Cut*: Natural gems are mined as rough stones. They need to be cut into well defined faces and the faces are polished to produce their characteristic sheen and optical effects. The cutting requires a very high degree of skill – particularly when the individual pieces are small. Minimum loss of stone is to be ensured during cutting.

10 *Aggressive marketing*: Almost any gemstone can be sold irrespective of colour and cost, provided the basic criterion of rarity is met. Economically, demand of any gem is by and large elastic, i.e., they are luxury items, and not essential in our lives. Consequently, gems do not follow the conventional law of demand and supply according to which, demand generates first and supply follows. On the other hand, in case of gems, supply comes first and demand generates later in response to that. Emeralds and its sister gems are no exception.

USES

The above factors have made tourmaline useful both as gem and for certain special non-gem applications. These are as follows.

1. Gem:

(a) *Jewelry*: In this use, rubellite is the most prized tourmaline. It was all through a rare variety of tourmaline, and with dwindling of its mining activity in Myanmar it has become even more scarcer. This rarity combined with durability, clarity and attractive colours (light pink to ruby red) makes it a valued gem for use in jewelry. Other varieties of lesser values are also used depending on their colours and clarity.

(b) *Decoration*: Tourmalines not having any market value for jewelry, but nevertheless attractive to look at, are made into decorative showpieces and sold by sheer aggressive marketing.

2. Non-gem:

(a) *Polariscope*: Polariscopes are used for polarizing light and then, with its help, for seeing colours and other properties of minerals in thin sections. Most commonly used polariscope today is "*polarizing microscope*". However, a very simple polariscope for quick examination, is the "*tourmaline tongs*". In this device, two plates of tourmaline mounted on cork are fixed to the two arms of a pair of tongs. The thin section to be examined is pressed between these tourmaline plates and then seen with naked eyes.

(b) *Measurement of high pressure and fluid compressibility*: In this application, the piezoelectric property of tourmaline is made use of. The pressure generates electric charge within tourmaline and the electricity is measured. The latter gives the measurement of the pressure directly with the help of a calibrated manometer.

(c) *Thermal dosimeter*: The word "dosimeter" comes from "dose" – in this case amount or intensity of radium emanations. The thermal energy from the radium transforms into measurable electric charge because of the pyroelectric property of tourmaline. This instrument has ceased to be popular after advent of more sophisticated and sensitive instruments.

(d) *Boron-related experiments*: Due to its boron-inertness, tourmaline serves as a standard reference for comparing contents of water soluble boron in fertilizers and examining their effects.

Chapter 45

TRONA AND NAHCOLITE

Trona: Trona [sodium sesquircarbonate, $Na_3H(CO_3)_2$. $2H_2O$ or $Na_2CO_3.NaHCO_3.2H_2O$] is an evaporite mineral. Theoretically, trona contains 41.2% Na_2O, 38.9% CO_2 and 19.9% H_2O. The name trona comes from the ancient Egyptian word “ntry” through the Greek “nitron” and Arabic “natron” meaning salt. It is valued as the natural sources of soda ash or sodium carbonate (Na_2CO_3), an important industrial chemical used to make glass, paper, laundry detergents, various sodium compounds, etc. Theoretically, 1.67 tons of trona is equivalent to 1 tonne of soda ash.

Trona is a white to grey or yellowish brown crystalline mineral having Mohs hardness 2.5-3.0 and specific gravity 2.1. It has massive or columnar form with perfect cleavage.

Trona deposits occur in USA, Iran, Tibet, Canada, Kenya, Namibia, Egypt and Mongolia.

The trona near Green River, Wyoming, USA, discovered in 1938 in course of oil well drilling, is the largest known deposit in the world deposited in a lake during the Tertiary period, and estimated to contain 100 billion tons of 80-90% pure trona wedged in between layers of oil shale and extending to over 2500 sq. km. area. The trona deposit varies in depth from 250 to 1100 m below the surface and contains 42 layers of trona. Actual mining (Sweetwater County) is confined to a depth of 500 m in beds that are 2.5-3.0 m thick.

The first mine commenced production in Sweetwater county in 1946. Presently, it is supplying about 15% of the world’s soda ash demand. Trona is mined by conventional underground methods and also, being soluble in water, recovered by solution mining method using hot water. The refined soda ash produced from the trona is more than 99.6% pure.

So far as the remaining demand of soda ash is concerned, it is met by synthetic soda ash manufactured by *Solvay process* or *ammonia-soda process* developed in the 1860s by Solvay brothers of Belgium. In this process, ammonia is absorbed in brine (natural or made by mixing water with salt) and then CO_2 is reacted with the ammoniated brine. First ammonium bicarbonate is formed which reacts with NaCl to form sodium bicarbonate, which is filtered and dried to produce soda ash.

Nahcolite: In natural deposits, crystals of natural sodium bicarbonate *nahcolite* [$NaHCO_3$] usually occurs intimately mixed with trona , but during mining, nahcolite is difficult to distinguish from trona as their physical properties are similar. They can be distinguished by only optical or X-ray techniques. Its uses are as follows.

1. Food and beverages: Sodium bicarbonate, also called baking soda, is a key ingredient in manufacture of effervescent salt and beverages. It reacts with acids to release carbon dioxide according to the reaction:

$$NaHCO_3 + HCl \rightarrow NaCl + H_2O + CO_2$$

2.Electrostatic precipitator (ESP): It is suitable for reducing industrial pollution . Industries now-a-days equip their plants with *electrostatic precipitators* (ESP) for capturing SO_x emissions and suspended particles. Nahcolite is used as granular filters behind an ESP. It works by reacting with SOx to produce solid waste sodium sulphate or sodium sulphite:

$$2NaHCO_3 + SO_3 \rightarrow Na_2SO_4 + H_2O + 2CO_2$$
$$2NaHCO_3 + SO_2 \rightarrow Na_2SO_3 + H_2O + 2CO_2$$

Besides, nahcolite filters trap the suspended particles. Thus it serves to enhance the efficiency of modern ESPs in reducing the levels of polluting emissions.

3. Deodorizing: Sodium bicarbonate reduces odour by neutralizing acid by-products of bacteria. This makes it suitable for use in health and beauty applications and in household cleaning.

Chapter 46

VERMICULITE

When subjected to heat vermiculite has the unusual property of exfoliating or expanding into worm-like threads, and the name vermiculite has been derived from Latin ‘vermiculus’ meaning ‘worm’ (or 'vermiculare' - to breed worms). It is a complex hydrated aluminium and magnesium silicate and its average composition can be represented by the formula [$(MgFe,Al)_3(Al,Si)_4O_{10}(OH)_2.4H_2O$]. It possesses a mica-like laminar structure. In fact, it is an alteration product of biotite or phlogopite micas, but is nowadays regarded in the industry circle more as a separate mineral than as a member of mica group. It is formed by hydration of certain basaltic minerals when most of their alkalis are replaced by water. The individual flakes of most of the commercial grades of vermiculite are of around 2-3 mm size although larger sizes are also in demand.

For a long time, the world production was dominated by one mine, namely, Libby mine of Montana, USA which was the largest and oldest vermiculite mine operating during the period from early 1920s till 1990, when it was closed down under public pressure. There, vermiculite was mined under the trade name *Zonolite*, and it was found to contain asbestos — a mineral infamous for its carcinogenic effect on workers and banned in many countries. For a considerable time, this generated public concern against vermiculite mining. But, it has now been confirmed that vermiculite produced from no other mine contains asbestos.

In 2005, South Africa was the top producer of vermiculite with about 40% of world share followed by the USA and China. Other important producing countries include Australia, Brazil, Kenya and Zimbabwe. So far as India is concerned, its production suffered from ups and downs throughout its mining history starting from 1950, when, for the first time a small quantity of 53 tons was produced in Karnataka. It attained a peak of 4933 tons in 1986 and during the year ending March 2006, a total of 4,774 tons was produced from the mines located in Andhra Pradesh, Tamil Nadu and Rajasthan. All mining is done by open cast method.

CRITERIA OF USE

Vermiculite is a translucent electrically non-conducting crystalline mineral with perfect cleavage, vitreous lustre, uneven fracture and generally having honey-like colour (the colour tends to change during expansion and is dependent upon the composition of the vermiculite and furnace temperature). But there are some critical properties that determine its industrial usage. They are as follows.

1. Chemical characteristic: The molecular formula of vermiculite is $[(MgFe,Al)_3(Al,Si)_4O_{10}(OH)_2.4H_2O]$, and the water-content in its crystal is responsible for its most important property i.e., exfoliation. Chemically, vermiculite is inert and it is a non-toxic substance.

2. Hardness: Vermiculite is soft material having hardness 2-3 on Mohs scale.

3. Specific gravity: Vermiculite is a light-weight material having specific gravity 2.4-2.7.

4. Grain size: Its use depends on the size (large, medium or fine) of the granules. Its softness facilitates low-cost crushing into different size fractions. The size varies from 12 mm down to (-) 150 micron. Larger granules will have lower bulk density due to air pockets and may be suitable for applications requiring light-weight material in high bulk . Fine-sized granules have larger surface area for chemical reaction or absorption and may be suited to applications requiring this attribute.

5. Exfoliation: Exfoliation is the property of being able to expand to many times its original volume when heated. Vermiculite differs from mica in its characteristic property of exfoliation. This characteristic of exfoliation is the basis for commercial use of the mineral, and it is the result of the mechanical separation of the layers by the rapid conversion of contained water to steam. When heated, increase in bulk volume (i.e., decrease in bulk density) commences at 150^0 C and continues as the temperature rises. Commercial grades of exfoliated vermiculite with 8 to 12 times increase in bulk volume (individual flakes may exfoliate as many as 30 times) is made by passing the crude vermiculite quickly through a furnace heated to about 1000^0C to provide a residence time of between 0.25 seconds and 8.0 seconds depending on shape and size of the particles.

6. Durability- Vermiculite does not rot or degenerate even after a long period of time, and it is not attacked by vermin.

7. Thermal properties: The air in the pores within the grains of expanded vermiculite traps heat and thus imparts to the latter thermal insulation capability. After exfoliation, it can withstand fairly high temperature of over 1100^0C.

8. Sound insulation: The pores provide zigzag interconnected paths for the air to pass through, thus slowing down the propagation of sound waves and imparting acoustic insulation.

9. Porosity and water absorption: After the escape of water, the expanded vermiculite becomes a porous mass. This porosity enables it to absorb and retain water for slowly releasing it later.

USES

Vermiculite has been used in various industries for over 80 years. It is used mostly in processed forms. Processing involves separation from gangue materials, exfoliation, crushing into granules, screening and classification into different granule sizes. Its important uses are:

1. Refractory
2. Thermal insulation applications
3. Fireproof material
4. Soil conditioner
5. Agriculture, plantation and hydroponics
6. Animal/poultry farms
7. Construction

These uses are discussed as follows.

1. Refractory: Refractory materials are defined as those resistant to heat and having a melting temperature of not less than 1580^0 C. The function of refractory lining is not only to withstand high temperature, but also to resist temperature fluctuation, slag and metal penetration, abrasion, and erosion by hot gases and molten slag and metal. Vermiculite, with its resistance to temperature of around 1100^0C, is used in furnaces and kilns up to only this temperature, and is, therefore, strictly not a refractory material. It is more apt to regard it as a high-temperature insulating material. However, its chemical immunity makes it resistant to attacks by molten slag and metal, and, in industry circle, it is seen as a refractory material. Medium-sized granules of exfoliated vermiculite are used both in the form of loose-fill and bricks. The leading Indian manufacturers prescribe the specifications as: *SiO_2 36 to 37%, Al_2O_3 14 to 16%, Fe_2O_3 10 to 14%, TiO_2 3 to 4%, LOI 6 to 8%, CaO 2 to 2.5%, K_2O + Na_2O 3 to 5%, Moisture 17 to 19% and size 1.0-2.8 mm (6-16 BS mesh).*

2. Thermal insulation applications: Larger exfoliated vermiculite granules are used as a loose-fill material between boards, wire-nets, sheets, etc. for thermal insulation of roofs and walls in homes, industrial structures and low temperature industrial equipment. Also, moulded shapes, bonded with sodium silicate are used as commercial hand-warmers and in other customized applications. The Indian industries specify 36% (min) SiO_2 , 16% (min) Al_2O_3, 15% (min) MgO and a minimum of 8-times exfoliation.

3. Fireproof material: The combination of the properties of high heat-insulation abilities and chemical inertness that prevents it from reacting with oxygen and catching fire, makes the loose granules of exfoliated vermiculite suitable for use in

i. fireproofing of structural steel and pipes;
ii. component of the interior fill for fire-stop pillows along with graphite for boiler-pipe lagging;
iii. building fire-resisting walls in deep mines.

Fine-sized granules are preferred.

4. Soil conditioner: Medium-sized granules are used as soil conditioner to lighten clay soil and to improve the moisture retention qualities of sandy soil. Fine-sized granules, by virtue of their ability to absorb and retain moisture and large surface area for doing so, are used as an anti-caking agent in fertilizer.

5. Agriculture, plantation and hydroponics**:** Finer granules of exfoliated vermiculite, by virtue of their ability to absorb and retain liquids and large surface area for doing so, are used as carriers for agricultural chemicals like pesticides, herbicides, insecticides and liquid fertilizers. They help in dry handling and slow release of the chemicals. Besides, their high water-retention power makes them a suitable growing medium for hydroponics (i.e., growing plants without soil).

6. Animal/poultry farms: Large-sized granules are suitable as a substrate for various animals and also for incubation of eggs. The large granules with many air pockets trap heat and help to provide warmth.

7. Construction: Low specific gravity, low bulk density of medium-sized granules, efficient thermal and sound insulation powers, ability to retain and slowly release water and chemical inertness with inability to catch fire make vermiculite in its exfoliated form a suitable additive for making light-weight concrete aggregates, plasters and tiles with acoustic and thermal insulation properties, fire-stop mortars and cementitious spray fireproofing. In the latter application, vermiculite has proved to be a good substitute for the environmentally hazardous and now-banned asbestos-based spray. Thus made concrete, mortars, plasters, etc are also used for making the base of swimming pools with a view to maintaining the temperature of the water. Also, beams made of such concrete being light-weight, are safer and less expensive to use than conventional beams. The Indian industries specify 36% (min) SiO_2, 16% (min) Al_2O_3, 15% (min) MgO and a minimum of 8-times exfoliation.

Products based on mixtures of cement, sand, exfoliated vermiculite and binding agents, such as gypsum plaster, are applied on structural steel members in commercial buildings and also on gypsum boards.

8. Other uses:

(a) *Packing material*: Medium to large granules of exfoliated vermiculite are used in fireproof and thermally insulating packing.
(b) *Paints and lubricants*: Fine-sized granules of exfoliated vermiculite granules are used for the same purpose as above.
(c) *Plastics and wall paper*: Exfoliated vermiculite is used as a light-weight filler and also for the fireproofing functions.
(d) *Sealant*: Exfoliated vermiculite is used in conjunction with antimony dioxide (SbO_2) in fireproofing sealing material.
(e) *Glass industry*: It is used for regulating the cooling rate of hot pieces in glassblowing, lamp-work, and glass bead-making.
(f) *Drilling mud*: Unexfoliated vermiculite is used. Its flat scales stick to the drill-hole walls and help in smoothening the circulation of drilling mud.
(g) *Annealing steel*: Annealing is the process of gradually heating and cooling. Here, unexfoliated vermiculite is used for regulating the cooling rate.

Chapter 47

WOLLASTONITE

Wollastonite (also known as *tabular spar*) is a meta-silicate of calcium having the formula $CaSiO_3$ (48.3% CaO and 51.7% SiO_2). It usually occurs as aggregate of bladed or needle like crystals that may contain small amounts of iron, magnesium, and manganese partially substituting for calcium. It is named after the English chemist and mineralogist William Hyde Wollaston (1766-1828). It forms when impure limestone or dolomite is subjected to high temperature and pressure in the presence of silica-bearing fluids as per the following reaction:

$$CaCO_3 + SiO_2 \rightarrow CaSiO_3 + CO_2$$

It has also formed due to inclusion of limestone in volcanic eruptions. Contact metamorphic rocks are its most favourite locale. Associated minerals include garnets, vesuvianite, diopside, tremolite, epidote, plagioclase feldspar, and calcite.

Wollastonite has as many as seven polymorphs having the same chemical composition but differing in crystal structure. However, the commonest of all is that having triclinic symmetry followed by the monoclinic *parawollastonite*. Commercially, all the polymorphs are referred to as wollastonite only.

Important occurrences of wollastonite in the world are known in the states of New York, Texas, California and New Jersey, USA; in the volcano Monte Somma, Vesuvius, Italy; in Ontario and Quebec, Canada and in Finland, Rumania, Germany, Mexico, Greece, China and Switzerland. China is the leading producer in the world with over 70% share followed by India and the USA (status in 2001).

In India, occurrences of wollastonite are known in Rajasthan, Gujarat and Tamil Nadu, but its production comes from only Rajasthan. Its production started in 1969 with 447 tons and after frequent ups and downs, it has reached a level of 128,582 tons during the year ending March, 2006.

CRITERIA OF USE

Wollastonite is a colourless to white or grey medium hard (Mohs hardness around 5) mineral having vitreous to pearly lustre and having specific gravity 2.8. But the most important properties of wollastonite from the user industries' point of view are:

(a) Colour if the powder is brilliant white.
(b) Fired colour is cream to white.
(c) Wollastonite crystals have acicular structure with aspect ratio (i.e., the length to breadth ratio of the individual aciculae) varying from 3:1 to 20:1 (cf., aspect ratio of asbestos varies from 20:1 in case of low grade to as high as 1000:1 in case of chrysotile). Structure of wollastonite with aspect ratio 15:1 to 20:1 can be termed as semi-fibrous.
(d) It has high resistance to heat melting at 1540^0C and low thermal expansion as well as low shrinkage on cooling.
(e) It has low moisture and oil absorption.
(f) It is insoluble in water.
(g) Its refractive index is about 1.63.
(h) Chemically it is inert.
(i) It has low volatile content (unlike calcite which gives off CO_2 on heating).

USES AND SPECIFICATIONS

Wollastonite that is sold in India contains a minimum of 94% $CaSiO_3$, 0.76% (max) Al_2O_3, 0.49% (max) Fe_2O_3, 0.4% (max) MgO and 2.71% (max) LOI. The important uses of wollastonite are:

1. Ceramics
2. Friction products
3. Electrodes
4. Mineral or rock wool
5. Adhesive
6. Plastics and rubber
7. Paint

These uses are elaborated as follows.

1. Ceramics: Wollastonite is an important constituent in all its ceramic applications by virtue of its high melting temperature of $1{,}540^0$ C, white to cream fired colour and low volatile-content. Volatiles tend to leave blemishes on the surface while escaping. In such applications, the acicular structure of wollastonite is not of relevance and that with low aspect ratio of less than 5:1 can find use.

(a) *Refractory ceramics*: These are ceramic products that are resistant to heat such as refractory tile.

(b) *Refractories*: Melting point of wollastonite is higher than that of steel and this makes wollastonite suitable for use as a filler in refractory linings of steel mills.

(c) *Earthenware tiles*: Wollastonite is used as a filler or minor constituent in earthenware tile based mainly on ball clay. Such tiles find use as ceramic floor and wall tiles, marine wall board etc.

(d) *Glaze*: The purpose of glazing is to provide a uniform firmly adhering coating on the surface of the ceramic body concealing defects such as pinholes, bubbles etc. Glaze may be "*raw glaze*" or "*fritted glaze*". Raw glaze consists of insoluble material applied as such (soluble components crystallize in the mixture and cause blemishes on the treated surface), while fritted glaze is heated beforehand to cause chemical change in the components. Glaze should not only melt but also spread uniformly. The glaze is made of the same ingredients but with predominance of quartz and feldspar. The ingredients are mixed, finely ground and mixed with water, and this mixture is the glaze. The moulded raw body of the product is dipped into the glaze and then fired to a high temperature. Wollastonite is used as a component in fritted glaze for providing a lime matt finish (by virtue of its lime-content).

2. Friction products: In such products, fibrous materials with high strength and heat-resistance are suitable because of their flexibility and resilience. Ideally, chrysotile variety of asbestos with aspect ratio in the region of 1000:1 is the preferred substance used for making woven brake linings and clutch facings. In India tremolite and actinolite varieties of asbestos (aspect ratio low but above 20:1) are also used for these purposes. But, on account of the health hazards associated with mining and use of asbestos, wollastonite with aspect ratio of its aciculae 15:1 to 20:1 is used as a partial replacement for short-fiber asbestos in certain applications by virtue of its high thermal resistance.

3. Electrodes: Wollastonite is used in the coating to prevent current loss due to eddy currents. The high dielectric strength combined with high heat resistance of wollastonite is the criterion. Wollastonite containing 96-98% $CaSiO_3$ is generally used by Indian industries.

4. Mineral/rock wool: Mineral wool is a general term meaning fibers made from inorganic substances that may include minerals, rocks and metal oxides — synthetic or natural. When the substance is a natural mineral or rock it is called rock wool or stone wool. It is a fibrous netlike substance produced by blasting steam or air through the molten mass of a mineral or a rock, and cooling. Alternatively, the molten mass is subjected to high-speed spinning on wheels. The result is a mass of fine inter-wined fibers the diameters of which can be as low as 6-10 nanometres. Sometimes, a resinous binder (e.g., phenol formaldehyde) is added to strengthen the wool and oil may also be added during processing to prevent dust formation. Wollastonite, by virtue of its acicular structure and low volatile content, yields good-quality wool. Besides, wollastonite has high dielectric strength. So wollastonite wool is suitable for use for insulation and for filtering. Besides, it can be used for heat and sound insulation, in brake pads, in gaskets and in fireproofing systems. Because it can retain water, it is nowadays used in hydroponics (growing plants on only water and without soil). In this wool, the individual fibers are not more than 3.5 micron in diameter and not less than 10 micron in length, and a typical net made of it consists of 3 fibers per cm^3.

5. Adhesive: Adhesive is an organic or inorganic substance capable of bonding together other substances by surface attachment. Wollastonite is used as an additive in certain adhesives. It plays the following role.

i. By virtue of its brilliant white colour, it acts as an extender in pigments of high brightness.
ii. Acicular crystal structure reinforces the media and increases impact strength (due to the cushioning effect provided by the aciculae), tensile and flexural strengths (due to the tendency of the aciculae to orient themselves along the flow of the resins which moves when applied).
iii. It imparts high dimensional stability due to low thermal expansion and low shrinkage on cooling.
iv. Low viscosity is achieved with high loadings of its solid powder.

Wollastonite is finding favour with the industries after the use of asbestos has been largely discontinued on account of the health hazards associated with mining and use of asbestos.

6. Plastics and rubber: Wollastonite used as a reinforcing agent due to the reasons as above.

7. Paint: The principal criteria that make wollastonite suitable as a filler in certain paints are its high brightness and whiteness, chemical inertness and low moisture and oil absorption.

Chapter 48

ZEOLITE

The name zeolite owes its origin to the Greek words “zein” (means "to boil") and “lithos” (means "a stone"), i.e., "a stone that boils", and it was originally coined in the 18th century by a Swedish mineralogist named Axel Fredrik Cronstedt who observed, upon rapidly heating a natural mineral, that it began to bubble and appeared to boil as the water evaporated. Today, the term zeolite is used to denote a group of 48 naturally occurring complex hydrated silicates of aluminium containing a wide variety of loosely held cations like sodium, potassium, calcium, magnesium, etc. Some of these minerals are of economic significance. These include clinoptilolite [$(Ca,K_2Na_2)O.Al_2O_3.10SiO_2.6H_2O$], analcime [$Na_2O.Al_2O_3.4SiO_2.2H_2O$], chabazite [$(Ca,Na_2)Al_2Si_4O_{12}.6H_2O$], heulandite [$(Ca,Na_2)O.Al_2O_3.6SiO_2.5H_2O$], natrolite [$Na_2Al_2Si_3O_{10}.2H_2O$], phillipsite [$(K_2,Ca)_2Al_4Si_8O_{24}.9H_2O$], apophyllite [$KFCa_4Si_8O_{20}.8H_2O$] and stilbite [$(Na_2,Ca)Al_2Si_6O_{16}.6H_2O$].

Chemically, zeolites are similar to clay minerals which are also alumino-silicates. They differ, however, in their crystalline structure. The latter have a layered crystalline structure (similar to a deck of cards) and are subject to shrinking and swelling as water is absorbed and removed between the layers. In contrast, zeolites have a rigid, three-dimensional crystalline structure (similar to a honeycomb) consisting of a network of interconnected tunnels through which water moves freely in and out, but the structure remains rigid.

Natural zeolites are secondary minerals having been formed either by alteration of feldspars, feldspathoids and volcanic tuff or as a result of reactions between volcanic rocks and ash layers with alkaline groundwater or by crystallization in post-depositional environments in shallow marine basins. In nature, they are found as infillings and amygdales in cavities, fractures, vesicles and veins in basalt, diabase, etc. Natural zeolites are rarely pure and are contaminated to varying degrees by other zeolites and various minerals like quartz etc., and are excluded from many important commercial applications where uniformity and purity are essential.

Currently, the world’s annual production of natural zeolite is about 4 million tons of which about 65% is consumed in China alone for its construction industry. So far as India is concerned, some varieties of zeolite occur as amygdales in Deccan Trap basalt in western Maharashtra (Pune-Lonavla area). The most abundant zeolite in India is stilbite followed by apophyllite, heulandite and others. Traditionally, natural zeolites in India have been no more than collectors’ delight, and as for commercial use, mainly synthetic zeolites and some substitute materials are used.

CRITERIA OF USE

The different types of zeolite have varying physical and chemical properties. Crystal structure and chemical composition account for the primary differences which result in differences in cation selectivity, molecular pore size, strength, etc. For example, clinoptilolite, the most common natural zeolite, has 16% more void volume and pores as much as 0.2 nm larger than analcime, another common zeolite. Source plays a large role in these variations and a zeolite mineral from one source will not necessarily have the same properties as the same one from another source. Environmental conditions during and following the deposition of zeolites are rarely the same in different occurrences. The types and number of impurities present and the way in which the zeolites are cemented together are all dependent on the unique conditions during their formation. Thus, some zeolite may help to assist plant growth while some other may make excellent filtration medium, but the same zeolite will not necessarily do both well. It is, therefore, important to know the specific type of zeolite that will be the most appropriate for each of its applications. Zeolites are now a subject of intensive research in UK and other countries. The following properties are important in determining the various industrial applications of zeolites.

1 *Porous structure:* Zeolites are characterized by its typical microporous structure comprising interconnected pores and tunnels of molecular dimensions (if all the channels in a teaspoon of zeolite were opened up and laid side by side, they would cover a football ground). These pores and tunnels are hosts to water molecules and a variety of positively charged ions (cations) of sodium, potassium, calcium, magnesium etc., but only those of appropriate molecular size to fit into the pores are selectively admitted while the other sizes are excluded. This unique sieving ability has earned it the nick-name *molecular sieves*. The maximum size of the molecular or ionic species that can enter the pores of a zeolite is controlled by the diameters of the tunnels. These are conventionally defined by the ring size of the aperture. For example, the term "8-ring" refers to a closed loop that is built from 8 silicon or aluminium atoms and 8 oxygen atoms linked in the shape of a tetrahedron. These rings are not always perfectly flat and symmetrical due to the strain induced by the bonding or due to adherence of some of the oxygen atoms of the rings to cations. Therefore, the pore openings for all rings of the same size are not identical. Their sizes roughly vary between 3 and 10 angstrom in diameter (1 angstrom is equal to ten billionth of a metre or one-tenth of a nanometre).

2 *Cation exchange capacity (CEC):* The large volume of micropores enable zeolites to absorb positively charged transition metals (mainly Na, K and Ca but also Mg) which get trapped and reside in these pores. Since they are loosely trapped without any chemical bonding, they are easily exchangeable. The type and amount of exchangeable ions (only Na, only K, mixture of Na, K, Ca etc.) distinguish one zeolite mineral from another.

3 *Catalytic power:* Zeolites have the ability to act as catalysts for chemical reactions which take place within the internal cavities. An important class of reactions is that catalysed by hydrogen-exchanged zeolites, whose framework-bound protons give rise to very high acidity. Zeolites can also serve as oxidation or reduction catalysts,

often after metals have been introduced into the framework. Underpinning all these types of reaction is the unique microporous nature of zeolites that enables it to control the access of reactants and products. Thus zeolites are often said to act as *shape-selective catalysts*. Further, the large surface area on the walls of their pores allows many chemical reactions to occur at least 50 times more efficiently than otherwise.

4 *Adsorptive ability*- The shape-selective properties of zeolites are also the basis for their use in molecular adsorption. The ability to adsorb preferentially certain molecules, while excluding others, has opened up a wide range of molecular sieving applications.

5 *Hardness:* Zeolites are not very hard with hardness varying from 3.5 to 5.5 on Mohs scale.

6 *Specific gravity:* 2.0-2.4.

USES AND SPECIFICATIONS

Conventional open pit mining techniques are used to mine natural zeolites. The overburden is removed to allow access to the ore. The ore may be blasted or stripped for processing by using tractors equipped with ripper blades and front-end loaders. In processing, the ore is crushed, dried, and milled. Crushing and milling are not very costly due to moderate hardness (3.5-5.5 on Mohs scale). The milled ore is air-classified as per particle size while the crushed product is screened for obtaining two fractions — granules and fines. The latter is sometimes made into pellets. Producers also may modify the properties of the zeolite or blend their zeolite products with other materials to enhance their performance. The cornerstone of the different industrial applications of zeolites is their microporous structure and consequent sieving ability at the molecular level. The important uses of zeolites are:

1. Nuclear waste treatment
2. Soil reclamation
3. Nursery, horticulture and silviculture
4. Animal husbandry
5. Paper
6. Heating and refrigeration
7. Purification of oil, gases, chemicals
8. Medical grade oxygen
9. Construction
10. Detergent
11. Water treatment
12. Fishery and aquarium
13. Zeoponic material
14. Catalytic agent
15. Gem
16. Perfect glass
17. Carbon sequestration

18. Beet sugar

These uses are discussed as follows.

1 ***Nuclear waste treatment:*** Zeolite can be used for radioactive waste products in two ways:

(a) The alumino-silicate frame of zeolites is extremely durable and resistant to radiation in spite of the porous structure. Additionally, once they are loaded with trapped fission products, the zeolite-waste combination can be hot pressed into an extremely durable ceramic form, closing the pores and trapping the waste in a solid stone block thus greatly reducing hazards associated with treatment of such wastes.

(b) The high cation exchange capacity (CEC) and high micro-sieving efficiency makes zeolites an excellent sorbent material with ability to selectively capture some ions to the exclusion of others. It can play a very important role in nuclear waste reprocessing by removing and permanently trapping many waste fission products like lead.

2 ***Soil reclamation:*** Potassium and nitrogen are two of the four major indispensable plant nutrients (the other two are phosphorus and calcium). Zeolites dominated by exchangeable K, therefore, may be well-suited for plant growth applications while those dominated by Na should be approached much more carefully as Na in high concentrations can be detrimental to plants. The natural zeolite clinoptilolite is used for soil treatment. It provides a source of slowly released potassium. If previously loaded with ammonium, the zeolite can serve a similar function in the slow release of nitrogen. It has been seen that certain zeolites can reduce nitrates and nitrites to free nitrogen by ion exchange.

3 ***Nursery, floriculture, silviculture:*** Zeolites can act as water moderators. They can absorb up to 55% of their weight in water and slowly release it according to plant demand. This property can prevent root rot and moderate drought cycles. In an experiment, a potting soil with 12% clinoptilolite was found to harvest morning dew and return it to the plant roots for reuse. The same bed was able to grow healthy leaf lettuce without external water in a sub tropical climate with daytime temperatures exceeding 30° C. Zeolite, by virtue of the absorbed and stored water, can also be used as a growing medium in hydroponic gardens (hydroponics is a technique of growing plants without soil, in water containing dissolved nutrients). By virtue of their ability to absorb, zeolites can be used for preventing cesium uptake in plants grown on contaminated soil.

4 ***Animal husbandry:*** Addition of as little as 1% of a very low-sodium clinoptilolite to livestock feed is known to be beneficial. It absorbs ions of some elements from the feed, stores them and releases them as per need within the body of the animal. This way it can store phosphorus and slowly release it as assimilation progresses for improved bone density. Clinoptilolite variety of zeolite is also used for cleaning the

environment around confined animals by absorbing airborne ammonia and toxins generated by fungi.

5 ***Paper:*** Micronized white (or bleached) natural clinoptilolite type of zeolite is used in USA, Japan etc. for imparting strength to paper. Because of the absorption capacity of zeolite, the surface particles of the paper become firmly bonded with it. The strength of the alumino-silicate frame of the zeolite species makes such papers strong.

6 ***Heating and refrigeration:*** Zeolites can be used as solar thermal collectors and for adsorption refrigeration. In these applications, their high heat of adsorption and ability to hydrate and dehydrate while maintaining structural stability are taken advantage of. This hygroscopic property coupled with an inherent exothermic reaction when transitioning from a dehydrated to a hydrated form (heat adsorption), make natural zeolites effective in the storage of solar and waste heat energy. By virtue of their heat-adsorption ability, zeolite can serve as a refrigerating agent.

7 ***Purification of oil, gases, chemicals:*** Zeolites (specially chabazite) are believed to have the potential of providing precise and specific separation of gases including the removal of H_2O, CO_2 and SO_2 from low-grade natural gas streams. Other separations include: noble gases, N_2, freon (chlorofluorocarbon or CFC) and formaldehyde. However, presently, this is still a subject of research. The hygroscopic positively charged cations (sodium, potassium, calcium, magnesium) trapped within the pores of zeolites have strong affinity for moisture, and by virtue of this affinity, they can selectively separate negatively charged particles of moisture and desiccate liquids and gases. Here, the selective absorption by zeolites is based not only on differences in size and shape but also on those in polarity. Due to the same factors, zeolites can also separate ions of one gas from another in a gaseous mixture and organic solvents from water. In some cases, different types of molecule enter the zeolite, but some diffuse through the channels more quickly, leaving others stuck behind, as in the purification of para-xylene.

8 ***Medical grade oxygen:*** Zeolite-based oxygen generation systems are widely used to produce medical grade oxygen. The zeolite is used as a molecular sieve to create purified oxygen from air, in a process involving the absorption of undesired gases and other atmospheric components, leaving highly purified oxygen and up to 5% argon.

9 ***Construction:*** Zeolites are used in two ways:

(a) *Asphalt mix*: In this application, the ability to hydrate and dehydrate while maintaining structural stability and an inherent exothermic reaction when transitioning from a dehydrated to a hydrated form are the key. When added in the production process of warm mix asphalt concrete, the exothermic reaction helps lower consumption of fossil fuels during manufacture and laying of hot asphalt concrete, thus releasing less carbon dioxide, aerosols and vapours. The development of this application started in Germany in the 1990s.

(b) *Ordinary portland cement*: When added to portland cement as a pozzolanic material, it reduces chloride permeability by virtue of its selective molecular sieving. Its low specific gravity (2.0-2.4) reduces weight. Also, its ability to absorb, store and slowly release water allows slower drying which improves break strength as well as workability.

10 ***Detergent:*** Sodium-containing zeolite is used in detergent powder as a water softener. The cation exchange capacity (CEC) of this zeolite helps it to exchange and remove calcium and magnesium.

11 ***Water treatment:*** By virtue of high cation exchange capacity (CEC) of some zeolites (sodium-containing clinoptilolite), they are widely used as ion-exchange beds in domestic and commercial water purification, softening (i.e., removal of the bicarbonates, sulphates and chlorides of calcium and magnesium), and other applications. In softening of hard water, the calcium and magnesium ions of the water are exchanged for sodium of the zeolite and content of sodium is, therefore, the key criterion. The other common applications are for ammonia removal in municipal sludge/waste water, for removal of heavy metals (cobalt, copper, manganese, cadmium, lead and zinc) in water filtration, in swimming pools, in acid mine drainage water and in septic leach fields. In experiments conducted by US Bureau of Mines in early 1990s, zeolites have been found to remove contents of lead up to 200 ppm, of copper from 147 ppb to 15 ppb and of arsenic from 14100 ppb to 5 ppb in contaminated water to produce potable water. A notable feature is that the loaded zeolites can be used repeatedly by stripping and regenerating with the help of sodium chloride solution and they showed no sign of any deterioration even after seven cycles of loading, stripping and regeneration. The sodium of the sodium chloride serves to replenish the depleted sodium content of the zeolite.

12 ***Fishery and aquarium:*** Zeolites are marketed by pet stores for use as a filter additive in aquariums. In aquariums, zeolites can be used to absorb ammonia and other nitrogenous compounds. However, due to the high affinity of some zeolites for calcium, they may be less effective in calcium-rich hard water and may deplete calcium—a nutrient for fish. On the other hand zeolite filtration is used in some marine aquariums to keep nutrient concentrations low for the benefit of corals adapted to nutrient-depleted waters. In the same way, zeolites are used in fish hatcheries for ammonia filtration .

13 ***Zeoponic materials:*** While zeolites have several properties that make them highly useful minerals, they can be chemically modified to make them even more effective. In fact, one of the most successful uses of zeolites have been in what are called *zeoponic* systems that utilize modified natural zeolite rather than strictly raw natural zeolite. The best example of this is zeolite used for plant growth applications. By changing the composition of the ion exchange sites and by loading the sites with selected nutrient cations, zeolites can become an excellent plant growth medium.

Other enhancements can also be done to modify the properties. Combined with slowly dissolving materials (such as synthetic and/or natural nutrient anions), these nutrient-enhanced zeoponic materials supply plant roots with additional vital nutrient cations and anions. Most importantly, these nutrients are provided to plant roots in a slow-release, demand-driven fashion. Basically, the process is a combination of dissolution and ion exchange reactions. The absorption of nutrients from the soil solution by plant roots drives the dissolution and ion exchange reactions, pulling away nutrients as needed. The zeolite is then "recharged" by the addition of more dissolved nutrients. In effect, zeoponic systems increase nutrient retention, reduce environmental nutrient losses and reduce fertilizer requirements through replenishment and balancing of nutrient supply in the plant root zone. Cuban studies in this emerging field of zeoponics suggest that some crops may be grown in 100% zeolite or zeolite mixtures in which the zeolite is previously loaded or coated with fertilizer and micronutrients.

14 ***Catalytic agent:*** Zeolites have the ability to act as catalysts for chemical reactions which take place within the internal cavities, with the help of some ions trapped within them. The two most common zeolite catalysts are:

(a) *Hydrogen-charged zeolite*: An important class of reactions is that catalyzed by hydrogen-exchanged zeolites, whose framework-bound hydrogen protons give rise to very high acidity. This is taken advantage of in many organic reactions in petroleum processing and petrochemical industries. Such zeolites are widely used as catalysts for cracking. In *cracking*, molecules are broken down under high temperature. Zeolites confine molecules in small spaces, which causes changes in their structure and reactivity. The hydrogen form of zeolites (prepared by ion-exchange) are powerful solid-state acids, and can facilitate a host of acid-catalyzed reactions, such as *isomerization* (i.e., the process of producing a similar but new substance by rearrangement of atoms within the hydrocarbon molecules of the original substance), *alkylation* (i.e., the coupling of an olefin and a butane or isobutane over a catalyst). Catalytic cracking uses a furnace and reactor. First crude oil distillation fractions are heated in the furnace and passed to the reactor. In the reactor the crude meets with a catalyst such as zeolite. In the process, it gradually cools down and then is sent to a separator, where the hydrogen is recovered for recycling. Finally, it is fractionated to get the petrochemical product.

(b) *Metal-charged zeolite*: Zeolites can also serve as oxidation or reduction catalysts, often after metals have been introduced into the framework. An example is the use of copper zeolites in NOx decomposition.

15 ***Gem:*** *Thomsonite* [$(Ca,Na_2)_2Al_4Si_4O_{16}.5H_2O$] nodules separated from host basalt by erosion and collected on beaches are valued as gems after polishing. These nodules have concentric rings in combinations of colors — black, white, orange, pink, red and many shades of green. Some nodules have copper as inclusions. When polished, they sometimes display play of colours.

16 ***Perfect glass:*** *Perfect glass* has been experimentally prepared in the University of Wales, USA by a process known as *amorphization*. In this process, pressure is applied to zeolite crystals under normal temperature. The zeolite crystals collapse slowly and transform into glass without melting. This glass is harder, but lighter and chemically more durable than ordinary glass.

17 ***Carbon sequestration:*** CO_2 emitted by burning of coal is a major source of air pollution, and is the single most responsible agent for global warming or, as it is called nowadays), the 'green house effect'. There are 5 green-house gases (or GHG), the emission of which is believed to be responsible for the green-house effect. These gases are: CO_2, NO_2, methane, CFC (chloro-fluoro-carbon), and water vapour. Out of these, CO_2 is the mostly widely produced gas directly related to burning of coal. It absorbs infrared coming from the sun, but does not allow it to go back to space; and an increased density of CO_2 in air causes increase in the temperature of the earth. This CO_2 is nowadays being regarded as an economic commodity. Its potential use is in food processing, fish farms, agricultural greenhouses, conversion to fuels, manufacture of stable products such as carbonate minerals and secondary recovery of petroleum Scientists are therefore trying to develop what is called *carbon sequestration* technologies to capture CO_2 from industrial emission streams and to store it for future use. One of the methods currently being explored for CO_2 separation is its absorption onto the pores of chemically modified zeolites.

18 ***Beet sugar:*** This was the first use of natural zeolites dating back to 1896. Beet sugar juice was rich in potassium compounds which prevented formation of sugar crystals. By virtue of their high cation exchange capacity, zeolites were used to replace the potassium by calcium and thereby increase formation of good sugar crystals.

19 ***Other uses:***

(a) *Odour control*: Zeolites, by virtue of their molecular sieving efficiency, are effective in absorbing odorous matter from the household air. This usage is common in UK.

(b) *Fungicide*: Zeolite can be used as a carrier of fungicide. Zeolite stores the liquid in its pores and then slowly releases it.

(c) *Hazardous waste treatment*: Zeolites, by virtue of their molecular sieving efficiency, can selectively absorb pentachlorophenol (PCP) which is a carcinogenic chemical, from liquid wastes. It then becomes easier to dispose of the saturated zeolite.

SUBSTITUTION

1. Synthetic zeolite: A defining feature of zeolites is that their frameworks are made up of four connected networks of atoms in the form of tetrahedrons with a silicon atom in the middle and oxygen atoms at the corners. These tetrahedrons can then link together by their corners to from a rich variety of beautiful structures. In all, over 130 different framework structures are now known. In addition to having silicon or aluminium as the tetrahedral atom, more than 1,500 types of zeolite have also been synthesized. A synthetic zeolite is made out of the same elements as in natural zeolite, i.e., alumina and silica.

There are several types of synthetic zeolites that form by a process of slow crystallization of a silica-alumina gel in the presence of alkalis and organic chemicals. One of the important processes to carry out zeolite synthesis is sol-gel processing in which other elements (metals, metal oxides) can be easily incorporated.

A crystalline sodium-aluminium-silicate called *zeolite-A* has been made from kimberlite waste generated from diamond mining in India. This synthetic zeolite is suitable for use in detergent powder as a substitute for sodium tripolyphosphate (STPP) which is not environment-friendly.

Synthetic zeolites can also be made from fly ash — a waste product of coal generated in thermal power plants. Fly ash contains alumino-silicate glass or mullite ($Al_6Si_2O_3$). It has been possible to synthesize low Si/Al ratio Na-rich zeolites from fly ash by either: (a) treating ash with concentrated NaOH solution at elevated temperatures ranging from 150-200^{0}C and at high pressure, or (b) microwave radiation and fusion with NaOH followed by hydrothermal treatment. This synthetic zeolite is also called *NaOH-modified ash*.

Synthetic zeolites hold some key advantages over their natural analogs. These are as follows.

(a) The synthetics can be manufactured in a uniform, phase-pure state.

(b) It is possible to manufacture desirable zeolite structures which do not appear in nature.

(c) Since the principal raw materials used to manufacture zeolites are silica and alumina, which are among the most abundant mineral components on earth, the potential to supply zeolites is virtually unlimited. Nowadays, calcined china clay is being looked upon as a source of silica and alumina for this purpose.

However, their disadvantages include the inability to create crystals with dimensions of a comparable size to their natural counterparts.

Customized synthetic zeolites have, now-a-days, become popular for applications as catalysts in petrochemical industry and also as additive to asphalt concrete in construction work. But they are now finding use as virtual chemical plants for making some high-tech materials as follows:

(a) *Cadmium sulphide optical switch*: Cadmium sulphide super-clusters are made by injecting first cadmium ions and then hydrogen sulphide gas into zeolite pores within which reactions take place completely and efficiently. Thus made cadmium sulphide super-clusters become opaque or transparent depending on how much light shines on them, and have potential applications as *optical switches*. They are found to work much faster than cadmium sulphide made by conventional routes.

(b) *Optical memories*: These are tiny crystals of light-sensitive material created within a zeolite.

(c) *Chemical sensors*: These consist of thin layers of zeolite crystals

(d) *Polymer filament*: These are made of molecular sized filaments of some conducting polymers.

2. Non-zeolite substitutes:- In the commercial circle, apart from natural zeolites, the synthetic zeolite and some substitute material are included in the zeolite family. For water-softening, the non-zeolite substitute materials are as follows.

a) *Activated carbonaceous materials:* This is made by activating carbonaceous materials like coal, lignite and peat with sulphuric acid and certain synthetic resins. These are suitable in water-softening application.

b) *Glauconite:* This is the commonest natural mineral in usage for water softening. It I is a complex hydrosilicate of K, Mg, Fe and Al believed to have the formula $[K_2(Mg,Fe)_2Al_6(Si_4O_{10})_3(OH)_{12}]$. It is a yellowish to dark green coloured mineral found in Cretaceous *greensands* in the form of small angular grains. But unlike sodium ion, the potassium ion is not easily replaceable by the calcium ions of hard water. So natural glauconite is generally activated by treating with sodium chloride solution so as to substitute the potassium ion by sodium ion. Without activation, one cubic foot (cft) of glauconite can exchange for 3000-4000 grains of calcium carbonate while after activation, the exchange capacity increases to over 5000 grains (1 grain = 1/7000 pound or 64.799 mg).

c) *Alumino-phosphates:* Microporous alumino-phosphates, known as ALPOs, are in development stage.

Chapter 49

ZIRCONIUM MINERALS

There are two commercially important minerals of zirconium having the same uses — zircon and baddeleyite (also called brazilite). The name zircon owes its genesis to the Arabic word “sarkeen” and Persian word “zirgun” both meaning gold-coloured, the colour of a zircon gem known since long, and much later, the name zirconium has been given to the metal after zircon. Baddeleyite is named after Joseph Baddeley who was the first to study it. While zircon is a silicate of the metal zirconium having composition ($ZrSiO_4$), baddeleyite is the oxide having composition (ZrO_2). Primary zircon occurs mainly in granite, syenite and diorite, while the favourable rock for primary baddeleyite is phonolite. But the commercial sources of both are the secondary placer deposits(both beach and fluvial) known as heavy mineral deposits, in which zircon and baddeleyite grains become naturally concentrated because of their hardness and consequent resistance to weathering and erosion. While such beach placer deposits rich in zircon are found in many places, the only such deposit of baddeleyite is known in Brazil (hence, its other name brazilite, but recently South Africa has emerged as the leading producer of baddeleyite obtained as a byproduct of extraction of uranium, copper and phosphate minerals), and because of the latter’s limited availability, it is the former which is more popular. In the commercial beach placer deposits, they occur in association with various heavy minerals namely, monazite, ilmenite, rutile, garnet etc. In the commercially important placer deposits, zircon generally constitutes 0.6 – 18.7% of total heavy minerals.

The world production of zirconium minerals was of the order of 0.08 million tons (1990 figure) with Australia as the leading producer of zircon and South Africa of baddeleyite). World production of zirconia was of the order of 20,000 tons (South Africa 10,000 tons and USA 4,000 tons, 1990 figures).

HISTORY

A gem variety of zircon called *jargon* was known since long (it finds mention in Biblical writings), but discovery of zirconium metal had to wait till the beginning of 20th century. German chemist Klaporth succeeded in 1789 to separate zirconium oxide from a gem (jargon) and he named it “zirkonetz” (zirconia). From this oxide, some impure metal was first isolated by two Dutch chemists named Lely and Hamburger, and named it zirconium. Later, in 1824, Berzelius obtained the same metal by heating a mixture of potassium and potassium-zirconium fluoride. Two other Dutch chemists named van Arkel and de Boer improved the method and produced pure zirconium in 1925, albeit the process was slow and expensive for production of the metal in commercial scale. Meanwhile, in 1892, Joseph Baddeley collected a sample of a new mineral from Kommonnangam area of Sri Lanka which he found to be a natural oxide of zirconium and he named it baddeleyite. This proved to be another source of zirconium. In 1947, W.J. Kroll of USA developed a commercially viable process.

Regarding industrial zircon, it is recovered from beach placer sand, and one of the oldest discoveries of commercial beach placer deposits was made in India in 1909 when the beach sand deposit of Kerala was discovered — valued first for its monazite content and later for ilmenite. Coir workers of that region used to rub their hands in sand to get a grip of the coir. Some sand used to stick to the wet coir. Eventually, some sand found its way to Germany along with the exported coir. One day, in 1909, C. W. Schomberg, a chemist, by chance, stumbled upon this glistening sand. He could identify that the sand contained monazite, an important material for gas light mantle. He came to India and located the deposits. He established a separation plant in 1911, and in the following year exploitation also commenced, primarily for recovering monazite. The British took over it during World War-I (1914-1918). Afterwards, more sand-mining companies were set up. Meanwhile, by around 1918, such beach placer sands were being produced and concentrated in many countries, mainly for recovering ilmenite concentrates. In the Indian plant, recovery of zircon started in 1922, but production was irregular and intermittent. During the 25-year period 1922-1946 its total production was 38,700 tons. After independence (1947), in 1950, the Government of India created a new undertaking, namely the Indian Rare Earths Ltd (IREL) for mining and processing the heavy mineral sand resources of India. IREL started mining in 1952 and took over the separation plants in 1965, and since then processing of heavy mineral sand has been going on for recovering concentrates of not only monazite and ilmenite, but also the other minerals including zircon. During the year ending March, 2003, the production of zircon was 23,219 tons — all from the beach placer sands of Kerala, Tamil Nadu and Orissa. The world production of zircon and baddeleyite was about 1.04 million tons during the year 2000.

PROCESSING OF THE MINERALS

The beach placer deposits of India containing 10-25% heavy minerals comprising ilmenite, rutile, zircon, monazite, garnet, sillimanite and leucoxene are being processed. Beach sand is first washed to 50% heavy mineral concentration. This concentrate is subjected to spiral separation in a series of plants to get 90% concentration. Finally, this concentrate is dried and separated into the individual minerals including zircon, utilizing differences in physical properties of the minerals, such as electrical conductivity, magnetic susceptibility, specific gravity, grain size etc. Indian zircons analyze 63-66% ZrO_2.

The process is essentially the same in case of sand containing baddeleyite.

EXTRACTION OF METAL

The process of extracting zirconium metal from the natural minerals in essence, involves two steps as follows.

1 Decomposition of ore: This is achieved by heating zircon to a high temperature of about 2900^0C so as to volatilize the silica away leaving a residue of zirconia (in case of baddeleyite, this is not necessary). The zirconia is then sintered and digested with acid followed by chlorination producing $ZrCl_4$. This $ZrCl_4$ is then reduced by molten magnesium in an inert atmosphere consisting of argon or helium to what is known as commercial grade zirconium (Kroll process). Commercial grade zirconium contains 1-3% hafnium.

2 Separation of hafnium: Zirconium and hafnium are similar with respect to many physical and chemical properties, and their separation is one of the most difficult and very expensive processes (hafnium-free zirconium is as much as 10 times more expensive than its commercial grade). For obtaining hafnium-free zirconium, there are four processes:

(a) Liquid-liquid extraction: In this process the differential solubility of their thiocyanates in methyl isobutyl ketone is made use of.
(b) Fractional distillation
(c) Fractional phosphate-precipitation: It takes advantage of the fact that hafnium phosphate is less soluble than zirconium phosphate, and also that the former phosphate is granular in nature and can be easily filtered out.
(d) Fractional crystallization: In this process, ammonium hexachloride and oxychloride are used.

Out of these, the first two processes are currently popular; the first in USA and the second in Europe. The processes have to be repeated many times until the desired purity is achieved.

For extraction of zirconium, baddeleyite is preferable to zircon because of higher metal content in the former (74% compared to 60.2% in zircon).

CRITERIA OF USE

A. Zircon/Baddeleyite

1 *Chemical characteristics*: The chemical composition of zircon i.e., $ZrSiO_4$ is made up of 67.2% ZrO_2 or 60.2% zirconium (Indian zircons analyze 63-66% ZrO_2) while baddeleyite is a natural ZrO_2 containing 74% zirconium (in a very few literature, the chemical composition of zircon is erroneously mentioned as $ZrSiO_3$, perhaps because some silicate compounds of zirconium with Na, Ca and Ba like catapleiite, calciohilairite, bazinite etc. have $(SiO_3)_x$ as the radical). Both of them in their primary form in rocks is characterized by uranium-lead (U was originally present which, with

progressive radioactive disintegration, has transformed to more and more Pb) firmly trapped within their crystals. Traces (about 1%) of hafnium are invariably and intimately associated with zirconium in both the minerals — the two metals being in the same group in the Periodic Table and possessing similar properties.

2 *Crystal form*: Crystals of zircon are tetragonal and those of baddeleyite monoclinic.

3 *Geographical and geological occurrence*:- Economically significant placer deposits containing zircon are widespread in many countries while that of baddeleyite is limited to only one country i.e., Brazil. Geologically, both are common accessory minerals of rocks, but zircon being more thermally stable are found in both igneous and metamorphic rocks while baddeleyite is relatively more common in igneous rocks.

4 *Physical properties*: Zircon is harder than baddeleyite. On Mohs scale, the hardness of the former is 7.5 and that of the latter 6.5. But baddeleyite is heavier than zircon —specific gravity being 5.5-6.0 (average density 5.6 gm/cc) and 4.20-4.86 ,respectively. Zircon breaks in conchoidal fracture pattern.

5 *Colour and other optical properties*: Zircon exhibits a variety of colours like pale yellow, yellowish green, brownish yellow and reddish brown. Rarely it may be colourless also. Baddeleyite is brown to black and (very rarely) colourless. Refractive indices of both are fairly high — that of zircon varying from 1.923-2.015 and that of baddeleyite from 2.19-2.20 (cf., ordinary glass 1.53, diamond 2.42). Zircon is transparent to translucent.

6 *Thermal properties*: The tetrahedral zircon is stable up to 1800^0C above which it breaks up into zirconia (ZrO_2) and a siliceous glass with 25% increase in volume (decrease in density). But unlike natural zirconia or baddeleyite which is monoclinic, this zirconia is cubic. The natural zirconia baddeleyite, on the other hand, goes through three changes when heated. Its monoclinic crystal form and density (5.6 gm/cc) are stable up to 1000^0C. In the range $1000\text{-}1150^0$C, its form changes to tetragonal and density to 6.1 gm/cc and remain so till 2350^0C. Thereafter it becomes cubic with density 6.27 gm/cc. Thus each change is accompanied by decrease in volume. The cubic zirconia is stable and is called *cubic stabilized zirconia (CSZ)*. It finally melts at a high temperature of $2535\text{-}2700^0$C.

B. Zirconia:

The dense cubic zirconia, whether derived from zircon or baddeleyite, has the following properties:

1 *Hardness*: It is one of the hardest materials (hardness 8.0-8.5 on Mohs scale, next only to diamond, corundum and chrysoberyl).

2 *Toughness*: It is tough and can resist fracture well.

3 *Wettability*: It is not wetted by most molten metals.

4 *Thermal properties*: As such, zirconia is a refractory substance having a melting point 2535^0C. It also has low conductivity of heat (20% of alumina).

5 *Ionic conductivity*: Zirconia has the unique ability to allow oxygen ions to pass through it smoothly.

6 *Chemical characteristics*: It is chemically inert and resistant to corrosion. It is chemically very stable due to strong bond between zirconium and oxygen.
7 *Electrical properties*: It has very low electrical conductivity, but at 1500^0C, it starts losing its resistance at 2000^0C, it becomes an excellent conductor. Stabilized zirconia has the ability to produce an electromotive force (EMF) in response to the equilibrium partial pressure of oxygen.
8 *Optical properties*: Refractive index of zirconia is higher than that of zircon, and is 2.35.

C. Zirconium Metal:

Zirconium is soft lustrous grayish white metal. But the following properties make it useful in various industrial applications:

1 *Nuclear property*: It has low neutron absorption.
2 *Thermal properties*: It melts at a high temperature of around 1855^0C and boils at around 4409^0C. Like zirconia, it also has the unique ability when heated to allow oxygen ions to pass through it smoothly, which carry the heat along with them, making it a good conductor of heat.
3 *Chemical characteristics*: Zirconium is highly reactive with both nitrogen and oxygen as well as with other gases and sulphur. Due to its reactivity with oxygen, it burns brilliantly when heated in air. It has strong resistance to alkalis. It is non-toxic and not corroded by body fluids.
4 *Physico-mechanical properties*: Commercial zirconium is hard and brittle (due to hafnium which is so), but the pure metal is ductile, malleable and resistant to shock and fatigue.
5 *Electrical property*: Zirconium is a strongly dielectric metal (dielectric strength indicates the voltage that an insulating material can withstand before break-down) with low electrical conductivity of 3.4-4.2% IACS (IACS or International Annealed Copper Standard indicates the percentage value of electrical conductivity of annealed copper).

USES AND SPECIFICATIONS

Though zircon and baddeleyite are the sources of zirconium metal, both these minerals have some unique industrial applications, and hence they are classified under ‘industrial minerals’ rather than under ‘metallic minerals’. All three forms of the minerals, raw minerals, zirconia and zirconium, are used in industries. However, insofar as the raw mineral is concerned, zircon is by far the most popular because of its easy availability compared to baddeleyite. The important uses are:

A. Zircon and zirconia

1. Refractory
2. Crucible
3. Ceramics
4. Enamel
5. Foundry
6. Chemical
7. Zircon polishing
8. Alumina zirconia abrasive
9. Gem
10. Artificial diamond
11. Electrical insulator
12. Geological dating
13. Fuel cell
14. Beer refining

B. Zirconium metal

1. Alloys
2. Nuclear reactor
3. Surgery

These uses are discussed as follows.

A. Zircon and Zirconia

1. Refractory: Refractory materials are defined as those resistant to heat and having a melting temperature of not less than 1580^{0}C. The function of refractory lining on a furnace wall is not only to withstand high temperature, but also to withstand temperature fluctuation, and to resist penetration, abrasion, and erosion by hot gases and molten materials in the furnace, and over and above, it should not chemically react with those materials. Life of refractory lining has increasingly been becoming a critical parameter in the productivity of a furnace and economics of a plant, because each time the lining fails and needs replacement, the furnace has to be shut down.

Cubic zirconia, whether derived from zircon or baddeleyite, is an outstanding refractory material due to its high melting point (2535^{0}C), hardness (8.0-8.5 on Mohs scale), heat conductivity (prevents the refractories from getting overheated) and non-wettability by most metal melts. Following are the common types zircon-based refractories:

(a) *Zirconia bricks*: Zirconia refractories are used in the form of bricks of various shapes in electrical furnaces, burner blocks, nozzles, saggars etc. Zircon based refractories are particularly suitable in aluminium melting equipment, and not good for iron smelting furnaces.

(b) *Zirconia-graphite bricks*: These are widely used in billet casting.

(c) *Ramming cement or plaster*: Natural zircon sand mixed with some refractory clay and some bonding material like plastic clay or sodium silicate is used as ramming cement or plaster for giving a protective coating on the refractory lining of furnaces to improve resistance to heat and thermal shock.

(d) *Quick-setting refractory cement*: The cement can be made into a quick-setting one by using hydrolyzed silicon ester as the bonding material. Such cement is used for bronze casting by what was earlier called '*lost wax process*' and is now known as '*investment casting*'. In this process, first a wax model of the intended object is made. This model is then invested or coated with layers of clay (that is why now it is called investment process). The wax is drained out leaving a clay mould in which bronze is cast. Addition of zircon sand to the clay mixture makes the mould stronger and more refractory.

However, zirconia suffers from one disadvantage i.e., weak resistance to thermal shocks and metal penetration on account of microcracks developed due to the changes in density and volume it undergoes during transformation from the natural minerals to cubic zirconia. This problem is overcome by addition of MgO or CaO or Y_2O_3or Sc_2O_3 or Ce_2O_3 which can go into solid solution with cubic zirconia and stabilize it.

2. Crucibles: Compared to furnaces, crucibles are smaller in size. They are advantageous for processing small quantities of different products which are fed in small batches at a time, such as in precious metal metallurgy. Such processing involves repetitive heating and cooling, and requires the crucibles to withstand rigorous thermal shocks. It is easier to change a damaged crucible, as opposed to a furnace lining.

Zirconia crucibles are used for melting platinum and platinum-rhodium alloys. Melting temperatures of platinum and rhodium are 1773^0C and 1966^0C respectively, and zirconia melts at a temperature well above these. Also, after suitably processing with MgO or CaO or Y_2O_3, zirconia can be made strongly resistant to thermal shocks and to metal penetration. Moreover, zirconia is inert and non-wettable by these metal melts.

As in the case of furnaces, inner surfaces of crucibles are also sometimes plastered with a cement made of a mixture of natural zircon sand, some refractory clay and some bonding material like plastic clay or sodium silicate.

3. Ceramics: In ceramic industry, zirconia is mainly used in some special ceramic products for high temperature applications, in some electro-ceramic products and in glazing.

(a) *High-temperature ceramics*: The unique combination of high melting temperature and heat conductivity along with chemical inertness and hardness make zirconia suitable as an ingredient in the material for making heat- and chemical-resistant laboratory wares. Heat conductivity prevents them from getting overheated. Zirconia-based ceramic material is used for adiabatic coating of diesel engines and zirconia-lined ceramic scissors, blades, etc. They are stronger, sharper and more durable than their metal counterparts.

(b) *Electro-ceramics*: These include porcelain used for spark plugs, for cladding fuel cells, etc. High melting point combined with high electrical resistance at temperatures below 1500^0C are the main criteria. Alkalis, both sodium and potassium, are strictly deleterious because their ions are electrically conducting.

(c) *Glazing*: The purpose of glazing is to provide a uniform firmly adhering coating on the surface of the ceramic body concealing defects such as pinholes, bubbles, etc. Ordinary glaze is made of the same ingredients as the ceramics but with predominance of quartz and feldspar. The ingredients are mixed, finely ground and mixed with water, and this mixture is the glaze. The moulded raw body of the product is dipped into the glaze and then fired to a temperature of about 1400^0 C. Glaze should not only melt but also spread uniformly. Glaze may be "*raw glaze*" or "*fritted glaze*". Raw glaze consists of insoluble material applied as such (soluble components crystallize in the mixture and cause blemishes on the treated surface), while fritted glaze is heated beforehand to cause chemical change in the components. It is in case of special ceramics and in raw glaze that zircon (or baddeleyite) is added to the ingredients, but then the glaze has to be heated to a higher temperature so as to melt (the melting temperature is somewhat reduced by the feldspar which acts as a flux). The zircon adds to the glazed surface hardness, high density, high refractoriness, chemical resistance and low electrical conductivity.

(d) *Opacifier*: An opacifier consists of particles that scatter and reflect some of the incident light to give a nontransparent effect. The covering power of opacifier depends on: (i) difference between refractive index of the underlying glaze and that of the opacifier, and (ii) particle size of the opacifier. The refractive index of most glazes is 1.5, but the indices of some TiO_2 and SbO_2 which are used in some special glazes are 2.55 and 2.25. Compared to these, the refractive indices of SnO_2, zirconia and zircon, all of which are suitable as opacifier material for both the common and special glazes, are 2.04, 2.35, and 2.0 respectively. Out of these, SnO_2 and zirconia are costly and the relatively inexpensive natural zircon is commonly preferred (zirconia is used in some special cases for some additional requirements as mentioned above).

(e) *Zirconia-toughened alumina (ZTA) ceramics*: With a view to improving fracture toughness of alumina ceramics, zirconia is added by dispersing it in an alumina powder matrix, compacting the mixture and sintering at 1500-1600^0C. Zirconia-toughened alumina ceramics find use in a variety of mechanical applications that include cutting tools, wear-resistant components (bearings, valves, wire drawing dies, etc.) rocket radomes which house radar antenna, hip joint prosthetic devices, tooth and ear implants, armour-plating, bullet-proof vests, coin-polishing assemblies, etc.

(f) *Crucible*: Zircon-based ceramic products are used for making small crucibles for assay works involving gold and silver (meting temperatures 1100^0C and 1050^0C ,respectively).

(g) *Alumina zirconia silica refractories:* They contain 50% alumina and up to 40% zirconia and silica. They may either be moulded into bricks for furnace lining or made into an aggregate for ramming of contact zones. Their most important application is in glass furnaces.

4. Enamel: Chemically, enamel is a complex mixture of silicates, borates and fluorides of some metals like sodium, potassium, aluminium, etc. It is a glaze coating on metallic surfaces so as to give protection to the latter against high temperature and corrosion. It is prepared by mixing borax ($Na_2B_4O_7.10H_2O$), quartz, feldspar, fluorspar, soda (Na_2CO_3), sodium nitrate, oxides of cobalt, manganese and nickel and an opacifier substance (e.g., tin oxide, titanium silicate, antimony trioxide). This mixture is ground, melted and quenched in water to yield a glassy mass. To this glass are added clay and more quartz powder and the mixture is finely ground to powder and made into a slurry with water. This is called *"enamel slip"*. Metallic objects are dipped in it and fired to about 900^0 C. Two to three of such enamel coats are usually applied. In special cases where hardness, high density, opacity, high refractoriness, chemical resistance and low electrical conductivity of the enamelled surface are required, zircon (or baddeleyite) is added to the mixture, but then it has to be heated to a higher temperature so as to melt it and become zirconia (the melting temperature is somewhat reduced by the feldspar which acts as a flux). This zirconia then adds to the enamelled surface these unique properties.

5. Foundry: In foundry industry, zircon is used as a facing for foundry moulds to increase its strength, non-wettability, resistance to high temperature of metal penetration and afford a uniform finish to castings. However, in certain cases, a mixture of zircon and chromite is used due to better chilling ability and lower cost of the latter (for details about foundry see the chapter on bentonite).

6. Chemicals: The important chemicals made from zircon/baddeyite are:

(a) Zirconium boride: It is one of the strongest and the most heat-resistant substance. It can withstand temperature of over 3300^0C and its shearing strength at 1550^0C is nearly 5275 kg/cm^2; but, at this temperature, it oxidizes very rapidly and so, for taking advantage of this property, it has to be coated with some inert substance.
(b) Zirconium phosphate: It has pharmaceutical uses (e.g., in stomach ulcer).
(c) Zirconium carbonate: Used in ointments and in antiperspirants.

7. Zircon polishing: Hardness of zircon is 7.5 on Mohs scale, and this makes it a suitable material for use in grinding wheels for polishing optical glasses. Its natural availability in the form of sand is an added advantage as grinding cost is minimal.

8. Alumina zirconia abrasives: If a mixture containing 25-40% of zircon sand and the balance pure Bayer's alumina is fused together and suddenly cooled, a solid solution of zirconia and alumina results accompanied by growth of sharp dendritic microcrystalline structure in the grains. This abrasive can be used for sharpening purpose. Zirconia serves to provide the toughness and alumina, the hardness of the abrasive.

9. ***Gem:*** Gem includes both precious and semiprecious stones. The criteria that make a gem are:

(a) *Rarity*: By the law of demand-supply, the scarcer a commodity is , the higher is its value.
(b) *Durability*: The combination of hardness, toughness and acid-resistance makes a stone durable.

(c) *Colour and optical properties*: Colour, lustre and optical dispersion are the most important parameter of beauty.

(d) *Clarity*: Small bubbles, cracks and other flaws reduce the clarity of a gem, and consequently, its value.

(e) *Cut*: Natural gems are mined as rough stones. They need to be cut into well-defined faces and the faces are polished to produce their characteristic sheens and optical effects. The cutting requires a very high degree of skill – particularly when the individual pieces are small. Minimum loss of stone is to be ensured during cutting.

(f) *Specific gravity:* The value/volume ratio depends on this parameter.

(g) *Caratage:* Larger a gem is, rarer and hence more valuable it is. So the individual weight of a piece is important for determining its value.

(h) *Certification*: For a common retail buyer, the physical and optical properties of gems carry little sense, and he is most concerned, besides size, with the colour and sheen as judged with naked eyes. But both these characteristics can be replicated by unscrupulous people. So for him certification by some trusted authority or agency assumes importance.

(i) *Aggressive marketing*: Demand of gems being elastic, almost any gemstone can be sold irrespective of colour and cost, provided the basic criterion of rarity is met.

(j) *Therapeutic value*: Gems are traditionally believed to possess some indirect beneficial effects on body and mind if worn on the body. This branch of therapy known as gemmotherapy works on the hypothesis that different gems, when worn by a man on his body, react differently to different kinds of cosmic rays having different effects on the health of his mind and body. Besides, some gems have been found to produce beneficial effects on human skin.

(k) *Beliefs and superstitions:* Gems, many people believe, bring luck or misery to lives.

(l) *Stability of value*: Economic phenomena like inflation, stagflation, recession and even political instability which exercise adverse impact on other manufacturing and processing sectors, do not affect adversely the demand of gems—particularly the high-value ones.

Strictly considered zircon having hardness 7.5 is not a precious stone, but when pure, its refractive index is high [1.923-2.015 (diamond 2.42)], it is transparent to translucent and its specific gravity is also high (4.86) giving it a high value/volume ratio. On account of these favourable criteria, some rare colourless or attractively coloured varieties of it are valued as semiprecious gemstones, and it is the densest gem known (cf., specific gravity of diamond 3.53). The gem varieties of zircon are called:

(a) *Jargon*: Colourless to smoky zircon found in Sri Lanka, the oldest known zircon gem.

(b) *Hyacynth*: Orange, reddish and brown coloured transparent zircon.

(c) *Starlite*: Natural zircon with blue colour induced artificially by exposing it to hot fumes of cobalt nitrate and potassium ferrocyanide.

These natural zircon gems are collectively called “Tursava” in Indian language.

10. Artificial diamond: Artificial diamonds consist of elements that are naturally occurring, but combined in forms that are not found in nature. The most common and widely used artificial diamond is American diamond (also referred to as zircon), which is cubic zirconia (ZrO_2) specially made from zircon ($ZrSiO_4$). Zirconia is monoclinic at normal temperature, becomes tetragonal when heated to above 1800^0C, and reverts back to monoclinic form on cooling. It melts at a high temperature of about 2700^0C and is reactive with certain high melting crucible materials like platinum, iridium which cannot endure this high melting temperature. By some carefully controlled special process the zirconia is melted in what is called *skull melting system*, recrystallized in cubic form and prevented from reverting back to the original form. The "skull" is a hollow-walled copper cup. Water is circulated through the hollow walls to cool the inside wall of the cup, when this skull is filled with powdered ingredients and heated by radio frequency induction until the powders melt. Because the water cools the walls of the skull, the powdered material next to the walls do not melt acting as a buffer between the wall of the container and the reactive molten material, and the latter is contained within a shell of unmelted material. When the heat source is removed and the system is allowed to cool, crystals form with nucleation and grow until the entire melt solidifies.

11. Electrical insulator: Titanium, rutile (TiO_2) and titanates are poor conductors of electricity and possess high dielectric strength (indicates the voltage that an insulating material can withstand before break-down). Titanium has electrical conductivity of 1-3% IACS. Dielectric constant of rutile is about 12 indicating weak electrical conductivity (cf., value for air, one of the poor conductors of electricity, is 1) and it has the ability to stabilize electric arc by overcoming the tendency to splutter and flicker. Magnesium has weak to moderate electrical conductivity of 12.3-38.6% IACS and zirconium 3.4-4.2% IACS. When magnesium, titanium and zirconium are combined by firing a mixture of magnesite, rutile and Zirconia (ZrO_2), a truly efficient electrical insulator suitable for use as condensers in radios —magnesium zirconium orthotitanate ($Mg_2TiO_4.ZrTiO_4$), is formed .

12. Geological dating: Both zircon and baddeleyite in their primary form in rocks is characterized by uranium-lead (U was originally present which, with progressive radioactive disintegration, has transformed to more and more Pb) firmly trapped within their crystals, and this uranium is the key to use of these minerals in geochronology. Both being very hard and strongly resistant to weathering and erosion, are found intact in very old rocks of all types. But, zircon being relatively more thermally stable than baddeleyite is found in both igneous and metamorphic rocks while the latter is less common in metamorphic rocks. Zircon is therefore suited for age determination of both types of rocks while use of baddeleyite is limited to that of igneous rocks. The oldest terrestrial material dated is a tiny grain of zircon found in a gneissic rock in Jack Hills region in Australia which has been reported in 2005 to be 4.4 billion years old, i.e., almost as old as the earth (4.6 billion years). Incidentally, the age of the host rock is 3.7 billion years, i.e., it formed 7 million years after crystallization of the zircon. Now specialized ion probe techniques have been developed to analyze the growth zones of zircon microcrystals that have the potentiality to unravel the mysteries of the processes of planetary evolution.

13. Fuel cell: Fuel cell is a device that generates electricity through a non-combustion electrochemical reaction (oxidation of hydrogen or CO-gas) the former being more popular because of its environment-friendliness. The principle was first conceived by William Grove in 1839, who hypothesized that if water could split into hydrogen and oxygen by electric current then the reverse should also be true, i.e., combination of hydrogen and oxygen should produce electricity. He experimented and proved his hypothesis true. In 1889, Ludwig Mond and Charles Langer made the first practical model and named it fuel cell. It was further streamlined by W. Ostwald in 1894, and now it is believed that fuel cells will become the norm in many applications within the first quarter of the 21st century, be it for transport or energy supply or in industrial applications.

A fuel cell basically consists of four main components, namely, (-) anode (hydrogen), (+) cathode (oxygen), electrolyte and catalyst (usually nano-particles of platinum). The catalyst ionizes the hydrogen atoms into positively charged protons and negatively charged electrons. The electrons go into an external circuit and reach the anode where oxygen is supplied and ionized by the catalyst. Thus an electric current flows through the circuit for utilization. Meanwhile, either the positively charged hydrogen protons pass internally through the electrolyte and reach the anode or the oxygen ions move through the electrolyte and reach the anode. Eventually, all the oxygen and hydrogen ions reunite to form water, either in the cathode or in the anode. Since the fuels hydrogen and oxygen are continuously supplied into the cell, it never goes dead unlike a normal cell. The electrolyte is the key and its function is to selectively allow either oxygen ions or hydrogen protons to pass through, directly or by reacting. Depending on which material is used as electrolyte, there are six types of fuel cell:

(a) Solid oxide fuel cell (SOFC)
(b) Polymer exchange membrane fuel cell (PEMFC)
(c) Alkali fuel cell (AFC)
(d) Phosphoric acid fuel cell (PAFC)
(e) Direct methanol fuel cell (DMFC)
(f) Molten carbonate fuel cell (MCFC)

It is in the SOFC that zirconia is used in the form of a layer as the solid oxide electrolyte. By virtue of its high oxygen ionic conductivity, it selectively allows oxygen ions to pass through it from cathode to anode while blocking the hydrogen protons. The efficiency of a zirconia cell can be up to 60% and its output (DC current) can be up to 100 KW. So a number of such fuel cells are, therefore, assembled into a stack. The zirconia fuel cells operate at a high temperature range of 700-10000C, and the water is converted into superheated steam for moving turbines and generating additional electricity. This process is called cogeneration of heat and power or CHP.

14. Beer refining: Zircon is used to make a filter bed for this purpose. The filter bed is made up of three layers consisting of fairly coarse anthracite top layer, slightly fine beach sand middle layer and zircon sand bottom layer.

15. Other uses:

(a) *Semiconductor*: At 2000^0C, zirconia becomes an excellent electrical conductor making it a potential semiconductor.
(b) *Dental casting*: A thin layer of zirconia coated on a base of porcelain is a good material for casting artificial tooth.
(c) *White rubber*, *leather*, *paint and lacquer*: It is sometimes used as a filler.
(d) *Zirconia reinforced glass*: In this zirconia powder is dispersed in a glass matrix. It is a very hard material usable in cutting tools.
(e) *Oxygen sensor*: Stabilized zirconia has the ability to produce an electromotive force (EMF) in response to the equilibrium partial pressure of oxygen, and this property is made use of.

B. Zirconium Metal

1. Alloys: The important alloys containing zircon are:

(a) *Ferro-zirconium*: It contains 20-30% Zr and the rest Fe, and is made by reduction of a mixture of zircon and hematite either in the electric arc furnace or by alumino-thermic process. It is added to special steel for increasing ductility and resistance to shock and fatigue. It also removes oxygen, nitrogen and sulphur from molten steel by virtue of high reactivity with these elements, and thus improves grain-uniformity of the steel. Suitable in light armour-plates and in projectiles.
(b) *Ferro-silico-zirconium*: It contains 30-35% Zr, 55% Si and the rest Fe. The function and use are as above.
(c) *Aluminium-zircon alloy*: Characterized by medium-strength.
(d) *Magnesium-zinc-zirconium alloy*: If the magnesium content is 93-97% with 2.5-6.5% Zn and 0.7% Zr, the alloy is called *ternary casting alloy* and if it is 90% with 2.5-4.0% Zn+Zr, then *quaternary casting alloy*. The former has very high stress resistance and the latter has remarkable creep resistance at elevated temperatures.
(e) *Magnesium-zircon-cerium alloy*: Characterized by light weight and stress resistance. Used in structural and engine components of aircrafts.
(f) *Copper-zirconium alloy*: 5-10% addition of Zr improves the strength of copper greatly.
(g) *Gold-zirconium alloy*: Can replace platinum-iridium in fountain pen nibs.
(h) *Nickel-chromium-zirconium alloy*: Addition of a fraction of zirconium to nickel-chromium alloys extends their operational lives in industrial and domestic heating apparatus.
(i) *Zirconium-nickel alloy*: It is a hard alloy used in cutting tools.
(j) *Zirconium-zinc/niobium alloy*: Both Zr-Zn and Zr-Nb alloys show superconductivity and magnetism at low temperatures of below 35K and can be used in low-temperature superconductive magnets.
(k) *Zircalloy*: An alloy of zirconium, iron, chromium and tin.

2. Nuclear reactor: Zirconium is used in construction of *fuel element* in nuclear reactor. Fuel element is a sort of container or matrix within which the nuclear fuel (uranium) is placed. In case of uranium fuel, the heat is generated by fission within the fuel, and it flows from within outwards. Besides, radiation from the fission product and oxidation of the fuel by coolant materials (like CO_2) have also to be taken into account while selecting the material for fuel element.

Zircalloy (the alloy of zirconium, iron, chromium and tin) is employed in manufacturing the core structural material of the fuel element and also, zirconium in pure metal form is used for cladding it. The primary role of zirconium in the zircalloy core and in the cladding is to efficiently conduct and transfer the heat generated inside the fuel element to outside devices for utilization while, at the same time, it neither absorbs the neutrons released by fission (so that neutron economy of the fuel is maximized) nor itself melts. High melting temperature, efficient heat conductivity and low neutron absorption of zirconium are the key criteria.

Hafnium, on the other hand, has high neutron absorption and hence, the zirconium must needs be free from hafnium.

3. Surgery: Zirconium can replace tantalum in bone screws, suture wire, cranial plates and can be inserted in the chest to isolate cavity created by lung operation from the surrounding organs. Pure hafnium-free zirconium is required. Non-toxicity and resistance to body fluids along with malleability and strength are the key criteria. In suture wire, ductility instead of malleability is important.

4. Other uses

(a) *Explosives*: Zirconium powder, due to its high reactivity with oxygen and brilliant burning, is used as a primer in explosives.
(b) *Photographic flashlight powder*: Pure zirconium powder was a material for use in *zirconium flash light* due to its brilliant luminosity. But after the advent of electronic flash light, this use has become obsolete.
(c) *Photographic flash bulb filament*: Ductility of pure hafnium-free zirconium, its ability to burn with brilliant luminosity and high melting point make it suitable in this application. But this use is not popular due to the high cost of such zirconium.
(d) *Vacuum devices*: High reactivity of zirconium with oxygen and nitrogen and other gases enables zirconium to remove traces of gases from such devices (e.g., radio transmission tube).
(e) *Rayon spinnerets*: Hardness and strong resistance to alkalis make zirconium a suitable metal in spinnerets for passing and drawing rayon threads.
(f) *Incandescent limelight*: Brilliant luminosity of heated zirconium is the criterion.

WASTE UTILIZATION

1. Hafnium: After separation of hafnium from uranium, the former is a waste metal product. It was used in the past only for laboratory experiments and a little in carbide cutting tools. But now, its high neutron-absorption capability and its possible use in control rods in nuclear reactors have been recognized. Control rods are meant for regulating heat in reactors. If the rods are lowered down in the reactor, more neutrons will be absorbed and the process of fission will slow down, thus reducing the heat. On the other hand, if the rods are pulled up out of the reactor, then less number of neutrons will be absorbed, and consequently process of fission will accelerate, thus increasing the heat. Presently materials like boron, cadmium etc. are used in making of control rods.

2. Zirconia-based silica: This material is derived from zirconia and silica which are co-precipitated during zircon-manufacturing processes. It contains 80% SiO_2 and 20% ZrO_2 (cf., in natural zircon the corresponding figures are 35% and 65%). Of the contained ZrO_2, 6-12% is active. But, its durability and corrosion- and chemical-resistance can be enhanced by processing it with certain organic polymers. Moreover its refractive index is high. It has been used as a substitute of TiO_2 as an extender in paint for application under water and under salty conditions. Being recovered from a waste material, it is relatively inexpensive.

PART II:
INDUSTRIAL ROCKS

Chapter 50

DIMENSION STONE

Rock constitutes practically the whole of the earth's crust, and it is the most abundant of all material things. According to one school of opinion, when rock is fabricated in some way for some commercial purpose, it is called stone. American Geological Institute calls the large natural masses as rocks, small quarried masses as stones, and the finer types as gravels, sands ,etc. If the rock is broken into fragments it is called crushed stone (see a separate chapter), and if it is cut and shaped to dimensions of specified sizes it is called dimension stone. The dimension stones used to be regarded as a a type of building stone. However, now, their utility is much more than that for mere building purpose. In legislative parlance in India, these stones are often referred to as ornamental or decorative stone. Dimension stones may be derived from different kinds of rock, a few of which are of commercial importance.

TYPES OF DIMENSION STONE

The commercial dimension stones are familiar by the names granite, marble, slate, sandstone and limestone. However, in commercial parlance, each of these commodities signify a group of petrologically distinct rocks as below.

1. **Granite:** It includes (in addition to true granite) diorite, basalt, dolerite, gabbro, anorthosite, pyroxenite, charnockite, porphyry, rhyolite, leptynite, andesite, syenite, gneiss, schist, diabase, felsite, monzonite and khondalite.
2. **Marble:** It includes (besides true marble) calcite marble, dolomite marble, magnesium marble, onyx marble, massive serpentine (mined as Verde Antique in Vermont, USA and as *green marble* in Rajasthan, India) and travertine marble.
3. **Sandstone:** It includes both sandstone and quartzite (including the green coloured *fuchsite quartzite).*
4. **Limestone:** To distinguish this splittable limestone from the massive limestone commonly used for cement manufacture, etc., it is generally referred to in industrial parlance as *flaggy limestone* or simply *flagstone*. It usually signifies the argillaceous, siliceous and dolomitic varieties of limestone which are hard. Its most well known Indian example is Kota stone.
5. **Slate:** It includes both slate and phyllite.

Much depends on amenability to cutting and polishing and certain basic characteristics of the rock, innovative ideas of the producer and his salesmanship. And it is possible that with time, more and more unconventional types of rock may be exploited for manufacturing dimension stones. The list given here is by no means exhaustive.

All these varied types of rock are grouped under one economic commodity namely, dimension stone, because there are certain common physical and economic criteria transcending the chemical and mineralogical definitions that impart some seemingly distinct petrological identity to each of them.

HISTORY

History of Use

Stones have been in use since over 12,000 years ago, for construction of human sheltersand of various structures and monuments. In the prehistoric era, during the civilizations of Egypt, Incas, Maya and Indus valley, use of stone for construction of buildings and other structures was much in vogue. The pyramids of Egypt and various archeological findings bear testimony to this. In the historic era, dimension stones became much sought after commodity for construction of the beautiful cathedrals of Europe.

Granite: The name granite owes its origin to the Latin “granum” meaning grain. In the older Dravidian temples of southern India, crystalline rock belonging to the commercial granite family were extensively used both in construction and statuary. Some of the examples of popularity of granite as a building stone during the prehistoric and ancient historic periods are the Sphinx in Egypt, Angkor Vat in Kampuchea, the rock caves of Ellora and the sculpture of Hampi in India etc. In India, granite has got so much mixed up with the imagination of artisans for generations that many exotic names have been given to appearances of its different grades—Golden Brown, Yellow Paradiso, Green Onyx, Indian Mahogany, Imperial Galaxy and so on.

Marble: The name marble has come from the Latin “marmor” and the Greek “marmaros” meaning shining stone. Quarrying and use of marble blocks for building purpose has a very long history. There is archaeological evidence pointing towards use of cut and dressed marble blocks around 3000 BC in Mohenjo Daro, Pakistan. That marble is believed to be a product from Makrana area of Rajasthan, India. Quarrying of white saccharoidal (coarse granular) marble from the beds of Delhi and Aravalli systems in Raialo, Alwar, Rajnagar, Nathdwara and Makrana in Rajasthan is an age-old activity. The marble from Rajasthan has been used for building many memorials, palaces and temples—Tajmahal of Agra, believed to be built with marble from Makrana, is the most famous amongst them.

Sandstone: In India, the fine-grained compact Kaimur sandstone belonging to the Vindhyan System were extensively quarried and used during the reign of emperor Ashoka (269-232 BC) as tablets for inscribing royal edicts. Monoliths weighing over 50 tons are known to have been used. The same variety of sandstone quarried in the form of slabs

10-12 m in length were used in the construction of the Buddhist stupas. The domes, railings, monolithic pillars and highly ornate gateways of the Sanchi stupa in central India were constructed out of this material. In the construction of the ancient forts and palaces of the central part of India, the Kaimur sandstone was extensively used.

The uppermost series of the Vindhyan System, known as Upper Bhander Series also provided very good sandstone for building purpose and in India, it used to be quarried in Bharatpur and Rupbas in Rajasthan and in Fatehpur Sikri in Uttar Pradesh. This sandstone found use during the Mediaeval period in the construction of Akbari palace in Fatehpur Sikri, Jumma Masjid in Delhi, and the various palaces, mosques and tombs of Agra, Delhi, Lahore etc. It was used in the famous Jodhpur fort where not only the walls, but also the floors and the roofs were made of it, but also the supporting beams.

The relatively soft and coarse-grained sandstone belonging to the Gondwana System was used in the construction of the ancient temples of Orissa (India). Though this sandstone was much less durable and much less pleasing in appearance than the Vindhyan sandstones, it was available locally and cheaply. For the same reason, the quartzitic sandstone of the Iron Ore Series was used in Singbhum district of Jharkhand state, Jurassic sandstone was used in Kachchh district of Gujarat, and gritty calcareous sandstone of sub-Recent origin was used in construction of the ancient temples and the churches in Thirunelveli district of Tamil Nadu.

Limestone: So far as the dimension limestone is concerned, its use has been widespread in India in construction of columns, pillars and floors of temples, palaces, buildings and other architectural works in many parts of India. The fine-grained white to buff coloured foraminiferal limestone of aeolian origin which is quarried in Saurashtra region of Gujarat, the Lower Vindhyan flaggy grey to black coloured limestone of Bijapur and Gulbarga regions of Karnataka, the crystalline limestone of Archaean age quarried in Warangal district of Andhra Pradesh, the argillaceous Aravalli limestone of Udaipur area of Rajasthan, the Jurassic limestone of Jaisalmer area of Rajasthan, the coralline limestone of the Cretaceous Bagh beds quarried along Narmada valley in central India, the extremely fine-grained compact bluish grey to black coloured highly amenable-to–polish argillaceous limestone quarried from the Kurnool Series in Cuddapah area of Andhra Pradesh, the dark bluish limestone of Lower Vindhyan age quarried in Durg district of Chhattishgarh state, the limestone of Cuddapah age available in Chandrapur district of Maharashtra, the limestone belonging to the coral formations of the southern coast in Tamil Nadu and the splittable flaggy limestone of Kota belonging to the Lower Vindhyan Semri Series — all, in the past, have been used in the vicinity of their occurrences.

Slate: There does not appear to be much of historical evidence suggesting use of slates in India much earlier than mid-nineteenth century. One of the oldest mining activities was in the outer Himalayan regions of Dharamsala and Mandi districts of Himachal Pradesh. There, grey to greenish grey coloured siliceous roofing slate belonging to the Chail formation used to be mined by the Kangra Valley Slate Company Limited in the 1860s. This company also quarried an excellent band of slate in Gurgaon district of Haryana from 1867 onwards. This slate belonged to the Ajabgarh Series at the top of the Delhi System. Slightly metamorphosed phyllite, suitable for use as flooring slab, switchboard, school slate etc. which belong to the Archaean age, was known as early as the middle of the nineteenth century, in Kharakpur hills of Munger district of Bihar. In the Kurnool and Nellore districts of Andhra Pradesh, the

Cuddapah formation contains good slaty bands, and manufacture of school slates started here in 1918.

PRODUCTION HISTORY

There is no record of production statistics in India pertaining to dimension stones in the historic past. Even during the late British period i.e., 1930s, data used to be maintained in respect of only the large companies. The production of some of the varieties of commercial dimension stone in India since 1932 is as follows:

Year	Production of dimension stones				
	Granite	Sandstone	Slate	Marble	Limestone
1932 (data pertains to India, Pakistan and Myanmar)	1.22 million tons	0.42 million tons	10,200 tons	6,000 tons	---
1942 (data pertains to India and Pakistan)	1.09 million tons	0.41 million tons	---	17,000 tons	---
1948	0.15 million tons	---	20,600 tons	27,000 tons	---
1965	---	---	1,408 tons	---	---
1970	---	---	633 tons	---	---
1975	---	---	3,661 tons	---	---
1980	---	---	15,264 tons	---	---
1985	1.29 million tons	4.00 million tons	8,628 tons	2.76 million tons	---
Year ending March 1992	0.99 million tons	4.41 million tons	3,000 tons	1.97 million tons	0.62 million tons
Year ending March, 1995	4.46 million tons	3.30 million tons	9,000 tons	2.63 million tons	1.41 million tons
Year ending March 1999	5.00 million tons	6.31 million tons	7,000 tons	3.76 million tons	143 million tons

CRITERIA OF USE

The acceptability of dimension stones for various uses is determined by geological nature, physical and mechanical characteristics, aesthetic and psychological appeal, techno-economic factors and, in a lesser degree, chemical or mineralogical composition. The various criteria are discussed here.

A. Geological Factors

The nature of the source rock as observed in the field gives the first clue regarding the suitability of a rock for use as dimension stone. The principal criteria that are considered by the prospective dimension stone manufacturer are as follows.

1. ***Size of occurrence***: The rock may occur in the form of a large massive pluton, in the form of batholiths or as a sedimentary bed extending for tens and hundreds of kilometers. Also, many rock bodies including igneous intrusives, may be as small as a few metres in length. Size of the source rock body intended to be mined for making dimension stones has a deciding influence on the economics of the end-use industry.
2. ***Depth of occurrence***: By far the larger mass of the rocks are located deep inside the earth's crust. A few rock bodies, nevertheless, occur at very shallow depths, and a still fewer ones outcrop. The depth of occurrence of the source rock body has a profound bearing on the technical and economic feasibility of dimension stone industries.
3. ***Bedding planes***: These are depositional features of sedimentary rocks. Originally they formed in horizontal fashion. But due to structural disturbances, the original orientations might have been distorted in all possible manners. Spacing of these planes may vary from a few millimetres to several metres and sometimes the inter-bedding spaces are filled by secondary mineralization or by crushed rock matter. Orientation of such bedding planes determines the exploitability of blocks.
4. ***Intensity and nature of jointing***: Joints are common features observed in rock bodies, and these are expressions of the failure of the outer shell of the earth due to tension or rupture. Joints may originate due to tension generated as a result of contraction of cooling magma or due to various external forces like shearing, faulting, etc. In igneous rocks, joints may be parallel or may be irregular and multidirectional. In sedimentary rocks, there may be joints parallel to bedding planes. Further, the joints may be closely spaced or far apart. The blocks of rock bound by joints are called *joint blocks*. Joint pattern of a rock body considerably influences the economics of its exploitation in the form of blocks. Large scale systematic structural mapping of rock bodies showing details of the patterns, frequency and spacing of joints generally go with good planning for exploitation. For example, too many crisscrossing joints at close intervals make a rock worthless for exploitation as blocks, on the other hand, optimally spaced regular joint planes facilitate quarrying of good-sized blocks from large batholithic bodies. In fact, if in a rock body suitably spaced joints are absent, then artificial joint planes are created by drilling and controlled explosion.
5. ***Sheeting***: Sheeting phenomenon is similar to jointing except that the sheeting surfaces are generally curved and parallel to the topographical surfaces. Sheeting phenomenon generally occurs in some large granite and sandstone deposits extending to great depths. Although the sheeting intensity generally decreases with depth, sometimes weak structural planes develop parallel to sheeting surfaces. These weak planes are helpful in exploitation of blocks economically.
6. ***Fissility***: Fissility is caused by foliation which is the property of rocks whereby they break along approximately parallel surfaces. It is also called *rock cleavage*. Foliation

in igneous rocks is a primary feature developed due to parallel arrangement of the platy minerals during flow stage of the magma. In fine grained sedimentary rocks, rock cleavage may develop either parallel or inclined to bedding planes. The rock cleavage in recrystallized schist or gneiss is called *schistosity* and, if the degree of metamorphism is low, the structure is called *slaty cleavage*. Slaty cleavage is caused by parallel arrangement of platy minerals like micas or chlorites or by that of ellipsoidal grains of certain minerals like quartz and feldspar. Due to presence of cleavage, a rock can easily break into thin well defined parallel sheets.

7 ***Faults***: In a rock body, there may be macro- and micro-faults. They create weakness and instability in the rock and their presence is generally considered detrimental to recovery of dimension stone blocks. Even if recovered, the blocks will remain prone to spall.

8 ***Unconformities***: Unconformities indicate discontinuities in deposition and are erosional surfaces separating younger rocks from older ones. Their presence is generally considered detrimental to recovery of dimension stone blocks.

B. Physico-Mechanical Factors

The characteristics discussed here mainly relate to strength, durability, workability and ultimate usability of the stone. The tests in respect of these characteristics are conducted on sample products and, in some cases, under microscope.

1 ***Compressive strength***: It is the load per unit area under which a block fails by shear or splitting. It is resistance to volume stress that tends to produce change in volume. For rocks, it is expressed in terms of pounds per square inch (psi) or kg/cm^2. It may be either confined (compressive load acting on all sides) or unconfined (compressive load acting on one side). In case of dimension stones, the unconfined compressive strength is tested. According to the standard procedure laid down by the American Society of Testing and Materials or ASTM (1958), three specimens of at least 2 inches size (2.5 inches in case of coarse grained rock) should be tested parallel to bedding, either dried at 105^{0}C for 24 hours or wetted after immersion in 20^{0}C water for 48 hours, and the rate of loading should not exceed 100 psi/second. The compressive strengths of some common Indian dimension stones are:

Granite	1000-2500 kg/cm^2
Grey granite	1100-2600 kg/cm^2
Pink granite	2 1000-2400 kg/cm^2
Porphyritic granite	1000-2500 kg/cm^2
Syenite	2 1200-2500 kg/cm^2
Diorite	1800-3000 kg/cm^2
Basalt	2 1500-3000 kg/cm^2
Dolerite	2000-3500 kg/cm^2
Gabbro	1800-3000 kg/cm^2
Charnockite	2000-3500 kg/cm^2
Gneiss	500-2000 kg/cm^2
Schist	400-950 kg/cm^2
Marble	1000-2500 kg/cm^2
Slate	2 1000-2500 kg/cm^2
Sandstone	20-1700 kg/cm^2
Quartzite	1500-3000 kg/cm^2
Limestone	300-2500 kg/cm^2

These figures are of general nature for giving some rough idea.

2. ***Tensile strength***: It is a measure of the coherence of the mineral grains within a rock by which the rock can resist pulling force. It depends on the strength of the grains, on the cementing material and on the areas of contact amongst the grains. It is also called resistance to longitudinal stress, because this kind of stress tends to produce unidirectional change in a body. Like compressive strength, tensile strength of rocks is also expressed as pounds per square inch (psi) or kg/cm^2.
3. ***Poisson's ratio***: This is closely related to both compressive and tensile strengths. When a bar is pulled or compressed, not only its length alters but also the transverse dimension. Thus when pulled, it becomes thinner or when compressed, it becomes thicker. Such alteration is called *transverse strain*. It is expressed (much the same way as longitudinal strain) as follows:

$$\text{Longitudinal strain} = \frac{\text{Change in transverse dimension}}{\text{Original transverse dimension}}$$

Now, for a given material, the ratio between transverse and longitudinal strains has been found to be more or less constant and this ratio is called *Poisson's ratio*. Poisson's ratio for some common Indian dimension stones are:

Granite	0.05-0.20
Marble	0.1-0.2
Slate `	0.1-0.3
Sandstone	0.1-0.3
Limestone	0.1-0.3

4. ***Shearing strength***: This is the resistance to tangential force. It is also called *rigidity*. In other words, a body is said to be in shear when it is subjected to a pair of equal forces which are opposite in direction and which act along parallel planes. Shearing strength of rocks is expressed in psi or kg/cm^2 as in the case of compressive and tensile strengths. The shearing strength of some common Indian dimension stones are:

Granite	246-457 kg/cm2
Marble	91-457 kg/cm2
Slate	141-253 kg/cm2
Sandstone	21-211 kg/cm2
Limestone	56-253 kg/cm2

5. ***Modulus of elasticity***: When any force, compressive or tensile or shearing, is applied to a body, the body undergoes some deformation. If a body can be easily deformed by a small force and it does not regain its original shape and size even after the force is withdrawn, it is called a plastic body (e.g., clay). On the other hand if a body completely regains its original shape and size after withdrawal of the applied force, it is called a perfectly elastic body, and this property is called elasticity.

When deformation takes place, the change in dimension per unit original dimension is called *strain*, and the internal restoring force per unit area is called *stress*. The maximum stress to which a body can be subjected without permanent deformation is called its *elastic limit*. According to *Hooke's Law*, within the elastic limit, stress is directly proportional to strain, and the constant ratio stress/strain is called *modulus of elasticity*. For rocks, it is usually expressed in units of psi or kg/cm^2.
Corresponding to the three kinds of force, tensile, compressive and shearing, there are three kinds of stress and strain and three kinds of modulus of elasticity. These three elastic moduli are:

i. Young's modulus,
ii. Bulk modulus, and
iii. Modulus of rigidity.

Liquids and gases have neither length nor shape, and nor do they have Young's modulus or modulus of rigidity. They have only bulk modulus. But, solid bodies like rocks can have all three types of modulus. The values of Young's modulus for some common Indian dimension stones are:

Granite	0.28 X 106 to 1.13 X 106 kg/cm^2
Marble	0.35 X 106 to 0.82 X 106 kg/cm^2
Slate	0.42 X 106 to 1.13 X 106 kg/cm^2
Sandstone	0.05 X 106 to 0.7 X 106 kg/cm^2
Limestone	0.21 X 106 to 0.63 X 106 kg/cm^2

The values of modulus of rigidity for these rocks are:

Granite	0.14 X 106 to 0.42 X 106 kg/cm^2
Marble	0.14 X 106 to 0.32 X 106 kg/cm^2
Slate `	0.18 X 106 to 0.42 X 106 kg/cm^2
Sandstone	0.02 X 106 to 0.28 X 106 kg/cm^2
Limestone	0.07 X 106 to 0.28 X 106 kg/cm^2

6. ***Rupture modulus**:* This is the resistance of a rock slab to bending or flexure. Such bending stress may be brought into play: (i) by the impact of wind blowing on a fixed beam or slab or (ii) by load of snow or other material acting on a beam or slab resting on supports at the two ends. The stress may first cause elastic deformation, then plastic deformation, and finally rupture. In case of brittle objects (as the dimension stones usually are), there will be no plastic deformation and the object will break as soon as the elastic limit is crossed. Modulus of rupture is expressed in terms of psi or kg/cm^2 of the bending stress under which an object breaks. It is usually measured at room temperature and under atmospheric pressure in short-time experiments. Values of the modulus of rupture for some common Indian dimension stones are:

Granite	0.09 X 103 to 0.39 X 103 kg/cm^2
Marble	0,04 X 103 to 0.28 X 103 kg/cm^2
Slate `	0.35 X 103 to 1.13 X 103 kg/cm^2
Sandstone	0.05 X 103 to 0.16 X 103 kg/cm^2
Limestone	0.035 X 103 to 0.366 X 103 kg/cm^2
Syenite	0.16 X 103 to 0.225 X 103 kg/cm^2
Gneiss	0.08 X 103 to 0.22 X 103 kg/cm^2
Quartzite	0.08 X 103 to 0.32 X 103 kg/cm^2
Gabbro, diorite ,diabase and basalt	0.14 X 103 to 0.56 X 103 kg/cm^2

Testing of this property assumes importance if the stone slab is meant for use in load-bearing applications like kitchen tops, table tops, park benches etc.

7. ***Rock creep***: Contrary to rupture which is a short time phenomenon, creep is a time-dependent deformation, and it is measured in long-time experiments. It is the result of constant stress conditions over a long period of time (like say, 10 years). Under such conditions, slow but permanent deformation may take place even if the stress is small. Ordinarily, the term is restricted to deformation resulting from stresses below the elastic limit.
8. ***Fatigue***: This is somewhat related to creep. The difference is that while in case of creep, the stress acts for a long time continuously, in case of fatigue it acts discretely. For example, if a small stress acts a hundred thousand times or a million times, rupture may take place. *Fatigue limit* or *endurance limit* is defined as the limiting stress below which a specimen can withstand hundreds of millions of repetitions of stress without fracture.
9. ***Toughness***: This is the resistance to sudden impact. The impact toughness of a rock is measured by the minimum height at which a standard drop weight breaks a standard specimen of the rock. According to the standard procedure laid down by the

American Society of Testing and Materials or ASTM, the standard drop weight is 2 kg, and the standard specimen is 25 mm (diameter) X 25 mm (height). Toughness is expressed in inches per square inches. Even if the compressive strength of two rocks is the same, they may differ in toughness which, inter alia, depends on inter-granular bonding. The impact toughness for some common Indian dimension stones are:

Granite	7-28 inches/inch^2
Marble	2-23 inches/inch^2
Sandstone	2-35 inches/inch^2
Limestone	5.0-8.6 inches/inch^2
Syenite	6.3-14.0 inches/inch^2
Gneiss	3.7-8.4 inches/inch^2
Quartzite	5-30 inches/inch^2
Gabbro, diorite, and diabase	5.6-34.0 inches/inch^2
Basalt	5-40 inches/inch^2

10. ***Hardness***: Hardness is basically a measure of resistance to permanent deformation by mechanical wear and is a surficial characteristic. The mechanical wear may be in the form of scratch, indentation or abrasion and depending on the method of measurement, the hardness of a rock or a mineral is referred to as *scratch hardness*, *indentation hardness* or *abrasion hardness*. Hardness is a complicated function of elastic, plastic and frictional properties of the surface.

The oldest and simplest method of measuring hardness is with reference to Mohs scale (1822). In this scale, talc is the softest mineral and diamond is the hardest mineral and they have been assigned arbitrary values of 1 and 10 respectively. In between, there are 8 other minerals with intermediate hardness values. The Mohs scale is as follows:

1. Talc
2. Gypsum
3. Calcite
4. Fluorite
5. Apatite
6. Orthoclase
7. Quartz
8. Topaz
9. Corundum
10. Diamond

The relative hardness of an object is roughly measured using the principle that it will scratch a softer mineral and it will be scratched by a harder mineral. The hardness measured thus is often referred to as *scratch hardness*, and the values of some common dimension stones are:

Granite and gneiss	6-7
Basalt and felsite	5-6.5
Sandstone	2-7
Slate	3-5
Quartzite	7

Methods to determine hardness accurately are based on first, permanent indentation of the surface by a loaded spherical, pyramidal or conical indentor and then, measuring the load and the amount of indentation. There are instruments making use of this basic principle, and depending on variations in the technique and formula, the hardness values are called *Brinell hardness*, *Vickers diamond hardness*, *Knoop hardness* and *Rockwell hardness*.

Another method of determining hardness lays emphasis on resistance to abrasive wear. The principle involves rotation of the object under a standard load with a standard quantity of abrasive powder (corundum) for a predetermined period and at a predetermined speed. The value obtained is usually expressed as *abrasion hardness*. In the method prescribed by the American Society for Testing and Materials (ASTM) in 1958, the superimposed weight is 2000 gm and the following formula for measuring abrasion hardness is used:

$$H_a = \frac{10G(2000 + W_S)}{2000\ W_a}$$

where H_a is the abrasion hardness, W_S is the weight of the specimen, W_a is the loss of weight during grinding operation, and G is the bulk specific gravity of the specimen.

The softest and the hardest minerals in the Mohs scale, i.e., talc and diamond have Vickers hardness values of 47 and over 2085; Knoop hardness values of less than 46 and 8,000; and abrasion hardness values of 0.0037 and 140,000. Abrasion is by far the most important type of hardness measured for dimension stones. It is important to note here that this hardness of a rock depends on both the hardness of the constituent minerals and the strength of the cementing bond. A loosely cemented sandstone may easily yield to abrasion in spite of high value of hardness of the constituent quartz. The abrasion hardness indices of some common dimension stones are:

Granite	37-88
Marble	8-42
Sandstone	2-26
Slate	6-12
Limestone	1-24

Abrasion hardness is an important parameter when the stone is subjected to foot traffic as in footpath pavements, floors of airports, railway stations, etc.

11. ***Density***: It is defined as the weight per unit volume of the rock. *Apparent or bulk density* is the density of the rock as a whole including pores, and *true density* is that excluding pores. True density is determined by powdering samples of the rock. True density is expressed in units of gm/cc while bulk density in tons/m^3. Both true density and bulk density are determined for dimension stones. The bulk density of some common Indian dimension stones are:

Granite	2.6-2.7 gm/cc
Gneiss	2.6-3.4 gm/cc
Syenite	2.7-2.8 gm/cc
Diorite	2.7-3.1 gm/cc
Dolerite	2.8-3.1 gm/cc
Gabbro	2.8-3.1 gm/cc
Charnockite	2.6-3.4 gm/cc
Marble	2.5-3.2 gm/cc
Quartzite	2.75 gm/cc
Limestone	1.78-2.94 gm/cc
Slate	2.7-2.9 gm/cc

12. ***Texture***: Rock texture is determined by the shape, size and fabric of the constituent grains. The grain size may be anything from very fine to very coarse; the shape of grains may be angular or rounded; and the fabric of grains may be described as of various types such as loose, compact, interlocked, openly packed, even, uneven, equigranular, inequigranular, homogeneous, heterogeneous, etc. Rocks with uniform and compact granular texture are generally more durable than coarse granular and porphyritic ones. Inequigranular rocks show variations in the degree of weathering, larger grains having larger areas exposed to weathering than smaller ones.
13. ***Micro-fractures***: Micro-structural discontinuities are often not visible in rough blocks, but they show up as hairline fractures after polishing. These develop due to release of stresses from original rock blocks. Intensive petrographic studies are necessary to detect them beforehand, once detected, such rocks are generally rejected.
14. ***Porosity***: Porosity of a specimen is the total volume of the pore spaces expressed as percentage of the volume of the specimen. The shape, size and nature of packing of the grains determine the degree of porosity. Vesicles, micro-capillary pores occurring along intra-granular cleavage planes and micro-cracks developed along grain contacts due to unequal contraction of quartz and other mineral grains during cooling of magma contribute to porosity of igneous rocks. In sedimentary rocks, degree of compaction, roundness of grains, range of variation of grain size and (in carbonates) presence or absence of vugs and channels determine the degree of porosity. In metamorphic rocks, cleavage planes contribute to porosity.

    Effective porosity of a specimen can be determined by immersing it in mercury and measuring the volume of mercury intrusion under pressure. However the micro-capillary and the isolated inside pores into which mercury does not penetrate, remain excluded and unaccounted for. In order to determine true porosity, the specific gravity of the rock sample as a whole and that of the powdered sample are considered as follows:

$$P = \frac{G_1 - G}{G_1} \text{ X } 100$$

Where P = porosity
G = specific gravity of rock as a whole
G_1 = specific gravity of powdered rock

The porosity volumes of some common Indian dimension stones are:

Granite	0.5-1.58%
Syenite	0.5-1.9%
Diorite	0.5-1.5%
Gabbro	0.1-0.5%
Dolerite	0.1-0.5%
Felsite	4.0-15.0%
Gneiss	0.4-1.5%
Charnockite	0.25-1.0%
Marble	0.6-2.5%
Sandstone	5.0-40.0%
Limestone	0.25-4.0%
Slate	0.1-1.7%

High porosity generally goes against the definition of dimension stones, but such porous rocks can also be used as dimension stones after some treatment. For example, the highly porous type of sandstone known in commercial parlance as *freestone* which is susceptible to damage by water, has been used for construction of the White House of Washington DC, USA after sealing the surface with a wash of salt, rice and glue.

15. *Water absorption:* It is the capacity to absorb water and is expressed as percentage of weight. It includes adsorption also, and it is sometimes referred to as water sorption. Porosity influences the water absorption to some extent inasmuch as water molecules enter and occupy the large capillary pores (not the micro-capillary ones) connected and opening up to the surfaces. For testing the water absorption of dimension stones, the American Society for Testing and Materials (ASTM) has prescribed in 1958 that a specimen having at least 3 smooth surfaces and of 2-3 inches size should first be dried at 105^0C for 24 hours and weighed (say, weight = A), then it should again be weighed after soaking in distilled water at 20^0C for 48 hours (say, weight = B) and the percentage of water absorption can be calculated using the formula [100 X (B-A)/A]. The water absorption values thus determined for some common Indian dimension stones are:

Granite	0.02-0.58%
Marble	0.02-0.45%
Sandstone	2-12%
Limestone	1-10%
Slate	0.01-0.06%

In practice, however, an easy and quick method for qualitative assessment of the degree of water absorption is often followed. In this method, water is poured on the surface of the rock. If this water is absorbed, then the wet surface will appear dull, otherwise if the water particles remain unabsorbed on the surface, the latter will appear shining.

16. *Thermal expansion:* Due to changes in temperature, substances undergo changes in volume. Changes in temperature may take place due to:

(a) Natural diurnal cycles of day and night
(b) Changes in seasons
(c) Excessive heating in deserts, industrial surroundings and densely populated cities
(d) Excessive cooling in arctic and sub-arctic areas
(e) Fire, etc.

In case of rocks, it is the expansion of the constituent minerals due to heat that contribute to the thermal expansion, and differential expansion of the minerals or differential heating of different parts may even result in damage of the rock. The coefficient of thermal expansion is measured by the ratio of the change in volume to the original volume per unit change in temperature (^{0}C or ^{0}F). Coefficients of thermal expansion of some common Indian dimension stones are:

Granite	3.6 X 10-6 / ^{0}F to 4.6 X 10-6 / ^{0}F
Marble	3 X 10-6 /^{0}F to 8.5 X 10-6 /^{0}F
Sandstone	3.9 X 10-6 / ^{0}F to 6.7 X 10-6 / ^{0}F
Limestone	2.8 X 10-6 / ^{0}F to 4.5 X 10-6 / ^{0}F
Slate	3.3 X 10-6 / ^{0}F to 5.6 X 10-6 / ^{0}F

17. *Thermal conductivity:* When heat energy is incident on the surface of any solid body, part of it is absorbed, part of it is reflected and the remaining part is transmitted by conduction. The ability to thus transmit is called thermal conductivity, and is the opposite of *insulating capacity*. It is obvious that the more of heat is absorbed and reflected, the less will be the thermal conductivity and more will be the insulating capacity. The thermal conductivity can be calculated by the following formula:

$$K = \frac{QL}{A(T_1 - T_2)}$$

Where K is the thermal conductivity
Q is the quantity of heat flow per hour
L is the thickness of specimen measured along a direction perpendicular to the isothermal surface
A is the area of the isothermal surface
T_1 is the temperature of the hot surface
T_2 is the temperature of the cold surface

Thermal conductivity is expressed either in “cal.cm/sec/cm^2/ ^0C” or in “Btu. inch/hour/ft^2/ ^0F”. The thermal conductivity of some common Indian dimension stones in cal.cm/sec/cm^2/ ^0C are:

Granite	0.004-0.008
Marble	0.005-0.006
Sandstone	0.003-0. 008
Limestone	0.005-0.008

19. *Ultrasonic pulse velocity or P-wave:* Rock quality can be determined by the measurement of ultrasonic wave velocity of relatively low frequency pulses passing through the rock. This is a non-destructive test for detection of the presence of any crack, micro-crack or other defect in a block of rock without the necessity of drawing small samples out of it (in any case absence of any such defect in a small sample does not ensure its absence in the whole block). Such test is particularly useful for getting important information in a non destructive way on the mechanical properties of large valuable blocks like say, stone monuments. Unit of measuring this velocity is kilometre or metre per second (km/sec or m/sec). It is determined using two piezoelectric crystal probes of frequency 2.2 MHz. (piezoelectric crystals are those that can change alternating mechanical strains into electrical impulses and vice versa). Initially, both the probes are kept in contact with each other and the travel time is noted. Then the probes are placed on both the sides of the rock and again the travel time is noted. Actual travel time is calculated by subtracting the travel time due to probe-probe contact from the travel time due to probes-rock contact. The P-wave velocity is calculated by dividing the thickness of the rock by the actual travel time. The P-wave velocity of some high-quality common Indian rocks which are relatively free from cracks and micro-cracks, are:

Granite	3.920-5.511 km/sec
Gabbro, dolerite	6.859 km/sec
Pink marble	3.96-9.63 km/sec
Sandstone	3.181 km/sec
Limestone	4.471

Ideally, the P-wave velocity (V) of a perfect rock is related to its modulus of elasticity (E), density in gm/cc (D) and Poisson’s ratio (P) as follows:

$$V = \sqrt{[E(1-P)/ D(1+P)(1-2P)]}$$

Lower velocity of P-wave means higher frequency of cracks and micro-cracks in the rock.

20. *Gloss/reflectivity:* Gloss is the percentage of the incident light beam that is reflected from a surface. It is measured by an instrument called *glossometer* using a reference plane. According to the American Society for Testing and Materials (ASTM), the reference standard is a highly polished plane of black glass with refractive index 1.567 for sodium-D line the gloss of which is assigned the value 100. The raw blocks are cut to a thickness of approximately 50 mm and their top surfaces are polished with abrasives till mirror-finish. Then the gloss is measured by positioning the polished surfaces beneath a glossometer. The measurement is determined by the ratio of the intensity of light reflected from a measured spot to that of the reference plane. Gloss depends on the angle of observation with respect to the plane. The higher the angle, higher is the gloss. So the gloss values are measured at angles 20^0, 60^0 and 85^0 (20-gloss, 60-gloss and 85-gloss) and the average gloss is calculated. The gloss indicates the ability of the rock to take polish as can be seen from the following test conducted on Kota limestone:

Rough Stone

Type of Kota limestone	Gloss values at different angles of measurement		
	20^0	60^0	80^0
Kotah Brown	0.58	1.20	0.40
Kotah Blue	0.60	1.54	0.66

Polished Stone

Type of Kota limestone	Gloss values at different angles of measurement		
	20^0	60^0	80^0
Kotah Brown	63	87	100
Kotah Blue	61	87	97

Based on gloss value, surfaces are classified as follows:

i. *Gloss***:** Smooth and almost mirror-like surface when viewed from all angles. Films with a high degree of reflectance. Gloss meter readings in excess of 65.

ii. *Semi-Gloss*: Films with an intermediate range of reflectance (readings between 30 and 65).

iii. *Eggshell***:** Low sheen films with gloss meter readings between 5 and 30.

iv. *Flat***:** Practically free from sheen even when viewed from oblique angles. Gloss meter readings will be less than 5.

Gloss values of some common Indian polished stones are:

Gabbro, dolerite	92.00
Sandstone	42.00
Limestone	79.33-83

21. *Electrical conductivity:* Insofar as dimension stones are concerned, this property is of very minor significance. It assumes importance only in some rare uses.

C. Psychological Factors

Dimension stones are used more or less in their natural form and they are valued because they add to ornamentation and decoration of the buildings and structures somewhat in the same way as gold jewelry ornaments the person of a human being. A lot therefore depends on the psychology of the user—whether he will like one stone or another. The criteria may depend on some external parameters like colour and texture, or may be the manifestation of the desires, complexes and emotions within minds of the users. However, one thing is common amongst all these criteria, i.e., all of them defy any quantitative evaluation. These factors are discussed here.

1 *Colour:* Colour has three components namely, *hue*, value and *chrome*. The much familiar terms like red, blue, orange etc. denote the hue (or the type of colour). The value indicates degree of lightness or darkness and it is related to both the percentage of light reflectance and the degree of lustre. Obviously, pure black has the lowest value and pure white has the highest value. Chrome indicates the degree of departure of a particular hue from neutral grey of the same value. In other words, it indicates the degree of saturation of the hue with reference to neutral grey. Thus, the familiar terms like ‘weakly red’, ‘strong red’, ‘deep red’, etc. are expressions of chrome.

However, these technicalities apart, the psychological perception of colour by a person depends on the combined effect of all these three attributes produced unconsciously and instantly within his mind. Someone may like one colour or one combination of colours, and someone else may dislike the same. Again, the same person may like one colour at one time, and may dislike it another time or under another circumstance.

Nevertheless, in the minds of consumers, some dimension stones have been permanently associated with some colours. Examples are black granite, pink granite, multi-coloured granite, red sandstone, golden yellow sandstone, green marble, white marble, etc.

2 *Shape:* Like colour, shape of dimension stones does not follow any rule or standard, and much depends on the likes and dislikes of a customer. For the same object (say, a tabletop), one person may prefer square-shaped stone, another person may like circular shape, and a third person may go for an octagonal or hexagonal shape.

Name of area of origin*:* For consumables, customers often tend to go by brand names. In a similar way, the names of areas from where the dimension stones are mined often play an important role in consumer acceptance. Consumers develop a sort of psychological bias in favour of traditional sites and a natural inertia to go for a product originating from a new site. Sometimes, dimension stones are more known to the users by their places of origin than by any physico-mechanical characteristic. Examples are Cuddapah slates, Andhra granite, Kota limestone, Jodhpur sandstone, Jaisalmer sandstone, Makrana marble, etc., all from India.

3 *Superstitious belief:* When dimension stones are used for making tombstones, superstitious belief may often influence the users' choice of size and colour. Such beliefs may not be confined to individuals and may be passed on from generation to generation, even to become ultimately community-specific. Thus, we may find that one kind of stone is preferred for use in Jewish cemeteries while another may be sought by Chinese, and still another by Christians or by Muslims.

4 *Sales promotion:* Human psychology is vulnerable, in a greater or lesser degree, to publicity campaigns that go with salesmanship. Since psychological factors play an important role in use of dimension stones, sales promotion campaigns do influence the users' decisions. Dimension stones being natural commodities, are highly unpredictable with regard to availability in shapes, sizes and colours of an user's preference. Often, products are to be made according to availability of natural blocks instead of according to the user's order. It is under such circumstances that sales promotion campaign plays an important role in making the products acceptable to the users.

D. Chemical and Mineralogical Factors

Chemical and mineralogical composition of a dimension stone determine its colour and also some of the physico-mechanical properties like hardness, texture, durability, amenability to sawing and polishing, etc. A knowledge of interrelationship between the chemical and mineralogical constituents on one hand and the characteristics that are directly responsible for the commercial potentiality of the stone on the other hand, is often helpful in making proper selection of sites for mining and subsequently, of blocks for cutting and polishing. Depending on the use of the stone, some of the constituents may be helpful in augmenting its value, while others may be deleterious. Also, the same constituents may be considered as desirable in one use and deleterious in another. The constituents that are either directly or indirectly crucial to the usability of a dimension stone, are:

> FeO, Fe_2O_3, CaO, quartz, hornblende, augite, pyroxene, plagioclase, orthoclase, biotite and other types of mica, pyrite, chlorite, calcite, garnet, zircon.

The effects of these constituents on the use of dimension stones vary due to their various intrinsic properties like colour, degree of resistance to weathering, coefficient of thermal expansion, chemical resistance, form, etc. Quartz does not undergo weathering easily, but minerals like feldspar alter with accompanying changes in physical properties, dislocation of positions and development of micro-fractures. These changes affect durability of a rock. Hard minerals like garnet and zircon will hinder uniform polishing. High silica content makes a rock more shiny.

D. Economic Factors

It is true for all commodities that certain favourable economic factors contribute to the volume of utilization. But in case of dimension stones, the economic factors may sometimes outweigh the other considerations, especially in a country like India, where dimension stone industry is by and large export-oriented, and when international competition is becoming tougher everyday. The factors may be macro-economic, i.e., region-specific or micro-economic, i.e., deposit-specific. These are as follows.

1. Macro-economic factors

(a) *Infrastructure*: For any export-oriented industry, its distance from port is an important economic factor, and so it is for the dimension stone industry in India. In fact, this distance matters more particularly in this industry because heavy blocks are required to be transported involving heavy freight charges. Conditions of roads and bridges are also very important. It is reported that stone blocks of up to 40 tons weight are exported from South Africa, China and South Korea while, in contrast, Indian industries can hardly transport blocks heavier than 13 tons, mainly because of poor conditions of roads and bridges. Though mining of dimension stone is to a large extent labour-intensive, the cutting and polishing industry is both labour- and power-intensive. Besides, cutting and polishing require continuous supply of water. So, both power and labour are required in sufficient measures. The importance of power can be gauged from the fact that an Indian firm with annual turnover Rs. 120 million worth of polished granite and Rs. 120 million worth of uncut granite (1990 price) consumed 200-3500 HP of power daily. The same firm consumed 5000 litres of water per minute. Though for cutting operation, recycled water to the extent of 50% could be used, for polishing, the entire requirement was for fresh water.

(b) *Industrial culture*: Polishing of cut blocks of dimension stones is more of an art than technique, and the art of polishing needs a high level of craftsmanship acquired through generations. The polishing industry in Italy has a history of more than 100 years and that in Japan, of more than 50 years. In each of these countries there are about 1,000 polishing units. Thus there is a well established culture in those countries, as a result of which the expertise and art of polishing have been perfected there. There is no dearth of the right kind of labour there, and ancillary industries manufacturing machinery spares and consumables have flourished. Over the years, consumers have also developed confidence in the products manufactured in these countries. This culture is an important factor in promoting the use of polished end products made out of stones.

2. Micro-economic factors

(a) *Mining and processing losses*: Dimension stones are mined in the form of large solid blocks and then, after cutting and polishing, marketed also in the form of blocks. Any run-of-mine product in the form of pieces or cracked blocks is rejected in the mine itself. Similarly, during processing, if any unwanted odd-shaped piece comes out of the raw blocks, the same has to be rejected. Such rejects constitute the losses during mining and processing. In India, the losses in some of the granite mines of southern states vary up to 60-70% during mining, and 30-60% of the mined raw blocks is rejected during processing. Thus, the total loss out of the in situ granite may go up to over 90% starting from mining up to the stage of the final polished product. It is obvious that lower losses will ultimately be a favourable factor for usability of a deposit.

(b) *Size of blocks*: If the blocks are large-sized, then there will be flexibility regarding shape, size and type of final products to be derived therefrom. So the deposits capable of yielding large defect-free blocks of stone are favoured by the industry.

(c) *Drillability*: Drillability or drilling hardness of a rock is related to its hardness and toughness. As has already been mentioned, hardness is the resistance to mechanical wear and toughness is the resistance to sudden impact. Efficiency of rotary drilling depends on the hardness, while that of percussion drilling on the toughness. Sometimes, the characteristic of a deposit is expressed in terms of drillability just as that of the rock samples in terms of hardness, toughness and other physico-mechanical attributes. This helps the stone industry in arriving at cost estimates of drilling operations to be undertaken for reserve assessment and for drawing samples for various tests. The frillability is a function of drilling rate. In case of rotary drilling, this rate is expressed in terms of number of rotations necessary to cut a hole 10 micron deep and, in case of percussion drilling, it is the penetration rate in inches per minute. A low drilling hardness may facilitate easy and cheap drilling operation, but will obviously decrease the suitability of the rock for use as a dimension stone.

USES AND SPECIFICATIONS

The uses of dimension stones may be broadly grouped as follows:

1 Engineering construction

- Bridge piers
- Bridge superstructure
- Beams
- Curbstones
- Pavements
- Slag drainage channel lining

2 Architectural works

- Monumental structures
- Institutional buildings
- Commercial buildings
- Residential buildings
- Wall tiles
- Roofing tiles
- Flooring tiles
- Steps
- Tombstones
- Window sills
- Door frames

3 Art work

- Statuary
- Carvings
- Sculpturing

4 Sanitary ware

- Wash basins
- Bath tubs
- Kitchen platforms

5 Furniture

- Tabletops
- Table frames
- Stools
- Shelves

6 Petty decorative and consumer items

- Writing slates
- Ash trays
- Pen stands
- Paper weights
- Switchboards

7 Metrological reference objects

- Prisms
- Parallels
- Surface plates
- Cubes

8 Ashlars

These uses are discussed in details with reference to their specifications, as follows.

1. Engineering construction: In this application, rugged strength and durability are the main consideration. The engineering structures like bridges, dams etc. are subjected to the impact of the most rigorous natural weathering and human handling, and are expected to last for hundreds of years. Moreover, the material for such construction work is required in bulk. So, for the dimension stones to be used in engineering construction, geological, physico-mechanical, chemico-mineralogical and economic factors assume importance and the psychological factors are of lesser relevance.

(a) *Geological factors*: Large sized blocks, slabs and beams are required and hence, large massive deposits free from joints and fissility are necessary. Also, since very large blocks are sometimes required to be transported out of the mines, shallow deposits are preferred to deep ones, not so much because of cost considerations as because of the risk of damage to the blocks. A slight defect, even invisible, inflicted during handling and transportation of the blocks may render them risky for use in heavy-duty public utility applications such as bridges, dams, etc. Another disadvantage of deep-seated deposits (as well as those occurring in tectonic zones) is that the rock remains in a strongly pre-stressed state before mining, and when afterwards the stress is relieved, over a period of time micro-cracks may tend to develop within the blocks. This behaviour is also noticed in metamorphosed and recrystallized rocks like marble, which were pre-stressed during metamorphism in the geological past. The relieving of this stress is hastened on slight heating resulting in expansion of the rock. Generally, the dimension stones most suitable for this use, come from igneous bodies.

(b) *Physico-mechanical factors*: In case of girder bed-stones in bridges and dams and in case of piers in bridges, there is a constant compressive load that acts on them continuously for hundreds of years. So, high compressive strength, high bulk modulus and low creep are specified for the stone. the piers of bridges are fixed at bottom and top, are subjected to a continuous pulling force due to the force of flowing water acting on them and the material must have high tensile strength, high Young's modulus and low rupture modulus. Since tensile strength of a rock depends on the coherence of its constituent grains, compact fine-grained texture, low porosity and high bulk density become automatically preferable. Again, the forces of the stream and the wind acting on the piers from different directions, may generate a sort of shearing force and in order to resist that, the rock must have high shearing strength and high modulus of rigidity. If the vertical pillars of a bridge are monolithic, then they are practically uni-dimensional and the compressive stress acts along the length resulting in development of transverse strain. Poisson's ratio should therefore be as low as possible.In the bridge superstructure, the beams resting on piers at the two ends, are subjected to a constantly high bending pressure over long periods of time, and hence low rupture modulus and low creep are necessary. Further, they have to resist the forces of the blowing wind which generates a pulling stress within the stone, and the latter, therefore, must have high tensile strength, compact texture, low porosity and high bulk density. In case of sea or riverwalls and curbstones, the stone is subjected to continual repetitive impacts of surging waves and traffic, respectively. In such cases, high impact toughness and low fatigue of the stone material used, assume much importance. In case of pavements, on the other hand, it is abrasive action of the traffic that the stones are subjected to most, and hence, high value of hardness is specified.In metallurgical industries, sometimes, the slag drainage channels are lined with dimension stones. The slags may not only be hot but they may also be very acidic, and so the stone must be resistant to both heat and acid. Moreover, in order to facilitate smooth flow of the slag, a highly polished stone lining is used. A low coefficient of thermal expansion is specified because, otherwise, frequent expansion and contraction of the lining may result in peeling off of chips. This may not only weaken the lining itself, but also may roughen its surface polish, and thus hinder the smooth flow of the slag. Also, fine-grained homogeneous texture and low porosity are desirable so as to enable the stone to take good polish. A heterogeneous porous rock consisting of constituent grains of uneven hardness does not take good uniform polish. Engineering constructions are such that the structures are often exposed to the open atmosphere. If they are in a cold place, then exposure to frost action will be common. Water particles may get absorbed, occupy pore spaces within the rock and later frost with associated expansion in volume. This may result in pushing apart of the constituent grains and weakening of the rock. Low water absorption is therefore a necessary specification for the stone for use in engineering construction works. Closely related to low water absorption are high bulk density and low porosity. In addition, when the structures are located in very widely varying climatic conditions, then coefficient of thermal expansion should also be low, because, otherwise, due to alternate expansion and contraction of volume over long periods of time, the rock may ultimately weaken and crumble.

(c) *Chemico-mineralogical factors*: Quartz imparts strength, but it has poor fire resistance. Alpha-quartz changes to beta quartz at temperatures ranging from 573^0C to 870^0C, and then to tridymite at temperature above 870^0C, and finally to cristobalite at 1470^0C. These changes are accompanied by changes in crystal form and volume. So, rocks containing quartz are not preferred in open constructions prone to fire. However, in structures which are not vulnerable to fire, like bridge pliers, sea walls, etc., quartz may not be objectionable.

An important advantage of the presence of feldspar in a rock is that it indicates freshness of the rock. If the rock is weathered, then the first constituent to alter is the feldspar which becomes flowery due to kaolinization. Feldspar is fairly hard and generally acid-resistant. However, orthoclase is susceptible to kaolinization through the action of carbonated or alkaline water, and sodium feldspar, i.e., albite is comparatively more fusible than other types of feldspar. All the same, feldspar is normally desirable, and anorthite type may be the most advantageous in engineering construction works.

- Carbonates are highly objectionable in engineering construction material due to four reasons. First, solubility of all carbonates rises rapidly with increasing CO_2-concentration in industrial and urban atmosphere, even at low temperatures. Second, carbonate is soluble in HCl acid, and is therefore extremely deleterious in stones intended for use in slag drainage channel lining. Thirdly, $CaCO_3$, on being burnt due to fire, reduces to CaO which is prone to hydration and slaking. Fourthly, crystalline $CaCO_{3,}$ i.e., calcite shows linear thermal expansion more along c-axis (about 2%) than along a perpendicular direction (about 0.5%). This simultaneous expansion and contraction may be disruptive in the rock even at temperature below 100^0C. Stones made of carbonates or otherwise containing calcite or siderite grains are therefore not suitable in engineering construction.
- Iron oxides are objectionable because they have a tendency to hydrolyze and limonitize over a period of time. Chips of limonitized portions tend to peel off and the stone surface become rusted and spoilt. Megascopically also, sometimes, thin films of iron oxide may be present in patches within stone bytes. This is more common in case of slates. These patches, being harder and with uneven boundaries, make smooth cutting difficult.
- Pyrite is considered deleterious. It is very unstable, and it readily alters by oxidation to iron sulphate or to limonite, large masses of pyrite exposed on the surface of rock may alter to a cellular mass of limonite, and the process of alteration continues till the whole of pyrite disappears. Further, this oxidation is highly exothermic and may generate considerable heat. Last, this process of oxidation sets free sulphuric acid,

which may react with other mineral constituents in the vicinity, thus aggravating the damage.

- Mica, particularly muscovite which is resistant to weathering is not ordinarily objectionable in some of the applications of the dimension stones in engineering construction work, where polishing is not required. Biotite, however, may sometimes tend to lose its iron on alteration and form rusty spots. But, if the cut stone is to be polished (as in the case of say, slag channel lining), then any type of mica is objectionable because its flakes obstruct polishing.
- Ferromagnesian minerals like hornblende, augite and pyroxene may be desirable because of their resistance to weathering. These impart strength and durability to the rock.

(d) *Economic factors*: The stones used in engineering construction are usually large sized and heavy. So, the crude dimension stones must be mineable in the form large blocks, and the road conditions should be good enough for transporting the heavy blocks from mine to industry and then to construction sites or ports.

- Strong and hard blocks are used in cut form (and sometimes polished form also). So, availability of adequate power, water and labour is a necessary prerequisite for the rock-cutting industries to be set up. In India, for example, the common experience is that for every Rs 10 million investment (1990 price), around 400 direct and 4000 indirect workers are required. Moreover, rock-cutting needs continual supply of various consumables, for cutting medium-sized to very large-sized blocks, usually mild-steel wires sprinkled with silicon carbide or diamond powder or special steel blades fitted with metal or resin-bonded diamond teeth are used (c.f., diamond saw for small blocks). The general life of these can be judged from the experience of one of the granite processing plants in India. This plant has reported that the wires can give a trouble-free service for up to one week and then their lives can be further extended for another two weeks by welding and repairing. This plant has also reported that the blades last about 250-300 square metre of cutting. It is apparent that for promotion of use of dimension stones in engineering construction work, well-knit network of ancillary industries ensuring continuous supply of special consumables required for processing work, is essential.
- Since, the stones used in engineering construction works are judged more by their intrinsic characteristics than by the consumers' psychology, the worldwide trend is to locate processing industries near mining sites. This serves to avoid transportation of very large and heavy blocks. Therefore, it is desirable that the infrastructural and other facilities required for processing, are available near the deposits.

Generally, the igneous rocks containing less of quartz and orthoclase and more of plagioclase such as diorites, dolerites, gabbros etc. (which belong to the type of dimension stones commercially known as granite) fulfill the necessary geological, physico-mechanical and chemico-mineralogical conditions, and these types of rock are preferred in engineering construction. The Bureau of Indian Standards in 1995 has grouped granites under two groups, namely, pink granite and multi-coloured/grey granite, and has recommended separate sets of specifications for these groups, and those with respect to some of the parameters have been reaffirmed in 1998. The specifications with regard to some important parameters are as follows:

(i) Pink granites: Moisture content 0.15% (max); dry density 2.58-2.63 gm/cc; water absorption 0.5% (max); porosity 1.02-2.5%; compressive strength 1000-1500 kg/cm^2; tensile strength 90 kg/cm^2 (min); shear strength 280-425 kg/cm^2; Mohs hardness 6-7; ultrasonic pulse velocity 5 km/sec.
(ii) Multi-coloured/grey granites: Moisture content 0.15% (max); dry density 2.60-2.68 gm/cc; water absorption 0.5% (max); porosity 1-2%; compressive strength 1300-2200 kg/cm^2; tensile strength 90 kg/cm^2 (min); shear strength 300-540 kg/cm^2; Mohs hardness 6-7; ultrasonic pulse velocity 5 km/sec.

But, in addition to the quality of the stone, proper installation using the right kind of cement or binder for fixation plays an equally important role in preventing failures.

2. Architectural works: In this application, the psychological factors come first, and all other factors, even economic factors, come next. Architectural works are valued prima facie for their appearance and aesthetic appeal, and without these, even durability becomes meaningless. Once the psychological conditions are fulfilled, then the other questions such as those of strength, durability, economics, etc. will arise.

Some of the architectural works are, like engineering works, exposed to atmosphere. The outside walls of buildings, roofs, monuments and tombstones, etc. fall in this category. Next to aesthetic appearance, strength and durability assume importance for such works. For other categories of architectural works like window sills, inside wall tiles, etc., strength may be of comparatively lesser significance. Some of the architectural works may not have any functional relevance, but may be simply decorative, and valued as a symbol of status and vanity. In such cases, cost considerations may recede to irrelevance. The specifications with regard to various factors are as follows.

(a) *Psychological factors*: Colour of the stone has to be pleasing. It is never possible to standardize this parameter in terms of exact hue, value or chrome. In fact, any colour or even combination of colours may appear pleasing to the user. Again, the aesthetic appeal of architectural works depends on the totality of the effect produced by the colour combination of the stones, the nature of the environ, the purpose of the work, the taste of the user and so on. What may be pleasing in case of a tombstone or a monument, may not be so in case of a hotel or an institutional building; what might have pleased people hundred years ago, may not be so hundred years after; what may be the right choice in an environ of natural greenery, may not at all suit an urban and industrial location. Thus, all colours such as white, cream, red, black and also combination of colours of different designs like spots, bands, etc. may be used. If the work is a symbol of status or vanity, then generally the colours that are rarely available in nature are the most sought after. If it is a tombstone or an institutional building, then sober and uniform colours are preferred whereas in case of commercial buildings like hotels, bright combinations of colours may not be unacceptable. In case of tombstones, superstitious beliefs that sometimes go with religious and national traditions, may have an overriding influence in the choice of stone.

The parameters usually influenced are colour, thickness and shape. For example, it has been reported that for use in cemeteries, the Jewish go for 12 inch thick spotless jet-black coloured stone slabs, the Muslims of Middle-East countries and the Christians go for 4-8 inch thick black coloured stone slabs, the Chinese prefer 3 inch thick red coloured stones and the Japanese seek hexahedral shaped stones. Of course, though superstition runs through generations, any preference guided by superstition may be highly susceptible to sudden changes due to rumours and preachings. In any case this criterion is irrelevant in application of dimension stones in other types of architectural works. Use of dimension stones in architectural works has a long history. The temples and monuments built in the ancient and mediaeval periods bear testimony to this. The best quality stones used in these works used to come from a chosen few quarrying sites, and these quarrying sites therefore has an equally long history. The name of each of these sites has consequently become a kind of brand name, being synonymous with high quality stones, and consumers tend to judge the stones more by these names than by other criteria. Makrana marble, Kota sandstone, etc. may be cited as examples of associating names of quarrying sites with the dimension stones preferred for use in architectural works.

(b) *Physico-mechanical factors*: Architectural works, though must look pleasing, have to last also. The temples and monuments built in the ancient and mediaeval periods continue to please the viewers even now. Nowadays also, institutional and commercial buildings are built keeping in view several decades (perhaps even a few hundreds) of years of life; residential buildings should also last one or two generations. So, there has to be a compromise between outer appearance on one side and intrinsic strength and durability on the other side. In other words, physico-mechanical factors are also important, but in a lesser degree than in an engineering construction. Fairly high compressive strength and bulk modulus and low creep are desirable for the stones which are used in the form of blocks to make solid stone walls, because these blocks have to bear the load of the superstructure. The desirable values of these parameters will depend on the height of the building. However, these parameters are not that important when the stones are used as tiles lining the walls.In case of roofing tiles, fairly high tensile strength and Young’s modulus and low rupture modulus may be necessary, because in this use, the stones in the form of long slabs are susceptible to flexure and pulling stress. Since tensile strength depends on the degree of coherence of the constituent grains, compact fine-grained texture is also important for stones thus used. However, since there is no extra load other than that due to the weight of the stone slabs themselves, a very high value of tensile strength or a very low value of rupture modulus is not essential as such. The stones used in flooring tiles and steps are subjected to abrasive action due to pedestrians walking on them. In this use therefore, a fairly high hardness value is desirable. However, since movement of heavy vehicular traffic is not involved, a very high value of hardness is not essential. In fact, a very hard rock surface hinders polishing, thus reducing its value as a raw material for architectural works. In pillars and door frames, bar-like long pieces of stone are used, which are subjected to compressive stress along the lengths, engendering possibility of development of transverse strain. So, for such uses, the stone should have low Poisson’s ratio. Stones used in architectural works are very often exposed to atmosphere. Blocks, tiles on outer walls, roofs, tombstones etc. are illustrative examples. In a cold place, the absorbed water particles may expand in volume due to frosting, and the result will be eventual weakening and erosion of the stone surface. Low values of water absorption of porosity and high bulk density are therefore essential. In climates in which the diurnal and seasonal temperatures are widely fluctuating, the effect of alternate expansion and contraction of the stones over a long period may be harmful. Low coefficient of thermal expansion is therefore necessary. If the stones are for use in residential buildings, they must protect the insides from heat and cold of the atmosphere, and low thermal conductivity is desirable. This is particularly true when the buildings are located in areas of extreme climatic conditions and also in hot industrial areas. Stones for architectural works are invariably used in polished form so as to render the necessary pleasing appearance and aesthetic effect. So, the stones must be able to take a high degree of polish and the texture becomes a vital criterion. Coarse grain size and loose heterogeneous fabric render the constituent grains liable to get detached from the rock surface during polishing. Fine to very fine-grained homogeneous compact texture is highly valued. Angular shaped grains remain interlocked and coherent, and consequently, are less liable to be detached during polishing than rounded grains.

(c) *Chemico-mineralogical factors*: Quartz is objectionable because it is hard and resistant to polishing. Being hard it is more resistant to weathering and solution in groundwater than many of its neighbouring constituents in the stone. Consequently, over a long period of time quartz, chert, etc. may form prominent reliefs on the stone surface. Also quartz has low fire resistance. Alpha-quartz changes to beta quartz at temperatures ranging from 573^0C to 870^0C, and then to tridymite at temperature above 870^0C, and finally to cristobalite at 1470^0C. These changes are accompanied by changes in crystal form and volume, as a result of which the rock ultimately gets weakened. Feldspar is no doubt the most desirable amongst the primary constituents in case of stones of igneous origin, because it is neither too soft nor too hard, and it is generally acid resistant. Further, it is stable under normal conditions of use, and is available in pleasing colours. Carbonates have advantages as well as disadvantages. Calcareous matter being homogeneous extremely fine-grained and soft, take very good polish. For this reason calcareous rocks like marble, calcareous slates and argillaceous limestone have been highly valued for different kinds of architectural works. Marble is used both as blocks and tiles for lining, while argillaceous limestone and calcareous slate are used as roofing, wall and flooring tiles. The disadvantages of $CaCO_3$ mainly pertain to its lack of thermal and chemical resistance and consequently, shortened life of the stone. First, due to fire, $CaCO_3$ is reduced to CaO and this CaO is prone to hydration . Second, crystalline $CaCO_{3,}$ i.e., calcite shows differential thermal expansion which is about 2% along c-axis and about 0.5% along perpendicular direction. This happens at temperatures even as low as 100^0C. In extremely fluctuating climatic conditions, this ultimately results in weakening of the stone. Third, $CaCO_3$ is chemically unstable in conditions of increased CO_2 concentration (as in urban and industrial areas). The famous Tajmahal of Agra was built in 1653 AD entirely with white marble. It remained intact for more than three centuries. But in 1970, Mathura refinery was set up about 50 Km north of Tajmahal. During this time, mushrooming of many foundry industries also took place in the region west of Tajmahal. Moreover, this monument is situated very near to railway track and earlier steam engines and later diesel engines have been frequently emitting CO_2 and other gases. Meanwhile, Agra city has also been continuously expanding with an ever increasing number of motor vehicles emitting exhaust gases. The net combined effect of all these factors is that this marble monument is nowadays exposed to an atmosphere vitiated with increased concentration of CO_2, CO, SO_2, NO_2 gases; and noticeable yellow tinges of hydrous nitrates and sulphates of calcium have appeared on some parts of this wonder monument. Iron oxides and pyrite are chemically unstable. Iron oxides and pyrite tend to limonitize very easily. Pyrite also tends to oxidize to iron sulphate. The process of oxidation generates both heat and free sulphuric acid which may act on other constituents of the stone. All these processes of alteration may eventually corrode the surface of the stone and also produce yellowish patches thereon. In stones used for architectural works, both surface polish and colour are very important, and even a slight damage to the surface is not tolerated. Hence, iron oxides and pyrite are considered highly deleterious. Megascopically also, sometimes iron oxide is present in patches within slate. This may obstruct smooth cutting of the slate into thin slabs and render it useless as a roofing or flooring stone. Any type of mica is objectionable because the flakes obstruct polishing, and ability of the stone to take polish is one of the most important criteria in architectural works. Moreover, mica is highly resistant to weathering and to action of groundwater. Due to differential weathering and ground water solubility of mica vis-a-vis other constituents of a stone, the mica flakes may, after a long time, show up as sharp blades on the stone surface. In the case of roofing and flooring slate, however, the flakes of mica (and also chlorite), arranged along the cleavage planes, may facilitate smooth cutting into thin slabs. For use in ordinary residential buildings, these slabs need not have a high degree of polish or a very long period of life and for such purposes, micaceous and chloritic slabs are considered good. Glauconite imparts green colour, hornblende imparts dark green colour and augite imparts black colour to a stone. Since there is no specification regarding colour except that it should be pleasing to the user, these mineral constituents are not objectionable as such, if green or black stone is desired.

(d) *Economic factors*: Unlike in case of stones used in engineering construction, those used in architectural works require a high degree of polish and finish, and also require consumer preference. Through cutting and polishing of raw blocks in India, value addition of the magnitude of 15-65% takes place. The risk of transporting through rail and road and that of handling are, is therefore, much more in case of polished blocks than in case of crude blocks. Also, it is advantageous if selection of blocks for polishing is taken up after ascertaining the consumer preference. It is therefore desirable that the processing industry should be located nearer to the consuming centre rather than to the mine. In case of export oriented industries, the processing plants should be as near to the port as possible. The infrastructure like water, power and labour and also the machinery and consumables necessary for processing of stones should therefore be available near some consuming centre or port.

Since various degrees of compromise are made between strength and durability on one hand and aesthetic appearance on the other hand, almost any kind of dimension stone viz., marble, sandstone, slate, granite are suitable for use in one or the other type of architectural work. The most important criterion that must be satisfied is that the stone should be homogeneous, fine-grained and compact. So, dolerite and gabbro amongst igneous rocks, marble and calcareous slate amongst the metamorphic rocks, and sandstone cemented by calcareous matter amongst the sedimentary rocks fit the bill widely.

3. Artwork: This may or may not be associated with architecture. Artists and artisans may carve out intricate designs like screens, flowers etc. on cut and polished wall, roofing and flooring tiles which are used in buildings, monuments and other architectural works. On the other hand, sculptors make statues out of cut blocks of stone or even out of in situ bodies of outcropping rock. For this kind of work, no sophisticated machinery is required, and tools like chisels and hammers are generally used. The products are generally preserved with care as showpieces, and are not subjected to rough handling. So, unless the carvings are on the exposed parts of buildings or unless the statues are erected outdoor for beautifying roads, parks etc., strength and durability of the stone are not of much significance, but colour and workability are. Such products are usually not turned out in an industrial scale. In this kind of work, as in any other kind of work of art, commercial considerations generally recede to background, and it is the inspiration and passion of the artist that count most. So, economic factors are relatively of less importance. The specifications with regard to different factors are discussed as follows.

(a) *Physico-mechanical factors*: Texture of the stone is by far the most important parameter that determines its workability. While chiseling a very small feature of an intricate design or the facial details of a statue, unwanted disruption of even a single grain may spoil the artistic value of the work entirely. Hence the texture of the stone should be fine-grained, compact and homogeneous. This also requires low porosity and low water absorption, thus ensuring reasonable durability of the stone. Besides texture, hardness is also an important criterion for workability of a stone. Too hard a surface makes chiseling difficult.

(b) *Chemico-mineralogical factors*: Quartz is not desirable because of two reasons. First, it is too hard to facilitate delicate chiseling. Second, it is more resistant than the cementing matrix and so, in course of time the unweathered quartz grains stand out as reliefs on the weathered surfaces, particularly on the works exposed to open atmosphere. This has happened to the sculptures on the outer walls of many ancient temples in Orissa and other parts of India which were made from sandstone blocks. In this way, many priceless works of art have been destroyed forever. Statues made of and carvings made in stones composed of $CaCO_3$ run a high risk of destruction if exposed to urban and industrial atmosphere vitiated with increased concentration of CO_2, CO, SO_2 and NO_2 gases. Increase CO_2 concentration causes chemical destabilization of $CaCO_3$, while SO_2 and NO_2 may cause formation of patches of yellow-coloured hydrous sulphates and nitrates of calcium. If exposed to very hot climatic conditions, crystalline $CaCO_3$ has a tendency of differential thermal expansion along two axes, that along c-axis being 2% compared to 0.5% along the perpendicular direction. However, these problems characteristic of $CaCO_3$ may not affect the artworks that are preserved indoor.

(c) *Psychological factors*: Uniformity of colour is the most important characteristic that needs to be ensured while selecting a stone for artwork. Whatever colour it may be — jet black, black, grey, white — it has to be uniform, and speckles, even a tiny dot of a different colour — on a carved design (of say, flower) or on a sculpted facial feature (of say, eye) may drastically reduce the artistic value of a work. This condition automatically precludes acceptance of stones with even very small grains of mineral constituents like pyrite, mica, etc. occurring within them.

(d) *Geological factors*: The statues and carvings seldom have any regular geometric configuration and much less, straight outlines. So, in order that the artists get maximum latitude to carve or sculpt any irregular-shaped figure out of the rock, the latter should be available in the form of massive bodies, and must not be cleavable. This condition precludes use of slate, flagstone, etc. for this kind of work.

Generally, pure diorite, dolerite, gabbro, anorthosite and marble satisfy the above conditions. Of these, marble suits best the works of carvings on internal walls, ceilings etc. and also of statuary for indoor preservation, while the other types of stone suit outdoor works.

4. Sanitary ware: Kitchen platforms are nothing but flat pieces of stone slabs cut to different sizes, while articles like washbasins, bathtubs, etc. are manufactured by joining thin flat pieces of stone with the help of cement or some other bonding material. These are ordinary household articles for installation within residential buildings and are not subjected to any heavy load. Strength and durability are, therefore, of not much significance. On the other hand, these are supposed to serve the purpose of utility and show of status symbol. Since these articles are generally for constant rough use, a very high degree of polish is not required. The various specifications are discussed as follows.

(a) *Geological factors*: Since the stones are used in the form of thin flat pieces, they either should be available in nature in the form of massive blocks which can be cut into desired slabs or should be fissile. However, for manufacturing sanitary ware, only small pieces are required and very large crude blocks need not be a requisite condition.

(b) *Physic*o-*mechanical factors*: The stones must be amenable to machine cutting. Hence, texture is an important criterion. Fine-grained, compact and homogeneous texture facilitates smooth cutting into thin slabs, because there is little chance of dislodgement of grains during passage of the saw, wire or blades. This type of texture also facilitates polishing of the stone surface. Another important aspect in the use of sanitary wares is the constant wetting of their inside surfaces without any leakage of water. The stones should therefore have low water absorption and also low porosity. Further, in order that water particles do not stick to the inside surfaces and that the wares should dry up quickly, the ability of the stone to take polish becomes important. For this purpose, the stone should not be too hard.

(c) *Chemico-mineralogical factors*: Quartz is not preferred because of its high hardness value and consequent resistance to cutting and polishing. Mica in igneous rocks also resists cutting and polishing and hence considered deleterious. However, micaceous slate in which flakes of mica are arranged in parallel planes facilitates fissility and is often preferred. Patches of iron oxide in slate are highly objectionable because they resist cutting, and also it is difficult to ensure regularity and smoothness of surfaces by controlling the cutting process. Calcareous matter is preferable. First, it is not very hard and is amenable to polishing; second, due to its very fine grain size, it forms practically a homogeneous mass by filling up pore spaces of porous rocks; third, it is not as weak as argillaceous matter. Disadvantages of $CaCO_3$ like uneven thermal coefficient and chemical instability do not manifest themselves in case of sanitary wares because the latter are not subjected to the vagaries of open atmosphere. Grains of pyrite are not desirable, mainly because their bright yellow colour tends to disturb the uniformity of colour and appearance of the stone. Moreover, the sharp boundaries of such grains with the matrix may serve as favourable locales for water absorption.

(d) *Psychological factors*: Pleasing appearance is essential. The colour may be either uniform or may be in combination forming pleasing designs. Consumer preferences and sales promotion measures play an important role in promoting use of sanitary ware made out of stones.

(e) *Economic factors*: Sanitary wares are normally manufactured as byproducts of building stones, and processing plants are not set up exclusively for sanitary ware. So, there is no particularly special economic criterion influencing the use of these products. However, since these products are somewhat delicate and since their use depends to a large extent on consumer tastes, the manufacturing plants located near consumer centres have some advantage.

Amongst the igneous rocks, diorite, dolerite and gabbro fit the bill best and amongst the metamorphic rocks, dolomitic marble, pure marble and calcareous slate are suitable, while calcareous sandstone and argillaceous limestone are the most preferable amongst the sedimentary rocks.

5. Furniture: The basic characteristics of stone furniture are more or less the same as those of sanitary ware except two aspects. First, the former are not subjected to frequent wetting, and therefore, low water absorption and porosity are not of any particular significance. Second, the pieces of furniture in residential or other buildings are exposed to public, and therefore, they must have strong aesthetic appeal with pleasing colours, and high degree of polish. The ability to take polish being dependent on a fine-grained, compact and homogeneous texture, usually the same kind of stones find use in manufacture of furniture as those in sanitary ware.

6. Petty decorative and consumer items: Articles like ash tray, paper weight etc. are generally made by cutting small leftover pieces in stone processing plants in desired shapes and polishing them. Obviously, there is no specification for such stone pieces, the products being conceived according to the availability of raw materials and not the other way round . Use of these products depend practically cent per cent on consumer tastes and sales promotion measures. However, for making writing slates, black colour and a good even cleavage of the stone (slate) are valued most while for making switch boards, the stone should be a nonconductor of electricity.

7. Metrological reference objects: These are very low-bulk high-value products. The very utility of these objects requires that their shape and size must not undergo the slightest deformation due to day-to-day handling, fluctuations of humidity and temperature, and action of chemicals. So, low water absorption, low porosity and low coefficient of thermal expansion are necessary specifications for the stone, and also the stone should be devoid of calcite and pyrite grains which are chemically unstable.

Further, these objects must have perfectly smooth, regular and geometrically plane surfaces. So, the stone must be able to take a very smooth cut and a very high degree of polish, and for this, it should be fine-grained , compact and homogeneous.

The objects like cubes require that there must not be any cleavage within, so that the perfectly equal dimensions of the sides do not remain prone to getting disturbed. Again, the planes of a prism are at slanting angles. All such conditions require that the crude blocks of stone must be in massive form so that it is possible to cut them in any direction in a perfectly regulated manner.

Another special criterion is that manufacture of such objects needs a very high degree of skill and workmanship.

Marble, slate and sandstone are automatically precluded from use for making this type of objects. Only rocks of commercial granite family, particularly dolerite and gabbro, and massive quartzite can fulfil the necessary specifications.

8. Ashlars: These are roughly cut rectangular blocks having plane surfaces. They are neither accurately sized nor polished. These can be laid on pavements, and also can be used in fencings. The very nature of the use demands low quality, easily and locally available and inexpensive blocks of rock. There is no specification as such, except that the rocks should be fairly hard, available in fairly large-sized pieces and should be relatively inexpensive. Often, defective or substandard blocks produced during mining and processing of superior grade dimension stones for engineering construction, architectural work, etc., are used as ashlars.

SUBSTITUTION

Depending upon the purpose, some synthetic materials sometimes may be used as a substitute of natural dimension stones. The common substitutes are:

1. Cultured marble
2. Synthetic marble
3. Marble casting
4. Cement concrete
5. Ceramic material
6. Fiber glass

Scope of substitution of these materials is discussed as follows.

1. Cultured marble: This is the popular name for *polymer concrete* or *synthetic resin concrete*. Its essential components are:

(a) Rock dust (less than 0.1 mm particles of quartz, marble, chalk, limestone, slag, light expanded clay, etc. that serve as filler)
(b) Sand (0.1-2.0 mm size)
(c) Gravels (2.0-7.0 mm size)
(d) Synthetic resin (polyester, epoxy, polyurethane, phenol, etc.)
(e) Colouring agents.

The ratio of the different components vary depending upon the use. For rough use, as in the case of window sills and frames, basins, shelves, etc., both the resin content and the rock dust content may be low, varying from 9-12% and 10-17%, respectively, while the sand and gravel contents are high. For decorative use, as in the case of tombstone, monuments, etc.,contents of both resin and rock dust are relatively high, varying from 13-17% and 10-35% , respectively, while the sand and gravel contents are less.

Cultured marble products are characterized by the following properties:

i. Compressive strength 9956-21335 psi (cf., natural marble 8000-27000 psi)
ii. Rupture modulus 2560-4978 psi (cf., natural marble 600-4000 psi)
iii. Water absorption 0.05% (cf., natural marble 0.02-0.45)
iv. Thermal conductivity 0.002-0.006 cal.cm/sec/cm^2/^{0}C (cf., natural marble 0.005-0.006 cal.cm/sec/cm^2/^{0}C)
v. Density 87-150 lbs/ft^3 (cf., natural marble 165-179 lbs/ft^3)
vi. Young's modulus 2.84 X 10^6-4.98 X 10^6 psi (cf., natural marble 5 X 10^6-11.6 X 10^6 psi)
vii. Vibration absorption high — about 6 times more than that of steel
viii. Thermal stability of shape good
ix. Innumerable possibilities of colour
x. Resistance to chemicals like HCl, H_2SO_4, seawater, etc. (depending on the type of resin)
xi. Short curing time
xii. Excellent surface quality
xiii. Good electrical insulation

Functionally, cultured marble competes well with natural marble with respect to some of the physic-mechanical properties. Also, due to lower density, cultured marble is easier to transport, store and handle. Further, by selecting a suitable mould, cultured marble can be cast into any shape or size. But so far as psychological factors are concerned, it may not always be able to outweigh natural stones.

2. Synthetic marble: Synthetic marble is a strong, homogeneous, dense, translucent product which can be cast into different shapes and sizes. It finds use in bathrooms and as structural components. It is made by casting and heat-curing (in presence of a catalyst) a finely ground mixture of alumina and resin matrix with some filler material. The filler constitutes 50-85% of the weight of the mixture and includes calcite, silica, oxides of antimony and titanium and talc. Silica used is in the form of silica flour, onyx flour, glass flour, glass frit. The refractive index of the mixture vis-à-vis the resin matrix is so manipulated as to give an illusion of depth.

3. Marble casting: Marble is first crushed, mixed with some polymer binder and the mix is poured into the desired mould to give it the required shape. Such marble castings are used for making handicrafts.

4. Cement concrete: Conventional cement concrete is made up mainly of cement, water and aggregates. Its main advantage lies in economy. However, its strength and frost resistance are low compared to natural stones. Cement concrete is the most widely used material in engineering construction.

5. Ceramic material: It can substitute natural stone in some of the architectural works like flooring and wall tiles, ceilings, etc. However, its main disadvantage lies in low compressive strength and low impact toughness. Consequently, it is prone to cracking and breaking. Another disadvantage is that manufacturing of ceramic products is highly energy-intensive.

6. Fiber glass: There has been some reports of using fiber glass in tombstones. Its main advantage lies in its light weight and the ease with which it can be fabricated. However, it has low impact toughness and consequently, it may be prone to crack.

Chapter 51

CRUSHED STONE

Stone-crushing for construction purpose is one of the oldest activities that people have been engaged in. It is widely believed that crushed stone together with sand has turned out to be the second substance most widely consumed by man after water. According to the National Stone Association, USA crushed stone is that stone which is produced by mining big pieces of rock and then reducing them to a desired size, usually less than 2 inches, and which is, then, used for a wide variety of purposes. Stones for the purpose of crushing, eventually for some industrial use in the form of crushed stone, may be mined as such or obtained as rejects during mining and processing of dimension stones. In the former case, the rock bodies may be jointed, brecciated or discoloured. In the latter case, the rejects may be generated at different points by different modes as follows:

(a) Mine sites
(b) Processing plants

- due to damage of the raw blocks during transportation from mine to plant
- due to cutting, trimming, etc. of the blocks
- due to defects coming to light during post-processing checks

(b) Ports
- due to damage of the processed blocks during transportation from plant to port

The stones are either manually crushed with the help of hammer or mechanically crushed (and, sometimes, ground as per requirement) with the help of stone-crushers.

USES AND SPECIFICATIONS

1. Road metals: These are the broken pieces of rock used in the construction of roads. All rocks are not equally suitable. The medium- to fine-grained compact basic igneous rocks like dolerite, basalt, etc. are considered to be the best. They can withstand heavy traffic and the powders from their wear and tear get mixed with tar, produce a tough, yet smooth surface and add to the effectivity of the tar. Quartzite, on the other hand, though hard, produces sharp edges which stand out on the surface and tend to damage the tyres of vehicles. Limestone pieces, though soft, may be suitable because of their natural cementing tendency; but dolomite tends to generate lots of dust causing traffic nuisance. Coarse-grained acid rocks like granite are not generally preferred because of the tendency of the cleavages of their constituent mineral grains to open up with changes in temperature. However, pieces of such rocks may be used in auxiliary roads inside the premises of mines, factories, offices, etc.

2. Railway ballasts: Pieces of hard and durable rocks can be used as ballasts in railway tracks. Very hard pieces of quartzite with sharp edges can also be used, because, unlike road metals, these are not required to bear traffic loads.

3. Ship's ballasts: After unloading cargo, ships have sometimes to come back empty, and for maintaining them on even keel, they are filled up with some quantities of ballast. Since these ballasts are subjected to a continuously high degree of attrition, pieces of only very hard rocks like quartzite are best suited.

4. Rip-rap: These are irregularly-shaped large pieces of stone that are used for facing in bridge abutments, river banks, sea shores and also for laying in heaps around foundations, walls, etc.

5. Slate granules: Slate granules are generally marketed in 14-48 mesh size range. These are sometimes mixed with asphalt for coating the roofs. The angular granules of slate facilitate bondage with surrounding asphalt matrix, and these also improve the weather- and fire-resistance of the roof. Moreover, the different colours of natural slate such as grey, green, purple, etc. can be made use of to render pleasing appearance to a roof.

6. Slate powder: This is generally marketed in 250-300 mesh size range and also in micronized (dry-ground to 20 micron size) form. This is used as a filler in the following products:

(a) Acid-resistant bitumen and asphalt for use on roads
(b) Paints and varnishes (slate is inert and has low oil absorption)
(c) Carrier of insecticide (slightly abrasive surfaces of slate particles are supposed to ensure better contact with hard-skinned insects, thus increasing the effectivity of the insecticide)
(d) Carrier of fertilizer
(e) Plastics
(f) Rubber
(g) Acid-resistant sealants and adhesives (slate powder is softer than limestone and harder than clay — both of which are also used as fillers — and, consequently, it helps to adjust the elasticity of the polymer used as sealant/adhesive)
(h) Gramophone records
(i) Electrical insulation
(j) Grease

Slate powder mixed with lime, can also be used for manufacturing sand-lime bricks and acoustic tiles. Further it is used as one of the constituents of earthenware tiles based on ball clay.

7. Carbonaceous slate pieces: When heated to 1500^0C, such pieces show a tendency to form a light porous product due to burning of carbon and escape of the gases. This product may sometimes find use as a light-weight filler in concrete.

8. Marble flour: Marble flour can be used as a whiting substance and as a constituent of feed stock for fertilizer. Research has also suggested its potentiality for use in road construction, in cement making, as catalyst for SO_x removal, as de-icing agent ($CaCO_3$ reacts with water to form $Ca(OH)_2$ with release of heat), for amending acidic soil and as low-cost binding material.

9. Terrazzo and conglomerate marble: Marble chips can be used as *terrazzo* chips. Terrazzo is a kind of flooring made of marble chips set irregularly in cement and polished. They can also be used for lime-burning and for the manufacture of resin-bound *conglomerate marble*.

10. Compound or agglomerated stone: Chips of marble, granite, quartzite, basal,t etc. are mixed with liquid polymers, white or grey cement, silica sand, quartz, calcareous silicate and a little water just enough to hydrate the cement. The mixture is then compacted in vacuum. Absence of air precludes presence of any micro- or macro-pores and ensures perfect compaction. This product, called compact or *agglomerated stone*, is relatively cheap and is suitable for flooring, for decorative tops of furniture, for kitchen platforms, for bar counters ,etc. It has pleasing colour and fabric.

11. Marble dust/slurry tiles, bricks and panels: Various types of tiles, bricks and panels have been made using marble dust and slurry. These are:

(a) Tiles and door panels made with marble dust (up to 50%) and jute fiber bound with resin or cement. In some products, as high as 90% resin has been used.
(b) Building bricks have been developed using marble slurry.
(c) Fired tiles incorporating marble slurry/dust.
(d) Mosaic tiles made using marble dust.

12. Concrete aggregates and bricks: Aggregates consist of a mixture of stone chips, sand, cement and water. Certain other materials like granulated slag, fly ash, clay and dust may also be added. The size should be between 12.5 mm and 300 micron, with about 40% of the material in the range 4.75-10 mm. Mixing of these materials is generally done in concrete mixers to achieve uniformity in colour and consistency. Thus mixed concrete aggregates can be used either as such for casting roofs, pillars, beams, etc. of buildings or for making hollow and solid bricks for use in brick masonry in replacement of traditional clay bricks. For making concrete bricks, the concrete aggregates are pressed in moulds, cured with water for 70-80 hours and steam-dried. So far as the stone chips are concerned, igneous rocks like basalt, diorite, etc. are preferred.

13. Granite sand: Granite sand is a new material that has the potentiality to replace river sand for building purposes, especially in situations where river sand is in short supply or is highly expensive. According to a report of 2005, its production has been planned in Kerala, India.

SUBSTITUTION

1. Florolite: A synthetic product trade named *florolite* was developed by a firm in Louisiana state, USA in 1990 as a road-base material, and it has been used in construction of roads in the that state. It is manufactured from calcium sulphate. However it suffers from the disadvantage that it cannot be used in conditions where the road is in continuous contact with water.

2. Blast furnace slag: Blast furnace slag consisting principally of lime, silica and alumina was earlier considered as a waste material. But since around 1910-1915, it is being considered as a byproduct of pig iron manufacturing due to development of some major commercial usage. One of its uses is as a substitute of crushed stone.

The hot slag can be processed in three ways, and depending on how it is processed, it finds specific applications as follows.

(a) It can be air cooled gradually and crushed. Such crushed slag is used in concrete aggregates, road metals and railway ballasts.

(b) It can be converted to *granulated slag* by introducing perlite grains during cooling, to act as nuclei around which the molten slag coagulates in the form of granules. Granulated slag does not require further crushing. It finds use as road-fill (and also hydraulic cement manufacturing albeit not as a substitute of crushed stone).

(c) By applying controlled quantities of water and regulating the rate of cooling, it can be made into a foamed expanded cellular mass. After crushing this cellular slag, it is used as a component of lightweight concrete bricks.

Chapter 52

ROCKS - OTHER USES

Physical form of certain rocks, either natural or modified by physical operations like cutting, crushing, is the primary criterion for dimension stones and crushed stones. But there are certain rocks which possesses values mainly by virtue of their chemical composition. These uses are discussed as follows.

1. DUNITE

The name dunite has come from Dun mountains of New Zealand. It is a mono-mineral ultrabasic igneous rock made up entirely of olivine ($Mg_2Fe_2SiO_4$). Sometimes it may also contain serpentine ($H_4Mg_3Si_2O_9$), which is the partial alteration product of olivine. In some vein deposits, magnesite was formed due to complete alteration of the olivine/serpentine of dunite. In such deposits, dunite constitutes the host rock of magnesite (e.g., Chalk Hills of Salem area, Tamil Nadu and of Dodhkanya of Karnataka in India), and it is generated as waste after mining and sorting of magnesite.

Now, dunite is high in magnesia, typically containing 30-45% MgO. Its present and potential uses are as follows.

1. ***Metallurgical flux:*** Suitability as a fluxing material in pig iron manufacturing is being seriously explored, and some dunite can reportedly be incorporated as a component in the sinter feed for pig iron metallurgy through blast furnace (see the chapter on dolomite). But when the iron ore is high in alumina, as is the case in India, alumina content in the dunite should be low. In India some pig iron plants are using it as a partial substitute of dolomite. Its role is as follows.

   (a) By virtue of the MgO-content which is basic, it increases the basicity and hence fluidity of the slag. A fluid slag is desirable for efficient removal of sulphur and phosphorus and also for making it easy to pour out.
   (b) By virtue of the basic MgO and the basicity of the slag, it extends the life of the basic refractory lining of the furnace. For this reason, around 8% MgO in the slag is considered desirable in a blast furnace.

2. ***Refractories:*** Refractory materials are defined as those resistant to heat and having a melting temperature of not less than 1580^0 C. The function of refractory lining on a furnace wall is not only to withstand high temperature, but also to withstand temperature fluctuation, and to resist penetration, abrasion, and erosion by hot gases and molten materials in the furnace, and over and above, it should not chemically react with those materials. Dunite finds use in a type of refractory called *forsterite refractory bricks*. The composition of forsterite is $2MgO.SiO_2$. Such bricks are suited to application as refractory bricks in the roofs of copper-smelting furnaces. Forsterite is generally made by firing a mixture of talc ($3MgO.4SiO_2.H_2O$) and magnesite ($MgCO_3$) to temperatures of $1400\text{-}1500^0$C. They react to form forsterite as follows:

   $$3MgO.4SiO_2.H_2O + 5MgCO_3 \rightarrow 4(2MgO.SiO_2) + H_2O + 5CO_2$$

   Dunite can be used as a substitute of talc in this process. But because of its Fe-content a mixture of forsterite and fayalite (Fe_2SiO_4) is formed.

   In USA, dunite has been used, to a limited extent, in refractories.

3. ***Soil conditioning:*** Ground dunite is suitable for application to acidic soil by virtue of its basicity. It also improves porosity of the soil. Besides, it is a source of magnesium which is an essential element in the chlorophyll ($C_{55}H_{70}MgN_4O_{5\text{-}6}$) of the plants. But, for this purpose, silica is considered deleterious because it increases the grinding cost. Since the silica content in dunite may be as high as 40%, it is not a popular material unless dolomite is scarce and dunite is freely available locally.

In India, 168,121 tons of dunite was produced in the year ending March 2001, which has decreased to 37,314 tons in the year ending March 2006. The production is mainly for use as flux.

2. PYROXENITE

Pyroxenite is an ultrabasic rock of the gabbro family in which there is a concentration of the mineral pyroxene [generally $(Ca,Mg)SiO_3$, but variations containing aluminium, ferric iron or manganese are not uncommon]. The calcium and magnesium contents make it comparable to dolomite in the latter's use as a flux in iron/steel metallurgy and pyroxenite can substitute dolomite. Limestone ($CaCO_3$) is the principal flux and the CaO of pyroxenite will supplement this. In addition, its MgO, by virtue of its basicity, will perform the same functions as dunite (see above) or serpentinite (see below).

3. SERPENTINITE

Serpentinite or serpentine rock is an ultrabasic igneous rock containing not less than 10% of serpentine ($H_4Mg_3Si_2O_9$) which forms by partial alteration of olivine. In some places (e.g., California in USA) the serpentine content may be as high as 90 per cent. Serpentine contains

43% MgO, but the rock may contain less MgO depending on the percentage of serpentine in it. Its uses are as follows.

1. ***Flux:*** Like dunite, serpentinite also contains MgO and its content may be high in some cases. It can, therefore, be used as a metallurgical flux in the same way as dunite elaborated above.

2. ***Refractories:*** Like dunite (see above), serpentinite can also be used as a substitute of talc in the manufacture of forsterite refractory brick. The advantage of serpentinite containing high MgO-content over dunite is that the former does not contain iron and pure forsterite formed.

3. *Carbon sequestration:* CO_2 emitted by burning of coal is a major source of air pollution, and is the single most responsible agent for global warming or (as it is called nowadays) the '*greenhouse effect*'. There are five greenhouse gases (or GHG), the emission of which is believed to be responsible for the greenhouse effect. These gases are: CO_2, NO_2, methane, CFC (chloro-fluoro-carbon), and water vapour. Out of these, CO_2 is the most widely produced gas directly related to burning of coal. It absorbs infrared coming from the sun, but does not allow it to go back to space; and an increased density of CO_2 in air causes increase in the temperature of the earth.

   This CO_2 is nowadays being regarded as an economic commodity. Its potential use is in food processing, fish farms, agricultural greenhouses, conversion to fuels, manufacture of stable products such as carbonate minerals and secondary recovery of petroleum. Scientists are therefore trying to develop what is called '*carbon sequestration*' technologies to capture CO_2 from industrial emission streams and to store it for future use. Methods currently used for CO_2 separation include physical and chemical solvents (e.g., mono-ethalo-amine or MEA), various types of membranes, absorption onto zeolites and other solids and cryogenic separation. But it is equally important to store the captured CO_2 for which one of options being investigated is *mineral storage* or *mineral sequestration* (also referred to as *mineral carbonation*). Mineral storage is the process whereby CO_2 is reacted with naturally occurring substances to create a product chemically equivalent to naturally occurring carbonate minerals. It is for this purpose that serpentinite is investigated as a possible mineral feedstock.

   After mining, crushing and cleaning, the serpentinite has to be activated via a chemical or thermal treatment. It is then reacted in an aqueous CO_2 solution under high pressure to produce carbonate mineral plus sand in the form of finely precipitated solids, which are separated from the liquid and sent to the final disposal area. Laboratory tests have shown that mineral carbonates can be formed rapidly, in time periods of about one hour. However, this requires intensive thermal pre-treatment of the feedstock and subsequent carbonation at elevated pressures and temperatures. However, this would be cost-intensive. Also, the huge amount of materials handling that would be necessary to transport the silicates and dispose the carbonate would pose another major challenge to be resolved.

4. PERIDOTITE

The two minerals pyroxene [Ca,Mg)SiO_3] and olivine ($Mg_2Fe_2SiO_4$) constitute the rock peridotite (cf., in dunite, dominance of olivine and in pyroxenite, dominance of pyroxene). It can be used as a flux in the same way as dunite or pyroxenite (see above). Besides, like serpentinite (see above), its suitability for use as a mineral feedstock for carbon storage is under investigation.

5. BASALT

The name basalt has come from an Ethiopian word, which, in its turn, had come from the Greek name “basanite” meaning “from Basan” (Basan refers to the name of a town in Syria). Basalt is an igneous rock containing equal proportions of plagioclase feldspar and the group of mafic minerals augite, olivine and iron oxides.

Basalt can be used for making *rock wool* which is a type of *mineral wool*. Mineral wool is a general term meaning fibers made from inorganic substances that may include minerals, rocks and metal oxides — synthetic or natural. When the substance is a natural mineral or rock it is called *rock wool* or *stone wool*. Basalt wool consists in very thin glassy strings arranged into a spongy texture. For manufacturing basalt wool, basalt is first melted at 1000-1400^{0}C and then the molten basalt is drawn into long strings. These strings are cemented into a *fiber mat* with the help of some resin binder (e.g., phenol formaldehyde). In this wool, the individual strings are not more than 20 microns in diameter and not less than 50 cm in length. For efficiency of the process, basalt should melt to a easy-flowing homogeneous liquid with low viscosity.

Regarding specification of basalt for this use, it is stipulated in terms of interstitial glassy matter, percentages of SiO_2, FeO and Fe_2O_3. and the *modulus of acidity*. The basalt should contain less than 30% interstitial glass because it creates problems in ensuring homogeneity of the melt. SiO_2 tends to increase acidity and its content should not exceed 45 per cent (normally, basalt is basic and molten basalt is easy-flowing liquid due to this basicity). The total iron oxides (FeO + Fe_2O_3) should not exceed 13% because molten iron oxide is a heavy viscous liquid and will tend to make the drawing of strings difficult. Modulus of acidity is expressed as

$$Ma = (SiO_2 + Al_2O_3)/(CaO + MgO)$$

This value for the basalt meant for making rock wool should not exceed 2.5, because higher acidity will make the melt more viscous and difficult to be drawn into strings.

Basalt wool is a light weight, corrosion free, waterproof absorbent material capable of absorbing sound and heat. It can be used for heat and sound insulation, in brake pads, in gaskets and in fireproofing systems. Because it can retain water, it can also be used in hydroponics (growing plants on only water and without soil). Basalt is used in this way in Czechoslovakia.

6. DIABASE

Diabase is an ultrabasic rock formed by alteration of dolerite. In it, the plagioclase is altered to carbonates, albite, epidote etc.; pyroxene to chlorite or hornblende; olivine to serpentine and ilmenite to leucoxene. Diabase is a product of low-grade metamorphism. It can be used for making *rock wool* in the same way as basalt.

7. AMPHIBOLITE

Amphibolite is a hornblendic rock formed due to a high degree of dynamo-thermal metamorphism. It can be used for making *rock wool* in the same way as basalt.

8. NEPHELINE SYENITE

The term syenite has come from “Syene”, a place in Upper Egypt and nepheline has been derived from the Greek word “nephele” meaning “cloud” referring to the cloudy appearance of the mineral. Syenite is an igneous rock with a predominance of alkali feldspar and in nepheline syenite the feldspar is associated with nepheline (approximate composition $Na_8K_2Al_8Si_9O_{34}$). Nepheline is generally a colourless to white mineral (variations with green, reddish brown, etc. colours are also sometimes found) with greasy and vitreous lustre.

Its main industrial use is in ceramic glazing. The purpose of glazing is to provide a uniform firmly adhering coating on the surface of the ceramic body concealing defects such as pinholes, bubbles, etc. A glaze should have more or less the same coefficient of expansion as the ceramic body. If the expansion is higher then *crazing* will take place (i.e., cracks will develop) on the glazed surface, and if lower, then peeling of chips will take place. Glaze should not only melt but also spread uniformly.

Glaze may be “*raw glaze*” or “*fritted glaze*”. Raw glaze consists of insoluble material applied as such (soluble components crystallize in the mixture and cause blemishes on the treated surface), while fritted glaze is heated beforehand to cause chemical change in the components. The glaze is made of the same ingredients as the ceramic product being glazed, but with predominance of quartz and feldspar. The ingredients are mixed, finely ground and mixed with water, and this mixture is the glaze. The moulded raw body of the product is dipped into the glaze and then fired to a higher temperature of about 1400^0 C. Colours and decorative designing, if required, are painted after glazing and before firing.

Nepheline syenite is added to both the types of glaze mixture as a source of feldspar, soda, potash, alumina and silica. Its cloudy white colour goes well with the glaze. The soda is a flux and it reduces the melting point and viscosity of the molten mixture; potash has higher expansion than soda and thus tends to balance the coefficient of expansion. As such, alumina has a high melting point, but at even below the firing temperature (1300^0 C) it melts imperfectly to become a highly viscous fluid, facilitating a coherently bonded non-porous product.

9. PUMICE AND OTHER VOLCANIC EJECTS

These ejects are produced when the volcanic lava mixed with violently escaping gases form a kind of frothy materials in molten state. Due to the escaping gases these ejects, when solidified, contain vesicles and become porous rocks with foam-like texture. Such a rock, in Japan, is called *Shirasu* and fine foamed particles obtained by crushing and grinding it are called *Shirasu balloon*. The Japanese Shirasu generally contains 65-73% SiO_2, 12-16% Al_2O_3, 1-3% Fe_2O_3, 2-4% CaO, 3-4% Na_2O, 2-4% K_2O, 0.2-0.7% TiO_2 and 0.4-1.0% MgO. Thus it is a predominantly siliceous and porous, but not permeable, rock with a foam-like texture, and also it is lightweight with air trapped in its pores and with low water absorption . By virtue of these, Shirasu has excellent heat insulating and fireproofing abilities. At the same time, it is a low-cost material, being freely available around volcanoes, and is emerging as a new industrial material.

Shirasu balloon finds industrial applications in construction, agriculture and pottery. Its principal uses are as an additive to concrete aggregate for weight reduction, in top-coating mortar and plaster for heat insulation and fireproofing, as sprayed coating material for the same purpose, as soil modifier and seedbed material for providing the plant nutrients calcium, potassium and magnesium, and lightweight pottery.

PART III:
FRESHWATER

Chapter 53

GROUNDWATER AND SURFACE FRESHWATER

Water may not be a mineral according to the conventional definition of a mineral, but according to the laws of various countries, groundwater is a mineral just as oil and gas are. The Supreme Court of India in a judgement in 1996 has held: “Mineral means all substances which can be obtained from the earth by mining, digging, drilling, dredging, hydraulicking, quarrying or by any other operation.” In fact, groundwater is exploited everywhere by either digging wells or drilling bore-wells (similar to oil and gas exploitation). And as for its economic importance, it is beyond any question, be it human and animal drink, be it industry, be it agriculture, water is essential for survival of life and for the survival of all land creatures including man. Freshwater has no substitute. Many old civilizations flourished near water sources and many died after their drying up. The importance of water as such was reiterated by the United Nations Organization (UNO) in 1993 when it declared March 22 each year as the *World Water Day*, and the year 2004 was observed as the *International Year of Freshwater*. It is being said that wars will be fought in future over water in spite of the fact that the over 260 water basins of world transcending across national borders are covered by more than 3800 unilateral, bilateral and multilateral conventions and treaties.

RELATIONSHIP BETWEEN GROUND AND SURFACE WATERS

Hydrologically, the dividing line between groundwater and surface water is not clear, and is marked by constant interaction between the two. Such interactions take place by two-way subsurface lateral flow of water through unsaturated soil and underground fractures and solution channels. The flow takes by one or more of four mechanisms:

i. Translatory flow or plug flow or piston flow: This flow is engendered by lateral flow at the bottom of a water column when more water is added at the top. The head tends to remain constant as long as surrounding conditions allow.
ii. Macro-pore flow: This is fast flow through soil pores too large for capillary action to come into play.
iii. Groundwater ridging: This flow is due to increase in hydraulic gradient towards rivers by a rapid increase of the hydraulic head in relation to the river water level.

iv. Return flow: This is the discharge of subsurface water to the surface when the water table and capillary fringe are close to the surface and only a small amount of rainwater is enough to saturate the soil above the water table.

Because of the close interactions between groundwater and surface water, there is a transition zone called *hydrorheic zone*, which is nowadays receiving attention of hydrologists, ecologists, environment scientists and regulators. This zone is the one where mixing of the two takes place and has a profound bearing on the quality of the surface water because migration of contaminants (metals, micro-organisms, etc.) from the groundwater to the surface water takes place constantly. There is an increasing trend not to treat the two as separate environmental entities and instead treat them as one single system.

But the approach of the mineral economists is different. From the economic point of view, the differences between the two are as follows.

(1) Unlike surface water, groundwater is an invisible resource just as a mineral deposit is.
(2) Within a confined reservoir, the groundwater resource is a depleting asset like any other mineral deposit in the short run. In the long run, however, due to continual recharge taking place, the resource is renewable.
(3) While surface water is all the time flowing and migrating towards the seawater (save the water of the lakes), groundwater does not flow out of the reservoir.
(4) Because of this invisibility, sophisticated exploration techniques are required for assessing the potentials of the groundwater resources.
(5) While the methods of exploitation of surface water are non-invasive, groundwater cannot be exploited without digging or boring. Consequently, the cost of using the former is much cheaper than the latter.
(6) Groundwater is finding increasing use because of advantages of location and accessibility. Surface water sources and flows are confined by ground topography to specific locations and channels not accessible to one and all.
(7) Unlike groundwater, surface water is vulnerable to man-induced external pollution.
(8) Also, there is a difference between the two respect to international disputes. Both rivers and groundwater reservoirs transcend across international boundaries, but in the case of the former, the water availability is always a bone of contention between the concerned countries, and that is why there are so many international treaties and conventions (e.g., Indus Water Treaty between India and Pakistan). Although, groundwater tables are sensitive to drawal, both directly and indirectly through the river water exploitation, so far there is no apparent dispute amongst the states sharing the same reservoir (*groundwater table* or *hydrostatic level* is the upper surface of the zone of complete saturation of the reservoir rock). Somewhat similar is the situation within India in respect to rivers flowing across interstate boundaries.

RESOURCES

The total volume of water in the hydrosphere of the earth has been estimated to be 1.35 X 10^{18} kilolitres. This resource is constant with no addition or depletion (what takes place is only shifting of resource from one zone to another). Of the total resource, 97.21% is saline water in oceans and lakes, 2.15% is ice in icecaps and glaciers, 0.5% is freshwater comprising the surface water of the lakes and streams and groundwater and the balance 0.14% is comprised of soil moisture and atmospheric moisture (at sea level). If all the water on earth were to fit into a one-litre bottle, about one teaspoon is all the freshwater available for use.

Of the total freshwater resource, groundwater accounts for about 96.8% which works out to a total of about 8334 trillion kilolitres. Of this groundwater resource, only about half, i.e., about 4167 trillion kilolitres occur within a depth of 800m and major part of it is not usable because of pollution and prohibitive cost of exploitation. This groundwater resource represents the accumulation in the sediment interstices of porous and permeable rocks like sandstone and in fracture zones of other kinds of rocks (called *aquifers),* of millions of years of recharge tickling down through soil-pores from the overlying ecosystem.

In India, the total surface freshwater resource was estimated in 1994 at 1780 billion kilolitres out of which 310 billion kilolitres or only 17% was utilizable. In contrast the groundwater resource was 600 billion kilolitres out of which usable portion was less than 260 billion kilolitres or 43% could be utilized. Up to 40% of the water demand in urban areas and up to 80% in the rural areas is met through groundwater withdrawal.

PARAMETERS OF QUALITY AND USE

(1) ***pH value****:* It is the short form of “potential of hydrogen”. It is the negative logarithm of the effective hydrogen-ion concentration or hydrogen ion activity in gram equivalent per litre. It is used in expressing both acidity and alkalinity on a scale whose values run from 0 to14 with 7 representing neutrality. Numbers less than 7 indicate increasing acidity and those greater than 7 increasing alkalinity. Both very strong acidity and very strong alkalinity corrode the plumbing components in the water transportation system and hence this value should be within limits when the water is to be transported through pipe lines. Generally, it should be between 6.5 and 8.5 if the plumbing components are made of brass or copper, and between 2.5 and 8.5 if they are made of stainless steel or plastic.

(2) ***Hardness/softness****:* Hardness of water is caused by the presence of the insoluble carbonates and sulphates of calcium and magnesium, which tend to precipitate in the form of scales when the water is boiled. Roughly, it can be measured in terms of the content of these salts as:

Soft	0-20 mg/litre
Moderately soft	20-40 mg/litre
Slightly hard	40-60 mg/litre
Moderately hard	60-80 mg/litre
Hard	80-120 mg/litre
Very hard	> 120 mg/litre

But for a precise quantification of the hardness, *Langelier Saturation (or Stability) Index* or LSI values are calculated. With the help of LSI value of a water it can be predicted whether it will precipitate or dissolve or be in equilibrium with $CaCO_3$ which is then converted to a scale of hardness. In this, the pH of a water sample saturated with $CaCO_3$ is pre-calculated as a reference (pH_s) and then the pH of the test water (pH_w). LSI is the difference ($pH_w - pH_s$). LSI value of '0' means equilibrium, a negative value means no scaling potential (soft water) and a positive value means high scaling potential (hard water).

Hard water can be softened by treating it with a softener like zeolite or ion-exchange resins. The former has micro-pores which allow water to get inside but excludes the salts (see chapter on zeolite) while the latter contains sodium ions which exchange place with calcium and magnesium ions of their carbonates and sulphates to form soluble Na_2CO_3 and Na_2SO_4.

(3) *Microbial contaminants*: The most common microbes in water are the heterotrophs which include the bacteria that get their nourishment from the carbon and nitrogen of organic compounds. *Heterotrophic Plate Count (HPC)* is a microbial contaminant indicator — a measure of the total number of bacteria that will form colonies during a period of incubation in a nutrient. Its unit is cfu/ml , (i.e., colony-forming units per milliliter).

(4) *Chemical contaminants:* Some of these are considered harmful and some others desirable.

(a) Desirable chemicals: These are the disinfectants which kill the bacteria of water. These are sometimes present in water naturally. If not, they may have to be added. The naturally present disinfectants are chloramines, chlorine and ClO_2.
(b) Harmful chemicals: These are organic carbons and some inorganic elements and compounds like arsenic, fluoride, lead, mercury, etc.

The maximum limits of these chemicals are generally expressed as *maximum contaminant level (MCL).*

USES AND SPECIFICATIONS

Although, groundwater and surface freshwater can be used interchangeably depending on the accessibility and cost of collection, the dependence on groundwater is, nowadays, increasing continuously at an alarming rate because of progressive deterioration of quality mainly due to man-induced pollution triggered by increasing discharge of wastes associated with increasing industrialization. In 1985, it was roughly estimated that 70% of the surface water resource of the world was already unfit for use. The United Nations Human Development Report for 2006 has said that by 2025, if current global water consumption continues, more than three billion of the word's 7.9 billion people will be living in areas where water is scarce. And the United Nations Population Fund, in 2003, has predicted that the world will begin to run out of water in 2050.

It is true that groundwater is recharged continuously from portions of rains, snowfalls and used water, but apprehensions are also intensifying continuously that, due to mismatches between the rates of exploitation and recharge and due also to man-induced pollution as well as some natural factors, its availability is fast reaching a critical state.

The broad categories of the large scale utilities of freshwater are as follows.

1. Agriculture: According to a United Nations study of 1999, worldwide the agricultural activity consumes 65% of the total anthropogenic water withdrawals. In many countries, groundwater accounts for a substantial portion of this water consumption. According to another estimation, 48-50% of irrigated land is irrigated from groundwater. But this usage is technology-sensitive. For example drip-irrigation technique popularized by Israel and now practised in many countries including India requires substantially less water without affecting the productivity.

2. Industry: Of the total anthropogenic water withdrawal, 24% goes for industrial consumption. Daily water requirement for different industries is: production of one brick 0.5 litres; tanning one kg of raw hide 25 litres; making one kilogramme handmade paper 54 litres; dyeing one kg cloth 80 litres and dairy farming a cow 150 litres.

Now, in any large new industrial venture like steel and thermal power in India, water is fast becoming the third issue after land acquisition and mineral linkages. For such industries, groundwater is not feasible and river/reservoir water is the only option. But, many river-flows in India are committed to serve purposes of agriculture, drinking and only the balance is available for industries. And many rivers in India being extremely sensitive to the unpredictability of Monsoon rainfall, the water availability for the industries becomes very often tight. In order to optimize the consumption of water, recycling of the used water after treatment has become an established practice in many modern industries.

Hard water is highly harmful for industries, because it will tend to deposit scales of lime and magnesia on boiler pipes and machinery parts. Since large quantities of water are used continuously, the scale deposition will also become very large resulting in breakdowns and loss of productivity.

3. Potable water: Potable water is defined in a generalized way as the water that is not having impurities in amounts sufficient to cause disease, is safe for both humans and animals to drink and is not containing salts in excessive quantities so as to be called mineral water. Obviously, this definition will vary with locality and will depend on the intrinsic immunity of the people of a locality. What is safe to drink for a villager in India may not be safe for a European.

Humans feel thirsty after loss of only 1% of body fluid and is in mortal danger near 10 percent. A person requires potable water of about 3-5 litres for drinking and 20 litres for cooking per day and there is no statistics for quantities that the animals drink, but like humans, most birds and animals also cannot live without water. Designs of wildlife and bird sanctuaries must necessarily incorporate provision of water.

Potable water supplied by municipalities is sourced to both surface freshwater and groundwater and is generally treated because of pollution. In case of groundwater, pollution takes place when metals and minerals from underground rocks and deposits migrate into it. In most cases their natural concentration remains minimal. But their concentrations become apparent and significant either when their rate of migration into the groundwater becomes far in excess of the rate of recharging. or when the rate of drawal is excessive compared to the natural rate of migration. Their higher concentration may also be due to human activities like mining, use of chemical fertilizers and pesticides in agriculture etc. Excess concentration of arsenic, fluoride, nitrates, and pesticides have been reported in India from the states of West Bengal, Orissa, Gujarat and some coastal areas. General standards of quality of potable water are:

i. pH: 2.5-3.0 and in any case less than 7.0 (i.e., acidic)
ii. Hardness/softness: neither too hard nor too soft
iii. Disinfectants:
    Chloramines 4 mg/litre (max)
    Cl 4 mg/litre (max)
    ClO_2 0.8 mg/litre (max)
iv. Heterotrophic plate count (HPC): Up to 500 cfu/ml, but preferably up to 100 cfu/ml
v. Total organic carbon (TOC): 0.05 mg/litre (max)
vi. Inorganic elements and compounds:
    As 0.05 mg/litre (max)
    Pb 0.015 mg/litre (max)
    Hg 0.002 mg/litre (max)
    Fluoride 2.0 mg/litre (max)

Low pH or high acidity indirectly serves to kill certain water bacteria because action of chlorine disinfectants is most effective at pH less than 7. If the pH of a water is higher, then it is purposely acidified. According to World Health Organization (WHO), there is no evidence that water hardness causes adverse effects on humans; but both very hard and very soft water will corrode water pipes and additional metallic impurities like cadmium, copper, lead and zinc will enter the water from the pipes. Some amounts of natural disinfectants in the water is obviously desirable for preventing bacteria growth, but too much of them will be harmful to even humans and animals and hence their upper limits. Organic compounds provide carbon and nitrogen for nourishment and colonization of the heterotrophic bacteria and hence are not desirable. The inorganic substances cause various diseases and deformities in both humans and animals. However, a little fluoride is beneficial for the bones and teeth and hence its maximum limit is considerably high compared to the other substances.

4. Mineral water: Mineral water is of two kinds — *natural mineral water* and *fortified mineral water*. Natural mineral waters are obtained from natural springs rich in certain elements and salts like calcium, iron, magnesium, sodium, boron, fluorine and Epsom salt (see chapter on magnesite) and also some gases which have medicinal values. In contrast, fortified mineral water is generally what is nowadays sold in the market as bottled water and it is made by first distilling/desalinating ordinary water and then adding certain nutrients. For therapeutic value, mineral water should contain at least 25 ppm of dissolved salts.

5. Household activities: Of the total anthropogenic water withdrawal, 24% is consumed by households and other municipal users. A person requires about 150-250 litres of water per day for different household chores other than drinking and cooking (includes 50 litres for bathing, 50 litres for personal hygiene and 40-60 litres for laundry). This consumption is being reduced in the advanced countries by virtue of use of dishwater (15 litres), washing machine (40 litres for 5 kg), etc. Potable water is not necessarily required for these purposes, but the water should not be hard, because hard water does not yield enough lather easily and considerably more quantities of it will have to be consumed. Soaps and detergents contain emulsion-forming fatty acids which are responsible for the lather. If hard water is used, $CaCO_3$/$MgCO_3$ reacts with the fatty acids to form an insoluble greasy scum on the soap surface and this is the reason behind poor lather formation. This scum is called *soap scum* or *soap curd*. Moreover, if machines are used then hard water will tend to deposit scales of lime and magnesia on the parts and damage them.

6. Support to ecosystem: While surface water is characterized by light, dissolved oxygen and temperature fluctuations; the features of groundwater environment are darkness, less oxygen, dissolved organic carbon along with other nutrients, and stable temperature. Some aquatic species need to take advantage of both the environments and they thrive in the hydrorheic zones. Some microbes live on the dissolved organic carbon and they provide food for grazers which in turn provide food for invertebrate predators. Thus equilibrium of the ecosystem is maintained.

7. Thermal service: In semiarid regions, the cooler groundwater comes up and discharges into the hotter surface water through the hydrorheic zone. In this way the impact of the heat on aquatic animals is mitigated.

SUBSTITUTION

1. Sea/brackish water: In order to make up for the deficiency in freshwater, *desalinated seawater* or brackish water is an important substitute of natural freshwater. Cost of inland transportation of desalinated water is high and, hence, it is most feasible for consumption in the coastal areas. Besides, they are common in military bases located in remote islands and aboard sea-going vessels. In India, the Bhabha Atomic Research Center (BARC) has been engaged in research on desalination (also called demineralization) technologies economically since the 1970s. In the designs of modern nuclear power plants in India, composite desalination plants are being provided for.

In desalination, all the salts are removed for human consumption while removal is partial for animal consumption. Today, there are two most commonly used technologies for desalination as follows.

(a) *Multi-stage flash distillation (MSF)*: This technology accounts for 85% of the world's production of desalinated seawater. This is a modern version of the traditional *vacuum distillation* method that involved fast boiling water at less than atmospheric pressure. The principle underlying the multi-stage flash distillation technology consists in distillation of seawater by flashing one portion of the steam at a time and repeating the process for subsequent portions. The first-stage steam is condensed to water and passed and suddenly passed to a low-pressure container; as a result the water boils to steam rapidly in a flash; the process is repeated in multiple stages to obtain a high-quality desalinated water. The method is suitable for both low-salt brackish water and high-salt seawater. But, this process of desalination is energy-intensive. On account of this reason, many plants are located in Middle-East countries. Saudi Arabia alone accounts for 24% of world capacity and the largest plant in the world (300 million m^3/year) is in UAE. However, its main advantage is that its residue consists of solid salts and can be disposed anywhere.

(b) *Reverse osmosis (RO)*: This is the current trend and is the preferred technology in the new plants and those of Argentina and north-eastern Brazil are working on this technology. In this method electrolysis and selective permeability through a special membrane are combined. The membranes are generally made of either spiral wound fibers or hollow fine fibers. Various types of membrane are used like cellulose acetate, aromatic polyamides and thin films of polyester composites (this latter type is more popular nowadays). This technology is suitable for both low-salt brackish water and high-salt seawater.

The principle underlying the RO technology consists in passing pressurized saline water through a water-permeable membrane. The pressure is 250-400 psi for brackish water and 800-1000 psi for seawater. Employing high pressures of 13.6-17.0 atmosphere and limiting the rate of flow to 241 m^2/day, it has been possible to remove by this method up to 98% of the initial total dissolved salt (TDS) of 2500-3000 mg/litre and almost all the viruses, bacteria and chemical pollutants from seawater.

Unlike the MSF technology, this technology consumes low energy. But its main disadvantage is that the residue is in the form of a highly concentrated brine containing 35,000 mg/litre of TDS which finds its way back into the sea (unless useful salts can be recovered economically). To this, the environmentalists have voiced concern on the ground that this will be harmful to the aquatic animals living near the coast.

Even without desalination, seawater is used for certain purposes like cooling of industrial plants and machinery.

2. Rainwater: Where the ground cover overlying a groundwater reservoir rock is pervious, a part of the rainwater percolates down and recharges the reservoir. But, in many cases, especially in cities with metal/concrete roads and house yards, most of the rainwater flows away through the storm water pipes or as surface run-offs. In many places, it is becoming a practice (in some, it is even enforced legally) to incorporate in plans and designs what is called *rainwater harvesting*. It consists of a system to channelize the rainwater precipitating on rooftops and courtyards into collectors (tanks and wells) for use during times of water-scarcity.

3. Ice caps: 70% of the earth's freshwater resource is locked up in the icecaps of Antarctica and Greenland. However, if this ice melts and goes into the ocean water, it will not be potable and on the other hand it will result in a rise in sea level, marine transgression, shrinking of landmass and more congestion, besides contributing to global warming due to reflection of less heat back to the atmosphere by the leftover ice with reduced thickness. The only alternative appears to be to mine this ice in a regulated manner as per requirement, transport it and melt it to water.

> "The progress of science is to be measured not by the number of questions we can answer but by the number of answers we can question."
>
> —Eddington

GLOSSARY

Adhesive: An adhesive is an inorganic or organic substance capable of bonding other substances together by surface attachment.

Agglomeration: Agglomeration techniques include sintering, briquetting and pelletizing.

Alkylation: Alkylation is the coupling of an olefin and a butane (or isobutane) over a catalyst.

Alloy: An alloy is a metallic material consisting of atoms of two or more metals, or two or more elements of which most of the atoms are metal atoms. Thus, even a nonmetal can be an element in an alloy. In an alloy, the elements are admixed at the atomic level, and bulk of properties are those usually associated with metals. An alloy differs from a chemical compound inasmuch as there is no fixed formula in the former, and the contents of the elements can be varied and manipulated depending on the desirable properties to be achieved.

Base exchange saturation: Base exchange saturation of soil is the ratio [Exchangeable (Ca + Mg)] /[(Ca +Mg +Al +H) extracted from soil].

Baume$^{/}$ scale: Named after its inventor Antoinne Baume$^{/}$, Baume$^{/}$ scale is a quick technique for measuring specific gravity of liquids with the help of a hydrometer (a hollow sealed calibrated glass tube). It comprises two independent mutually exclusive scales—one for liquids with specific gravity less than 1(i.e., lighter than water) and the other for those with specific gravity greater than 1 (i.e., heavier than water). On this scale, the specific gravity denoted by the unit "^{0}Be$^{/}$", and the reference liquid for comparison is a solution of NaCl. The principle consists in measurement of the depth to which the hydrometer sinks when immersed in a liquid. The two scales are calibrated and they can be converted to specific gravity as follows:

For liquids heavier than water: 0^{0}Be$^{/}$ = distance the hydrometer sinks in pure water, and 15^{0}Be$^{/}$ = distance the hydrometer sinks in a solution of 15% NaCl by mass; Its conversion factor to specific gravity at 15^{0}C is

$$\text{Specific gravity} = 145/(145 — {}^{0}\text{Be}^{/})$$

For liquids lighter than water: 0^{0}Be$^{/}$ = distance the hydrometer sinks in solution of 10% NaCl by mass, and 10^{0}Be$^{/}$ = distance the hydrometer sinks in pure water; Its conversion factor to specific gravity at 15^{0}C is

$$\text{Specific gravity} = 140/(130 + {}^{0}\text{Be}^{/})$$

The Baume$^{/}$ scale is popular for measuring and expressing specific gravity of wine and brine.

Biscuit firing: In ceramics, the fired product before glazing is called biscuit and the firing is called biscuit firing.

Brightness: Brightness is measured in terms of the reflectance of blue wave of light (wave length 457 micron).

Briquette: Briquettes are made by pressing the fines with or without bonding material.

Capacitors: Capacitors store electricity for a short period of time and ensure that the current supplied remains within narrow range of parameters – particularly in low voltage applications.

Catalysts: Catalysts increase the rate of chemical reactions without themselves undergoing permanent change.

Cation exchange capacity: It means the quantity of positively charged ions (cations) that a clay mineral can accommodate on its negatively charged surface, and it is expressed as milli-equivalents per 100 gm. This is also called "*Base exchanging power*".

Chelating agent: It surrounds and holds the unwanted ions of the water-hardening substances calcium and magnesium, thus softening the water.

Chrome: It is a component of colour. It indicates the degree of departure of a particular hue from neutral grey of the same value. In other words, it indicates the degree of saturation of the hue with reference to neutral grey. Thus, the familiar terms like 'weakly red', 'strong red', 'deep red', etc. are expressions of chrome.

Coefficient of friction: It is the ratio of the friction force to the applied force. It acts perpendicular to the applied force. Higher the coefficient, more is the energy loss due to friction.

Compressive strength: It is the load per unit area under which a block fails by shear or splitting. It is resistance to volume stress that tends to produce change in volume. It is expressed in terms of pounds per square inch (psi) or kg/cm^2.

Corrosion: Corrosion is the degradation of a material by the environment, most people associate with rust.

Cracking: In 'cracking', molecules are broken down under high temperature (with or without a catalyst) into smaller units, and a new type of hydrocarbon namely olefin is produced.

Creep: Creep is a time-dependent deformation, and it is the result of constant stress conditions over a long period of time. Ordinarily, the term is restricted to deformation resulting from stresses below the elastic limit.

Curie: It is a unit of radioactivity equal to the amount of a radioactive isotope that decays at the rate of 37 billion disintegrations per second.

Curie temperature: Curie temperature is the temperature above which a substance loses its magnetism.

Diamagnetic materials: These cause the magnetic flux to move further apart, resulting in decrease in magnetic flux density compared to vacuum, the magnetic permeability of which is taken as the unit value.

Dielectric constant: It is the ratio of the capacitance of a specific sample of the material between two plates and a vacuum between the same plates. Stronger the electrical conductivity, higher is the dielectric constant. The value for air, one of the poor conductors of electricity, is 1.

Dielectric strength: Dielectric strength is a measure of the electrical insulation, and is the voltage that an insulating material can withstand before breakdown. It is expressed in terms of specific resistance. The unit of measurement is volts/mm.

Dispersion: Dispersion is the rate of change of refractive index with change in wavelength of the incident light, and is expressed with reference to some wavelength.

Dyne: The word has been derived from the Greek word "dynamics". It is smaller unit for force than Newton. One dyne is the force required to produce an acceleration of one centimetre per second per second to a mass of one gramme. It is 100000th of a Newton.

Electrolysis: If a strong electric current is passed through a chemical compound, its decomposition into elements or parts takes place. This is called electrolysis.

Electronegative element: Atoms of some elements collect in the positive pole or anode, and those elements are called electronegative.

Electrophoresis: Electrophoresis is the movement of an electrically charged substance under the influence of an electric field. *Gel electrophoresis* is a technique used for the separation of DNA, RNA or protein molecules through an electric charge and is used for analytical purpose and as a preparation technique to partially purify molecules prior to use of other methods such as mass spectrometry, DNA sequencing, etc.

Electroplating: Electroplating is the process of precipitating a metal in an anodizing bath through electrolysis.

Electropositive element: Atoms of some elements collect in the negative pole or cathode, and those elements are called electropositive.

Emery: Emery is a natural mineral comprising an intimate mixture of magnetite and corundum used in powder form for polishing, smoothing and grinding purposes. On an average, emery contains Al_2O_3 65% (min), magnetite 22% (max) and SiO_2 10% (max).

Emissivity: Emissivity is a measure of the energy (heat or some other form) appearing within a substance due to absorption of incident light.

Emulsion: An emulsion is a dispersion of liquid in another immiscible liquid.

Equivalent weight: It is the molecular weight of an element divided by its valency.

Eutectics: The constant proportion in which two constituents of a binary magma or a binary melt simultaneously crystallize, is called the eutectic.

Fatigue limit: Also called endurance limit, it is defined as the limiting stress below which a specimen can withstand hundreds of millions of repetitions of stress without fracture.

Fission: The ability of an atom to split due to collision with a free neutron is called 'fission'.

Fluorescence: Atoms of some luminescent materials emit light only during their exposure to exciting energy and they are called fluorescent.

Gems and gemstones: According to Webster's Second Edition Unabridged Dictionary, gem means any jewel having value and beauty that is intrinsic and not derived from its setting; and gemstones or gem materials are stones or materials from which a gem may be cut. By popular perception, a gem is a rarely encountered hard, durable, brilliantly shining and beautiful natural mineral which has high intrinsic value.

Glazing: The purpose of glazing is to provide a uniform firmly adhering coating on the surface of the ceramic body concealing defects such as pinholes, bubbles etc. Glaze may be "*raw glaze*" or "*fritted glaze*". Raw glaze consists of insoluble material applied as such (soluble components crystallize in the mixture and cause blemishes on the treated surface), while fritted glaze is heated beforehand to cause chemical change in the components. Glaze should not only melt but also spread uniformly.

Gloss/reflectivity: Gloss is the percentage of the incident light beam that is reflected from a surface.

Gravel::According to the definition of the American Society of Testing and Materials (ASTM), gravel is naturally occurring unconsolidated or poorly consolidated rock particles ranging in size from 4.75mm to 76.2 mm. But according to many sedimentary petrologists, granular gravels are of 2-4 mm size and gravels more than 4 mm.

Glost firing: Firing of a glazed product which has previously been fired at a higher temperature is called glost firing.

Hard (or permanent) magnets: Once magnetized, these magnets retain their magnetic field indefinitely even after the magnetizing field is withdrawn.

Heterotrophic Plate Count (HPC): Heterotrophs are bacteria that thrive on carbon and nitrogen of organic compounds. HPC is a microbial contaminant indicator and is a measure of the total number of bacteria that will form colonies during a period of incubation in a nutrient. Its unit is cfu/ml, i.e., colony-forming units per millilitre.

Hue: It is a component of colour. The much familiar terms like red, blue, orange, etc. denote hue (or the type of colour).

Hydroponics: It is a technique of growing plants without soil, in water containing dissolved nutrients.

International Annealed Copper Standard or IACS: This is the international standard for electrical conductivity with value of conductivity 2.8 microhm/cm^3 at 20^0 C.

Isomerization: Isomerization is the process of producing a similar but new substance by rearrangement of atoms within the hydrocarbon molecules of the original substance.

LAB parameters: The three letters ‘L’, ‘A’ and ‘B’ are used as parameters for denoting colours — ‘L’ value stands for whiteness; ‘A+’ value, for red colour; ‘A-’ value, for green colour; ‘B+’ value, for yellow; and ‘B-’ value stands for blue colour.

Langelier Saturation (or Stability) Index (LSI): Langelier Saturation (or Stability) Index or LSI values are calculated for a precise quantification of the hardness of water which is caused by the presence of the insoluble carbonates and sulphates of calcium and magnesium, which tend to precipitate in the form of scales when the water is boiled. With the help of LSI value of a water it can be predicted whether it will precipitate or dissolve or be in equilibrium with $CaCO_3$ which is then converted to a scale of hardness. In this, the pH of a water saturated with $CaCO_3$ is pre-calculated as a reference (pH_s) and then the pH of the test water (pH_w). LSI is the difference ($pH_w — pH_s$). LSI value of ‘0’ means equilibrium, a negative value means no scaling potential (soft water) and a positive value means high scaling potential (hard water).

Levigation: Levigation is the operation involving pulverization of clay to very fine size for liberating the clay particles from the impurities.

Lixiviation: Lixiviation (also called leaching) is the process of separating a soluble substance from one that is insoluble, by washing with water or some solvent.

Luminescence: Many substances easily gain energy and emit light without being heated very much. They do this through a process called luminescence.

Magnetic flux: These are the lines of force conceived as a “flow” from one pole of the magnet to the another (counterpart of current in electricity). Its unit of measurement is gauss (or Maxwell per cm^2) which is the magnetic flux perpendicularly intersecting an area of one square centimetre.

Magnetic permeability: It is the ability to acquire magnetism in a magnetic field.

Mesh size: It represents number of holes per square inch of area on a sieve. Approximately, 1250 mesh is equivalent to 10 micron and 125 mesh to 100 micron.

Metal matrix composites: A composite material is a materials system composed of a mixture of two or more materials deliberately combined to form heterogeneous structures with desired or intended properties. In composites, at least one of the constituents serves principally to strengthen or reinforce the composite, while another constituent, called the applications matrix, serves to confine the reinforcing constituent(s) and provides a means to distribute any applied stress. In metal matrix composites (MMCs), a metal serves as the matrix, while the reinforcing constituent can be a metal, a non-metal, an alloy or a compound.

Mineral wool: Mineral wool is a general term meaning fibers made from inorganic substances that may include minerals, rocks and metal oxides — synthetic or natural. Glass wool, lime wool, rock wool or stone wool, slag wool are all different types of mineral wool.

Modulus of elasticity: The maximum stress to which a body can be subjected without permanent deformation is called its *elastic limit*. According to *Hooke's Law*, within the elastic limit, stress is directly proportional to strain, and the constant ratio stress/strain is called *modulus of elasticity*. It is usually expressed in units of psi or kg/cm^2. Corresponding to the three kinds of force — tensile, compressive and shearing — there are three kinds of stress and strain and three kinds of modulus of elasticity. These three elastic moduli are:

Young's modulus
Bulk modulus and
Modulus of rigidity

Newton: Newton or 'N' is a unit of force. One Newton is the force required to produce an acceleration of on metre per second per second to a mass of one kilogramme. Compressive strength is expressed as N/mm^2.

Octane number: Octane number is a measure of 'anti-knock' value of a motor fuel i.e. the ability to resist the knock or sound produced due to its sudden and violent combustion in a spark ignition engine. For this measurement, a standard scale has been devised by assigning the value zero to heptane (C_7H_{16}) which has very poor knock resistance, and 100 to octane (C_8H_{18}) having a very high knock resistance. Octane number is the percentage of this isomer of octane in its mixture with heptane.

Paramagnetic materials: These concentrate the magnetic flux by a factor of more than 1 but less than or equal to 10 compared to vacuum, the magnetic permeability of which is taken as the unit value.

Pascal: Pascal or 'Pa' is a unit for denoting compressive strength, and is equal to N/m^2. One mega-Pa is 10^6 Pa.

Pellets: When very fine particles (size in microns) are formed into spherical objects called 'pellets', the process is called pelletization.

Permeability, coefficient of: The common method for measuring it is by Darcy's Law. According to it the coefficient of permeability is measured by the following formula:

$$K = V/I$$

where, ‘K’ is the coefficient of permeability in gallons per day per square foot, ‘V’ is the velocity of flow of water in feet per day and ‘I’ is the hydraulic gradient of the medium in feet per foot length.

pH value: It is the short form of “potential of hydrogen”. It is the negative logarithm of the effective hydrogen-ion concentration or hydrogen ion activity in gram equivalent per litre. It is used in expressing both acidity and alkalinity on a scale whose values run from 0 to14 with 7 representing neutrality. Numbers less than 7 indicate increasing acidity and those greater than 7 increasing alkalinity.

Phosphorescence: Atoms of some luminescent materials stay excited for some time before they de-excite and consequently, they glow in the dark long after they have received extra energy. They are called phosphorescent.

Piezoelectricity or electrostriction: Piezoelectric crystals can change alternating mechanical strains into electrical impulses :nd vice versa. The efficiency of transfer of energy back and forth between strain and motion is expressed by ‘Q’ factor which is defined as the ratio of energy stored to energy dissipated. The higher the Q, the lower will be the energy losses.

Pigment: Pigments serve various functions such as acting as fillers, stabilizing binders, protecting against ultraviolet light, reinforcing, controlling thermal expansion, controlling thixotropy, controlling shrinkage, colouring and beautification. There are 4 types of pigments: (i) pigment extenders , (ii) white hiding, (iii) inorganic and organic colours, and (iv) carbon black.

Poisson’s ratio: This is closely related to both compressive and tensile strengths. When a bar is pulled or compressed, not only its length alters but also the transverse dimension. Now, for a given material, the ratio between transverse and longitudinal strains has been found to be more or less constant and this ratio is called *Poisson’s ratio*.

Polarization of light: As white light waves propagate through space, the vibrations take place in all possible directions on all possible planes. But due to certain factors, these vibrations are modified so as to take place on a single plane only. This light vibrating on a single plane is called polarized light, and the phenomenon of such modification is called polarization. The polarizing factors are: (i) partial reflection, (ii) double refraction or birefringence, and (iii) absorption. When light is incident on an object, some of its rays are reflected back and some are refracted, and both the reflected and the refracted rays are polarized. When the object (e.g., Iceland spar) is doubly refractive, each of the two refracted rays is polarized. In case of absorption (as in case of a dark coloured object like tourmaline), light rays vibrating in all but one plane are absorbed within the object and the rays emerging out from it are thus polarized. Polarized light is used for seeing the colour of an object in thin section under microscope, otherwise in unpolarized light it will appear as almost colourless unless the object is very dark coloured.

Polymerization: Polymerization is spontaneous alteration of substances.

Proppant: Proppants are materials which are used for filling up the fracture cavities to prevent closure of oil wells, but without reducing the permeability of the reservoir rock, so that flow of oil or gas can be sustained.

Pyroelectricity: Pyroelectric substances are a kind of semiconductor. Semiconductors are materials with resistivity intermediate between metals (resistivity $< 10^4$ ohms/cm) and insulators (resistivity $>10^3$ ohms/cm). They contain only a small number of loosely bonded electrons at room temperature, and hence their conductivity is very poor (of the order of 100000 times less than that of conductor metals). However, their low electrical conductivity can be substantially improved by various methods one of which is by supplying thermal energy. This phenomenon of increase in conductivity with increasing temperature is called pyroelectricity.

Radioactivity: Radioactivity is the spontaneous disintegration of certain heavy elements accompanied by the emission of high energy radiation, which consists of three kinds of rays: 'alpha particles', 'beta particles' and 'gamma rays'.

Refractory: Refractory materials are defined as those resistant to heat and having a melting temperature of not less than 1580^0 C. The function of refractory lining is not only to withstand high temperature, but also to resist temperature fluctuation, slag and metal penetration, abrasion, and erosion by hot gases and molten slags and metals.

Rheology: It is the study of deformation and flow of matter under the influence of applied stress.

Rupture modulus: This is the resistance of a rock slab to bending or flexure. The stress may first cause elastic deformation, then plastic deformation, and finally rupture. In case of brittle objects, there will be no plastic deformation and the object will break as soon as the elastic limit is crossed. Modulus of rupture is expressed in terms of psi or kg/cm^2 of the bending stress under which an object breaks.

Sand: According to the definition of the American Society of Testing and Materials (ASTM), sand is naturally occurring unconsolidated or poorly consolidated rock particles ranging in size from 0.074 mm to 4.75 mm, and gravel is similar rock ranging in size from 4.75mm to 76.2 mm. But according to many sedimentary petrologists, sand is an unconsolidated granular material coarser than 1/16th of a millimetre and finer than 2 mm (cf. granular gravels are of 2-4 mm size and gravels more than 4 mm).

Sealant: A sealant is an organic substance soft enough to pour or extrude into an opening in an object, and capable of subsequent hardening to form a permanent bond with the object.

Semiconductor: These are materials with resistivity intermediate between metals (resistivity < 104 ohms/cm) and insulators (resistivity >103 ohms/cm).

Shearing strength: This is the resistance to tangential force. It is also called *rigidity*. In other words, a body is said to be in shear when it is subjected to a pair of equal forces which are opposite in direction and which act along parallel planes. Shearing strength is expressed in psi or kg/cm^2.

Sialon ceramics: It is an advance material comprising a mixture of silicon, aluminium, oxygen, and nitrogen (i.e. Si-Al-O-N). Sialon is suitable for applications requiring high mechanical strength at elevated temperatures, high specific strength (for weight saving without sacrificing strength), high hardness and toughness, low coefficient of friction and good thermal shock resistance.

Sinter: By application of just enough heat to fuse the corners of ore particles, they are made to join together to form a lumpy mass. This product is called 'sinter'.

Soft magnets: These can be magnetized easily, for example by electric current travelling in an electric coil wrapped around a soft magnetic core, but they lose their magnetism once the current is turned off.

Soldering: Solder is an alloy of tin and lead, which is used for joining two pieces of a metal by a process of welding called soldering.

Specific heat: Specific heat of a substance is the ratio of the amount of heat required to raise the temperature of one gram of it by one ^{0}C to that required to raise the temperature of one gramme of water by one ^{0}C.

Surfactant: is the acronym of "surface active agent", and it removes dirt from a soiled surface attracting the dirt particle to its surface by ion exchange.

Tensile strength: It is also called resistance to longitudinal stress, because this kind of stress tends to produce unidirectional change in a body. Tensile strength of rocks is expressed as pounds per square inch (psi) or kg/cm^2.

Thixotropy: It is the property of pseudoplastic fluids showing time-dependent change in viscosity. Longer the shear stress, lower is the viscosity (e.g., ketchup, some clays, gels)

Toughness: Also called impact toughness, it is the resistance to sudden impact and is expressed in inches per square inches.

Value of colour: The value indicates degree of lightness or darkness of a colour and it is related to both the percentage of light reflectance and the degree of lustre. Obviously, pure black has the lowest value and pure white has the highest value.

Viscosity: Absolute or dynamic viscosity or simply viscosity is that property of a liquid which is a measure of its internal resistance to deform under shear stress, and it is measured by the stress in dynes/cm^2 or Pascal (Pa) required to be applied to overcome that resistance and maintain a velocity of flow of one centimetre per second. This unit of measurement of viscosity is Poise which is 1 gm.cm.sec or 1 Pascal second (Pa.sec). It is often expressed in centipoise (cP). The viscosity of water at 20^0 C is 1.0020 cP. Kinematic viscosity is dynamic viscosity divided by density, and its unit is Stokes (S or St) or centistokes (cS or cSt).

Welding: Welding is a metal-joining process wherein coalescence is produced by heating to suitable temperature with or without pressure and with or without the use of filler metal.

Yield point: It is the point where a stressed material no longer deforms elastically, but begins to deform permanently. Its unit of measurement is lb/in^2 or kg/cm^2.

REPERTORY OF USES OF INDUSTRIAL MINERALS AND ROCKS

(This will serve as a product-wise ready reference for uses of those industrial minerals and rocks which are covered in this book; afer identifying the relevant mineral/rock corresponding to a particular end-use, the reader may refer to the concerned mineral/chapter of this book for details about the uses)

Abrasive/grinding (wheel, paper, cloth)	Bentonite, corundum, cryolite, diamond, diatomite, feldspar, limestone, magnesite, perlite, quartz, zircon
Activated carbonaceous material	Coal, lignite, peat
Adhesive	Attapulgite, barytes, calcite, crushed stone, dolomite, graphite, gypsum, kaolin, limestone, potash, quartz, sulphur, wollastonite
Aero gel	Quartz
Agriculture/ horticulture/hydroponics	Basalt, borax, Chile saltpetre, diatomite, dunite, magnesite, perlite, pyroxenite, rock salt, shirasu (volcanic eject), vermiculite, zeolite
Aircraft	Muscovite mica, phlogopite mica
Alloy	Graphite, muscovite mica, phosphorite, quartz , zirconium
Analytical chemistry	Borax
Animal/poultry feed	Ball clay, bentonite, diatomite, magnesite, phosphorite, rock salt, zeolite
Anti-skid	Feldspar, garnet
Artificial diamond	Celestite, strontianite, zircon
Asbestos paper	Asbestos
Ashlars	Dimension stone
Asphalt/bitumen	Asbestos, crushed stone
Ballast	Crushed stone
Bearing	Graphite, ruby, sapphire
Beet sugar	Zeolite
Beverage	Nahcolite, saltpetre
Bleaching	Attapulgite, limestone
Board/panel	Asbestos, gypsum, magnesite, muscovite mica, vermiculite

Boiler/steam pipes	Asbestos, magnesite, muscovite mica
Bone china	Feldspar, kaolin, phosphorite
Boron	Borax
Brake/friction material	Asbestos, basalt, graphite, wollastonite
Brick	Brick clay, brick shale, crushed stone, gypsum, limestone, quartz
Calcium metal	Limestone
Calcium silicate	Limestone
Capacitor	Muscovite mica
Carbon nano-tube	Graphite
Carbon sequestration	Peridotite, serpentite, zeolite
Casein	Potash
Cassette	Kaolin
Catalyst	Attapulgite, crushed stone, kaolin, zeolite
Caulking	Asbestos
Cell (including fuel cell)	Feldspar, graphite, quartz, phosphorite, zircon/baddeleyite
Cement	Asbestos, attapulgite, corundum, dolomite, fluorite, gypsum, kaolin, limestone, magnesite, muscovite mica, pozzolanic clay, quartz
Ceramics (including potteries, fired tiles, composites)	Asbestos, ball clay, bentonite, borax, diamond, diaspore, diatomite, dolomite, feldspar, fluorite, gypsum, kaolin, perlite, pottery clay, pyrophyllite, quartz, rock salt, roofing tile clay shirasu (volcanic eject), stoneware clay, talc, wollastonite, zircon/baddeleyite
Chemicals	Barytes, calcite, fluorite, potash, pyrites, rock salt, saltpetre, strontianite, sulphur, trona, zircon/baddeleyite
Chemical sensor	Synthetic zeolite
Climatology	Diatomite
Coal washing	Barytes, feldspar, quartz
Compass	Muscovite mica
Construction (including concrete, aggregate, building sand, structural material)	Barytes, bentonite, crushed stone, diamond, diatomite, dimension stone, dolomite, graphite, gypsum, perlite, quartz, shirasu (volcanic eject), vermiculite, zeolite
Cordierite (artificial)	Fireclay, talc
Cosmetics (including talcum powder)	Bentonite, borax, calcite, gypsum, kaolin, magnesite, muscovite mica, pyrophyllite, quartz, talc
Crucible	Fireclay, graphite, zircon/baddeleyite
Cutting/boring	Diamond, hafnium
Decoration (including art work, artifacts)	Calcite, crushed stone, gypsum, mica, muscovite, pyrophyllite, talc, tourmaline, terracotta clay, terracotta shale

De-icing	Crushed stone, magnesite, rock salt
Deliquescent	Lime saltpetre
Desulphurization	Limestone
Diesel	Lime saltpetre
Diet coke	Magnesite
Disinfectant	Rock salt
Drilling	Attapulgite, barytes, bentonite, celestite, graphite, muscovite mica, perlite, quartz, vermiculite
Dust suppression (including coal dust)	Gypsum, magnesite
Edible salt (includes table and iodized salts)	Rock salt
Electrical appliances	Magnesite, muscovite mica, phlogopite mica
Electric motor/generator/transformer	Graphite, muscovite mica
Electro-ceramics	Talc, zircon/baddeilite
Electronics (includes chip, clock, robot, computer, television)	Diamond, graphite, muscovite mica, strontium
Electrode	Calcite, graphite, wollastonite
Electroplating	Fluorite
Emery (artificial)	corundum
EMI-shield	Graphite, muscovite mica
Enamel	Borax, Chile saltpetre, cryolite, feldspar, fluorite, magnesite, quartz, sulphur, zircon
Epsom salt	Magnesite
Etching	Fluorite
Explosion/explosive/pyrotechnics (including gun powder, dynamite)	Attapulgite, barytes, borax, celestite, Chile saltpetre, diatomite, graphite, kaolin, lime saltpetre, rock salt, saltpetre, strontianite, sulphur, talc, zirconium
Fertilizer (including soil conditioner and plant micronutrients and their measurements)	Anhydrite, Chile saltpetre , crushed stone, diatomite, dolomite, dunite, gypsum, lime saltpetre, limestone, magnesite, perlite, phosphorite, potash, pyrites, pyroxenite, quartz, saltpetre, shirasu (volcanic eject) sulphur, tourmaline, vermiculite, zeolite
Ferro-boron	Borax
Filter/filtration	Asbestos, diatomite, dolomite, magnesite, perlite, quartz
Fishery	Zeolite
Fluorine	Fluorite

Food processing	Borax, rock salt
Foundry/casting	Bentonite, corundum, graphite, gypsum, muscovite mica, perlite, quartz, zircon
Fullerene	Graphite
Furnace/oven	Muscovite mica
Gear	Graphite
Geiger counter	Muscovite mica
Gem	Amber, andalusite, apatite, apophyllite, aqua marine, axinite, bowenite, chrysoberyl, coral, cordierite, corundum, danburite, diamond, diopside, emerald, enstatite, epidote, euclase, feldspar, fluorite, fuchsite quartzite, garnet, hambergite, idiocrase, jadeite, kyanite, lazurite, malachite, nephrite, olivine, pearl, piedmontite, phenacite, prehnite, pyrites, quartz, rhodonite, rutile, scapolite, sillimanite, sphene, spinel, sodalite, staurolite, topaz, turquoise, tourmaline, zeolite, zircon, zoisite
Geological dating	Zircon/baddeleyite
Glass (includes optical fiber)	Barytes, borax/ulexite/colemanite, calcite, Chile saltpetre, celestite, cryolite, dolomite, feldspar, fluorite, kaolin, kyanite, limestone, magnesite, phosphorite, potash, pyrophyllite, quartz, saltpetre, vermiculite, zeolite, zircon/baddeleyite
Glass-bonded mica	Muscovite mica
Glazing	Ball clay, barytes, borax, calcite, diatomite, feldspar, kaolin, limestone, magnesite, nepheline syenite, quartz, phosphorite, rock salt
Graphene	Graphite
Grinding	Quartz
Halogen bulb	Quartz
Heating	Zeolite
Handling/storage	Diatomite, perlite
Hydraulic brake	Borax
Hydrofluoric acid	Fluorite
Ice-cream	saltpetre
Ice-box	Perlite
Incandescent mantle	Lime saltpetre
Ink	Borax kaolin
Insecticide/pesticide/germicide/fungicide	Attapulgite, bentonite, borax, crushed stone, cryolite, diaspore, diatomite, gypsum, kaolin, muscovite, quartz, perlite, pyrophyllite, sulphur, talc
Insulator (heat) including fire-retardant	Asbestos, basalt, borax, diatomite, muscovite mica, perlite, shirasu (volcanic eject) , vermiculite
Insulator (electrical)	Asbestos, crushed stone, kaolin, magnesite, muscovite mica, talc, zircon/baddeleyite
Insulator (magnetic)	Muscovite mica
Insulator (sound)	Asbestos, basalt, borax/glass wool, diatomite,

	gypsum, vermiculite
Jointing sheet	Asbestos
Laser/maser	Graphite, quartz, ruby, sapphire
Leather	Limestone, dolomite, borax
Lime	Dolomite, limestone
Limelight	Zirconium
Lubricant/grease	Crushed stone, graphite, muscovite mica, talc, vermiculite
Magnetic tape	Graphite
Manometer	tourmaline
Matches	Diatomite, kaolin, lime saltpetre, phosphorite, saltpetre
Measurement of distances	Calcite
Medical	Borax, diatomite
Metakaolin	Kaolin
Metallurgy (includes iron, steel, ferromanganese, alloys, aluminium)	barytes, bentonite, borax, celestite, cryolite, dolomite, dunite, feldspar, fluorite, graphite, gypsum, limestone, magnesite, phosphorite, pyroxenite, quartz, rock salt, rutile/anatase/ilmenite, serpentinite, sulphur, vermiculite, zircon/baddeleiyite
Metallic glass	borax
Metrology	Dimension stone
Micanite	Muscovite mica
Microscope	Calcite, gypsum
Microwave transmitter	Muscovite mica
Mineral wool/glass wool/lime wool/rock wool/slag wool	Amphibolite, basalt, borax, diabase, limestone, wollastonite
Missile	Muscovite mica
Mortar	Pozzolanic clay
Night illumination device	Celestite, strontianite
Nitric acid	Chile saltpetre
Nuclear reactor	Barytes, borax/boron, graphite, hafnium, perlite, zirconium
Odour control	Nahcolite, zeolite
Opacifier	Fluorite, zircon
Optical instruments	Calcite, muscovite mica, synthetic zeolite, tourmaline
Ornament/jewelry/gem	Aqua marine, diamond, emerald, gypsum, phosphorite, quartz, ruby, sapphire, tourmaline
Oscillator	Muscovite mica, quartz
Oxygen-breathing equipment	Muscovite mica
Oxygen sensor	Zircon/baddeleyite
Packing (including gaskets)	Asbestos, graphite, vermiculite
Paint (including pigment, dye)	Asbestos, barytes, bentonite, calcite, celestite, crushed stone, diatomite, dolomite, feldspar,

	graphite, gypsum, kaolin, limestone, muscovite mica, ochre, perlite, phlogopite mica, pyrites, pyrophyllite, quartz, rutile/anatase/ilmenite, talc, vermiculite, wollastonite, zircon
Paper	Barytes, bentonite, borax, diatomite, dolomite, gypsum, kaolin, limestone, magnesite, muscovite mica, quartz, rock salt, talc, zeolite
Pencil/crayon/writing chalk	Graphite, gypsum, kaolin, limestone, pyrophyllite, talc
Petromax	Limestone, muscovite mica
Pharmaceuticals (including Ayurvedic medicine)	Attapulgite, bentonite, diamond, dolomite, gypsum, kaolin, limestone, magnesite, talc
Phosphorus	Phosphorite
Phosphoric acid	Phosphorite
Photography	Zirconium
Pipe	Pipe clay, stoneware clay
Plaster/stucco/putty	Gypsum, kaolin, limestone, magnesite, muscovite mica, potash
Plastics	Asbestos, ball clay, crushed stone, feldspar, kaolin, muscovite mica, perlite, talc, vermiculite, wollastonite
Polishing	Bentonite, corundum, diatomite, garnet, ochre, talc, zircon
Pollution control	Nahcolite
Polymer filament	Synthetic zeolite
Potassium	Potash
Potassium silicate	Potash, quartz
Preservation (includes food, metal)	Chile saltpetre, fluorite, limestone, quartz, rock salt , saltpetre
Purification/refining/cleaning	Attapulgite, bentonite, celestite, diatomite, limestone, magnesite, nahcolite, perlite, zeolite, zircon
Record player	Crushed stone, diamond
Radiation pyrometer	Muscovite mica
Radio	Lime saltpetre, pyrites
Refractory	Andalusite, bentonite, corundum, diaspore, diatomite, dolomite, dunite, feldspar, fireclay, graphite, kaolin, kyanite, magnesite, perlite, pyrophyllite, pyroxenite, quartz, serpentinite sillimanite, vermiculite, zircon/baddeleyite
Refrigeration	Fluorite, rock salt, zeolite
Rip-rap	Crushed stone
Road metal	Crushed stone
Rocket	Borax
Roofing material	Asbestos, crushed stone, muscovite mica
Rubber	Ball clay, barytes, bentonite, calcite, Crushed stone, diatomite, gypsum, kaolin, limestone, magnesite,

	muscovite mica, pottery clay, pyrophyllite, quartz , rock salt, sulphur, talc, wollastonite
Sand blasting	Garnet, quartz, staurolite
Sanitary ware (unfired)	Dimension stone, talc
Sealing/lining	Asbestos, attapulgite, bentonite, crushed stone, diatomite, graphite, kaolin, limestone, muscovite mica, talc, vermiculite
Searchlight	Phlogopite mica
Seawater magnesia	Dolomite, limestone
Semiconductor	Fluorite, zircon/baddeleyite
Sialon	Fireclay
Signaling device	Celestite, strontianite
Silane	Quartz
Silica gel	Quartz
Silicon carbide	Quartz
Silicon nitride	Quartz
Silicone	Quartz
Silly-Putty	borax
Slag granulation	Perlite
Smoke bomb	saltpetre
Soaps/detergents/toilet powder	Bentonite, borax, gypsum, kaolin, potash, rock salt, zeolite
Sodium chemicals (including silicate)	Diatomite, limestone, quartz
Space technology (includes satellite, rocket)	Diamond
Stowing	Quartz
Submarine	Muscovite mica
Sugar	Celestite, gypsum, limestone, sulphur, strontianite
Sulphuric acid	Anhydrite, gypsum, pyrites, Sulphur
Superconductor	Borax/boron
Surgery (including dental)	Gypsum , zircon/baddeleyite, zirconium
Synthetic cryolite	Fluorite
Synthetic/artificial gem	Garnet
Synthetic/imitation marble	Calcite, gypsum, quartz, talc
Synthetic zeolite	Kaolin
Terrazzo	Crushed stone
Textile	Borax, calcite, gypsum, kaolin, limestone, talc, zirconium
Therapy (including skin care, surgery, dentistry)	Aqua marine, diamond, diatomite, emerald, feldspar, ruby, sapphire
Thermal dosimeter	Tourmaline
Thermal regulator	Muscovite mica
Thermometer	Quartz
Thermoplastics/thermoset	Muscovite mica, phlogopite mica
Tile (unfired)	Crushed stone, gypsum, magnesite
Tooth paste/powder	Borax, corundum, diatomite, fluorite, kaolin,

	saltpetre
Toys	Barytes
Tracer bullet	Celestite, strontianite
Traction sand	Quartz
Ultra-hard material	Borax
Vacuum device	Zirconium
Varnish	Crushed stone
Vinyl sheet/linoleum/oil cloth	Asbestos, bentonite
Vodka	Asbestos
Vanaspati	Borax
Waste treatment	Zeolite
Water treatment	Calcite, glauconite, rock salt, zeolite
Welding	Bentonite, cryolite, feldspar, magnesite, mica, muscovite mica, potash, rutile
White carbon	Graphite
Window	Muscovite mica
Wire drawing	Diamond
X-ray/radiology	Barytes, graphite
Zirconium	zircon

INDEX