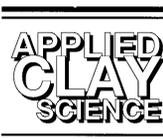




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Traditional and new applications for kaolin, smectite, and palygorskite: a general overview

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Abstract

Clays have been and continue to be one of the more important industrial minerals. Clays and clay minerals are widely utilized in many facets of our society. They are important in geology, agriculture, construction, engineering, process industries, and environmental applications. Traditional applications are many. Some of the more important include ceramics, paper, paint, plastics, drilling fluids, foundry bondants, chemical carriers, liquid barriers, decolorization, and catalysis.

Research and development activities by clay scientists in academia, government, and industry are continually resulting in new and innovative clay products. Many of these new applications are the result of improved processing, which provides clays of higher purity, more precise particle size and distribution, whiter and brighter color, modified surface chemistry, and other physical and chemical modifications. Some new and improved clay products include tailored or engineered paper coating kaolins, enhanced paint thickeners, nanocomposites for plastics, pillared clays as special absorbents and catalysts, clays for liquid fertilizer suspensions, clays for absorption of animal wastes, calcined kaolins with high brightness and low abrasion, faster casting clays, and clays with a very high modulus of rupture.

Improvement of mining and processing techniques will lead to the continued growth of traditional clay applications and to the development of new and innovative clay products. Value added products are the wave of the future for the traditional industrial clay minerals. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

The clay minerals kaolinite, smectite, and palygorskite and sepiolite are among the world's most important and useful industrial minerals. The smectites are more generally referred to as bentonites; bentonite being the whole rock term for rocks whose dominant clay mineral is smectite. Smectite is a family name, which includes sodium and calcium montmorillonites. Millions of tons of these clay minerals are used annually in a very large variety of applications. This paper focuses on the traditional applications and on the many new and improved products that are finding additional uses.

The industrial applications of the three most important clay mineral types are varied and in most instances quite different. This is primarily because of differences in their physical and chemical properties, which are dependent on structure and composition. The structure and composition of kaolins, smectites, and palygorskite–sepiolite are very different even though each has octahedral and tetrahedral sheets as their basic building blocks. The arrangement and composition of these octahedral and tetrahedral sheets account for the major and minor differences in the properties of these clay minerals and thus on their ultimate applications. A brief summary of some of the important characteristics and properties of kaolins, smectites, and palygorskite are shown in Table 1.

The particle size, shape, and distribution are important physical properties, which are intimately related to the applications of the clay minerals. Other important properties are surface chemistry, surface area, and surface charge. These, along with color and brightness, affect many use properties such as low

Table 1
Some important properties of clay minerals that relate to their applications

Kaolin	Smectite	Palygorskite
1:1 layer	2:1 layer	2:1 layer inverted
White or near white	Tan, olive green, gray, or white	Light tan or gray
Little substitution	Octahedral and tetrahedral substitutions	Octahedral substitution
Minimal layer charge	High layer charge	Moderate layer charge
Low base exchange capacity	High base exchange capacity	Moderate base exchange capacity
Pseudo-hexagonal flakes	Thin flakes and laths	Elongate
Low surface area	Very high surface area	High surface area
Very low absorption capacity	High absorption capacity	High absorption capacity
Low viscosity	Very high viscosity	High viscosity

and high shear viscosity; absorption; plasticity; green, dry and fired strength; casting rate; permeability; and bond strength. In almost every application, the clays and clay minerals are functional and are not just inert components in the system.

Improved processing techniques, which have evolved over the past 30 years, in particular have had a profound effect on the traditional and new applications. Some of the more important of these will be briefly discussed in this paper. Specific traditional and new applications are discussed in the sections related to each of the three clay mineral groups.

2. Kaolins

The most common mineral by far in the kaolin group of minerals is kaolinite. Its physical and chemical properties and applications are discussed in this section. The physical and chemical properties of kaolin determine its use as an industrial mineral. These uses are governed by several factors including the geological conditions under which the kaolin formed, the total mineralogical composition of the kaolin deposit, and the physical and chemical properties. As mentioned by Murray and Keller (1993) there are “kaolins, kaolins, and kaolins.” Kaolin deposits can be sedimentary, residual, or hydrothermal and in almost every instance the kaolin has different properties and thus must be fully tested and evaluated to determine its utilization.

The occurrences of kaolin are common, but commercially useable deposits are relatively few in number. The best known and most highly utilized deposits are in the Cornwall area of southwestern England, in Georgia and South Carolina in the United States, and in the lower Amazon region of Brazil (Pickering and Murray, 1994).

As shown in Table 1, kaolin is usually white or near white in color. There is very little substitution in the structural lattice and thus it has a minimal layer charge and a low base exchange capacity. The kaolinite crystals, which make up most of the kaolin deposits, are pseudo-hexagonal along with plates, some larger books, and vermicular stacks (Fig. 1). Particle size and particle size distribution are also very important in determining the industrial uses of the kaolin. A coarse particle kaolin has very different physical and optical properties relative to a fine particle size kaolin. Other properties that are important are the relatively low surface area in comparison to smectite and palygorskite–sepiolite, and the low absorption capacity, which relates to the minimal layer charge and the low surface area.

A relatively low viscosity at high solid concentrations is an important characteristic of some kaolins. This is particularly important in paper coating and paint applications. Viscosity of kaolin products is dependent on several factors including mineral content; particle size, shape and distribution; presence



Fig. 1. SEM showing kaolin plates and stacks. Bar = 1 μm .

of soluble salts; and dispersability. The presence of a small amount of smectite, illite or halloysite adversely affects viscosity.

What are the traditional applications of kaolins? The more important are ones shown in Table 2.

The largest use of kaolin is for coating paper. Properties that are important to the paper manufacturer are dispersion, viscosity (both low and high shear), brightness, whiteness, gloss, smoothness, adhesive demand, film strength, ink

Table 2

Traditional applications of kaolins

Paper coating	Plastic filler	Adhesives
Paper filling	Ink extender	Enamels
Paint extender	Cracking catalysts	Pharmaceuticals
Ceramic ingredient	Fiberglass	Crayons
Rubber filler	Cement	Molecular sieves

receptivity, and print quality. Thus, it can be seen that the kaolin properties listed in Table 1 are exceedingly important in controlling the factors that are important for paper coating. Many of the properties of kaolin can be altered and improved by processing, which is covered in the last section of this paper. The use of kaolin in paper coating formulations continues to grow at a rate estimated at between 2% and 3%/year. However, the use of kaolin as a filler in paper has significantly decreased in the past 10 years because of a major change in the production of wood pulp from using an acid to an alkaline process. This change has permitted a much more extensive use of calcium carbonate, which can survive an alkaline system but dissolves in an acid system.

The use of kaolins as functional fillers and extenders in paint, plastics, rubber, and ink continues to grow at a rate equivalent to the gross national product growths, except in plastics where the growth is estimated at 5% to 6% per annum.

A very large traditional use of kaolin is in ceramics, particularly in white-ware, sanitaryware, insulators, pottery, and refractories. Many kaolins have very good ceramic properties (Murray, 1986). There are many kaolin deposits that do not have the physical and chemical properties for paper coating but have very good ceramic properties. The ceramic use of kaolin continues to grow particularly in the tile and sanitaryware markets.

One other area of use of kaolin that has grown rapidly in the last 10 years is as a raw material in the production of fiberglass. The kaolin supplies both silica and alumina, which are needed in the fiberglass formulation. The kaolins that are used must have a relatively low iron and titanium content. The reason for the increased use of fiberglass is because of the restricted use of asbestos due to health considerations.

Growth markets for kaolins are tailored or engineered products for coating paper, calcined kaolins as extenders for titanium dioxide, and surface-modified kaolins that will disperse in organophilic and hydrophobic systems.

Tailored or engineered kaolins to enhance specific properties such as opacity, gloss, ink, holdout, brightness, whiteness, and print quality can be produced by special processing. These tailored products are increasing because of the demands of the coated paper manufacturers.

Calcined kaolins are value-added products used particularly by the paper and paint industries to extend titanium dioxide. There are three general categories of calcined kaolins: meta-kaolins calcined at about 650°C, mullite/spinel calcined at about 1050°C, and refractory grog calcined at about 1300°C. The major use of the meta-kaolin type of calcined product is as a filler in plastics used for wire coating. The meta-kaolin grade has a high dielectric capacity and good thermal insulating property. The mullite/spinel-calcined product has by far the largest use. The cost of titanium dioxide is very high (approximately \$1 per lb) and the mullite/spinel grade can replace 50% to 60% of the TiO₂ with little or no loss in opacity and brightness. These calcined grades have a high brightness (92 to

95), good opacity, and a relatively low abrasion. The cost is about one fifth of the cost of TiO_2 . The calcined kaolin that is used as a refractory grog is calcined at a high temperature to reduce shrinkage and to increase the refractoriness. This product is a granular product, whereas, the other two calcined products are pulverized to a fine particle size. As the price of TiO_2 continues to escalate, the more calcined kaolin will be used as an extender in paper coating and filling and in paint formulations.

Another growth area for industrial kaolin is in value added surface-treated products. Kaolins are hydrophilic and are easily dispersed in water by using small amounts of a chemical dispersing agent such as sodium hexametaphosphate or sodium polyacrylate. Ionic and/or polar non-ionic surfactants can be applied to the surface of the kaolin to make it hydrophobic or organophilic (Iannicelli, 1991). These surface-modified kaolins are used in the plastics and rubber industries to improve the dispersion and thus produce a more functional filler.

3. Smectites

The smectite group of clay minerals consists of several clay minerals, but the two most important industrially are sodium montmorillonite and calcium montmorillonite (Elzea and Murray, 1994). The most common occurrences of these two smectite minerals is in bentonite, a clay altered from glassy igneous material such as a volcanic ash or tuff (Grim and Guven, 1978). As shown in Table 1, smectites have very different properties than kaolins. Both the octahedral and tetrahedral sheets can have substitutions, which creates a charge imbalance in the 2:1 layer. Alumina substitutes for silica in the tetrahedral sheet and iron and magnesium substitute for aluminum in the octahedral sheet. Grim (1962) reported that many analyses have shown that the charge imbalance in smectite is about 0.66 per unit cell. This net positive charge deficiency is balanced by exchangeable cations absorbed between the unit layers and on the edges. If the dominant exchangeable cation is sodium, then the mineral in the smectite group is sodium montmorillonite, and if it is predominantly calcium it is calcium montmorillonite.

The high layer charge, the very fine particle size, the thin flakes, the high cation exchange capacity, and the high surface area result in the physical and chemical properties that determine the many industrial applications, the more important of which are shown in Table 3.

Fine particle size (Fig. 2), high layer charge, and large surface area of sodium montmorillonite when dispersed in water results in a very high viscosity and thixotropy. This along with the high swelling capacity makes the sodium montmorillonite the most important and necessary ingredient in fresh water drilling muds (Elzea and Murray, 1990). This market fluctuates with the price of

Table 3
Traditional applications of smectites

Drilling mud	Bleaching clay	Emulsions stabilizers
Foundry bond clay	Agricultural carriers	Desiccants
Pelletizing iron ores	Cat box absorbents	Catalysts
Sealants	Adhesives	Cosmetics
Animal feed bonds	Pharmaceuticals	Paint

crude oil. When oil prices are low, exploration and development are curtailed and so this market for sodium montmorillonite drops off. Conversely, when the price of crude oil is high, the market increases.

The molding sands used in foundries for molten metal consist of quartz and from 5% to 12% bentonite, plus some additives. The bentonite provides bonding strength and plasticity. A small amount of tempering water (3% to 5%) is added to the sand–bentonite mixture to make it plastic and to give it enough green compression strength to maintain its shape after the mold pattern is removed. Both sodium and calcium montmorillonite are used as foundry bond clays. Calcium montmorillonite has a higher green strength, lower dry strength, lower hot strength, and better flowability than sodium montmorillonite (Grim and

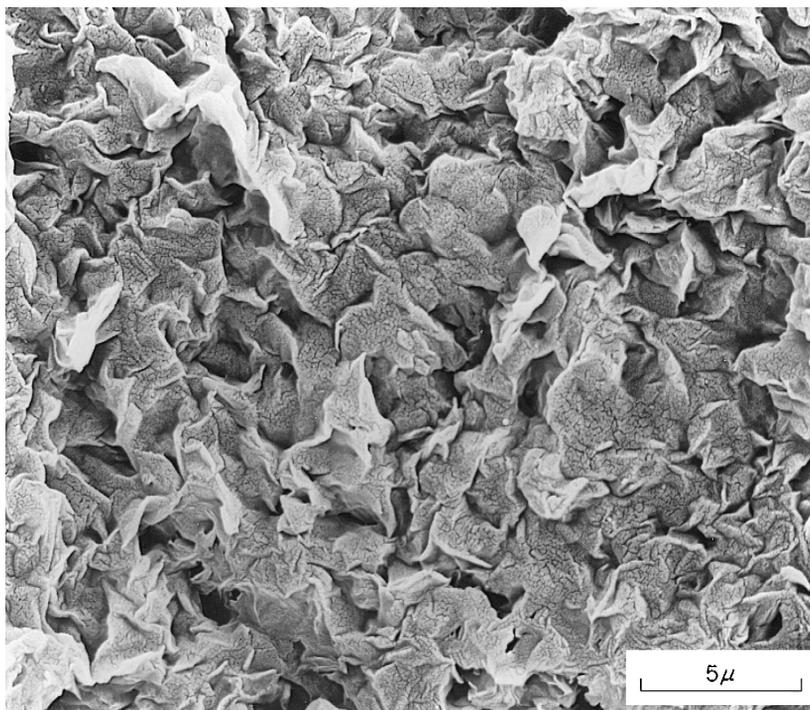


Fig. 2. SEM of sodium montmorillonite showing very fine particle size.

Güven, 1978). Therefore, blends of sodium and calcium montmorillonite are commonly used to gain the optimum properties for the molding sand, which is needed for a particular metal. The foundry sand market is mature and the growth is linked to increases in the various national economies.

Sodium montmorillonite, because of its superior dry strength, is used extensively to pelletize pulverized iron ore concentrates. This is done for ease of handling for shipment and to produce a superior furnace feed. Because many iron and other metal ores must be beneficiated to remove impurities, they are pulverized. The pulverization frees the impurities so they can be removed by magnetic separation, flotation, or another beneficiation process. The pulverized concentrate is then pelletized using 1 wt.% or less of sodium bentonite. This market is growing because more and more iron ores must be beneficiated to meet the iron percentage required for furnace feed.

Because of the high swelling capacity of sodium montmorillonite, this particular smectite is used in applications requiring barriers to water movement. Examples are earthen dams, liners for irrigation ditches, to prevent seepages and leaks in ponds, and to contain chemicals and toxic wastes in landfills (Keith and Murray, 1994). This is a growing market area for sodium montmorillonites to conserve water and to prevent contamination of water supply and aquifers.

Another growing use of high swelling sodium montmorillonite is in the slurry-trench or diaphragm-wall method of excavation in construction where unconsolidated soils and rocks are encountered (Lang, 1971). In this application, the trench being excavated is filled with bentonite slurry and the earth material being excavated is lifted through it. A thin filter cake on the walls of the trench prevents loss of fluid and the hydrostatic head of the slurry prevents caving and running of loose soil and sands, which makes costly shoring unnecessary.

Both sodium and calcium bentonites are used in binding animal feed into pellets. In addition to their binding ability, these minerals act as absorbents for bacteria and certain enzymes, which when removed promote the growth and health of the animal. Another large and growing use for both calcium and sodium montmorillonites is as a pet waste absorbent. This large market uses granules of calcium bentonite, which may be treated with deodorants and bacteriacides. A variety called clumping litter uses a mixture of calcium bentonite granules and sodium bentonite. The sodium bentonite swells and clumps when the waste moisture contacts the litter, which makes for selective and easy removal from the litter box.

Another large market for calcium montmorillonite is the decolorization of vegetable, animal and mineral oils. Most of the calcium bentonite used for filtering and decolorizing oils is acid activated (Odom, 1984). Acid treatment with sulfuric or hydrochloric acid removes the calcium ions from the surfaces and edges of the layers, which increases the overall negative charge. This makes the acid-activated clay more effective in removing anionic color bodies from the oil. A moderately large amount of natural smectite clay is used to remove

colloidal impurities in wine. These colloidal impurities are positively charged and are attracted and coagulated by the negatively charged smectite clays. Sodium montmorillonites having a light or white color with high dispersability are preferred for use in the clarification of wine, beer, vinegar, and fruit juices. A relatively new market for acid activated clay is in animal feed where it absorbs mycotoxins.

Both calcium and sodium bentonites are used as carriers for agricultural insecticides. This is a growing market because of the need to increase the production of grains used for food supply as the world's population increases.

A value added market for sodium montmorillonite is the use of organoclays. The exchangeable sodium ions are replaced with organic cationic molecules such as alkylamines (Rausell-Colom and Serratosa, 1987) and produce a hydrophobic surface. These organic-clad sodium montmorillonites are used as thickeners in paints, oil-based drilling fluids, to gel various organic liquids, to stabilize the gel properties of lubricating greases, and to thicken and gel certain cosmetics. This latter use requires a water-washed high brightness sodium montmorillonite as a starting material.

Another value added market for sodium montmorillonite is to make pillared clays, which can be tailored for specific catalyst and absorbent uses. Interlayer reactions using sodium montmorillonite are restricted to low temperatures because at high temperatures ($> 200^{\circ}\text{C}$) the layers collapse. By intercalating thermally stable cations the layers are propped apart. By varying the size of the pillar and/or the spacing between pillars, the pore size and space can be adjusted to suit a particular application. Hydroxy-aluminum and zirconium cations have yielded thermally stable clays with surface areas of 200 to 500 $\text{m}^2 \text{g}^{-1}$ and interlayer free spacings near 9 Å (Rupert et al., 1987). This relatively recent development will result in many new industrial markets because of the need to absorb and catalyze many toxic ions, anions, and chemicals to prevent their release into groundwater, soils, and the atmosphere.

Another recent development using sodium montmorillonite is the separation of the unit layers into almost unit cell thicknesses for use in plastic compositions called nanocomposites. These extremely thin, platy particles are exchanged using organic molecules to interact with the plastic polymers to produce very strong and heat resistant products. These nano-particles are currently being utilized in certain automotive plastic components and in plastic food wrappings and packaging.

4. Palygorskite and sepiolite

Palygorskite and attapulgite are synonymous terms for the same hydrated magnesium aluminum silicate mineral. The preferred name as specified by the International Nomenclature Committee is palygorskite but the name attapulgite

is so well entrenched in trade circles that it continues to be used by many producers and users. Sepiolite is almost structurally and chemically identical to palygorskite except it has a slightly larger unit cell.

The term fuller's earth is used to describe clays which have sorptive and bleaching qualities, so both palygorskite and some smectite clays (particularly calcium montmorillonite) are also called fuller's earth. Table 1 lists the important properties of palygorskite, which relate to its traditional industrial utilization. A most important property is its elongate shape (Fig. 3), which as seen in many of the applications described below, is a controlling physical property.

There is considerable substitution of aluminum by magnesium and iron in the octahedral layer, which gives the particles a moderately high layer charge. This layer charge and the high surface area give palygorskite an intermediate cation exchange capacity normally about 30 to 40 meq/100 g. The high surface area, the charge on the lattice, and the inverted structure, which leaves parallel channels through the lattice, give palygorskite and sepiolite a high absorption capacity. This, along with the elongate habit of the minerals, makes them particularly useful in many industrial applications. The high viscosity of liquids into which the palygorskite is added is a physical and not a chemical viscosity, and thus makes for a very stable viscosity of the suspensions.

The more important industrial uses of palygorskite and sepiolite are listed in Table 4 (Heivilin and Murray, 1994).

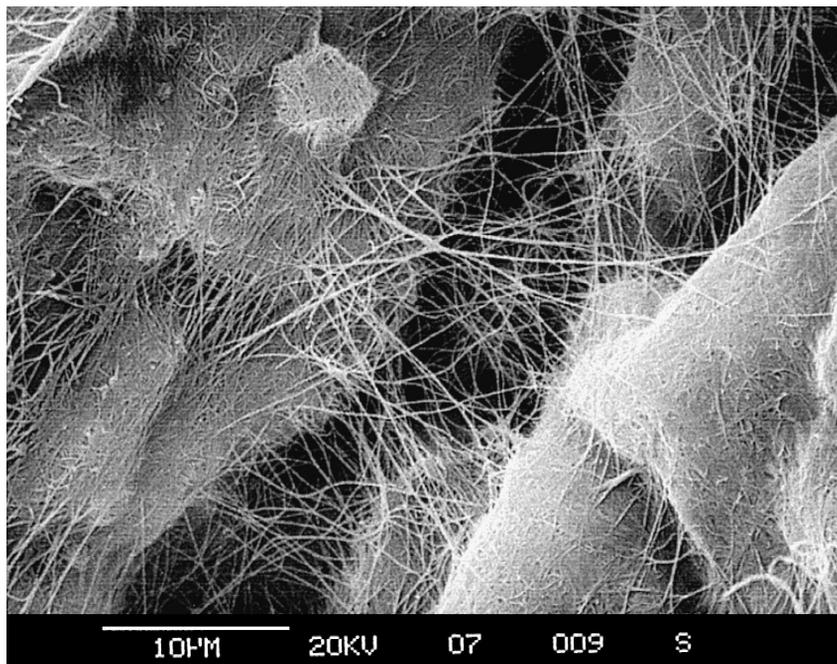


Fig. 3. SEM of palygorskite showing elongate particle shape.

Table 4
Traditional applications of palygorskite and sepiolite

Drilling fluids	Cat box absorbents	Paper
Paint	Suspension fertilizers	Pharmaceuticals
Agricultural carriers	Animal feed bondants	Anti-caking agent
Industrial floor absorbents	Catalyst supports	Reinforcing fillers
Tape joint compounds	Adhesives	Environmental absorbent

Galan (1996) recently reviewed the properties and applications of palygorskite–sepiolite clays and showed the relationship between the structure, composition, and physical properties to their industrial applications. As pointed out in Table 4, these two minerals have a variety of applications, which has resulted in sizeable annual production from the major deposits in the world (Murray, 1995). One of the largest uses of both of these minerals is as viscosity builders in drilling muds. The major advantage of palygorskite- and sepiolite-based drilling muds over sodium bentonite-based drilling muds is their insensitivity to salt water and other electrolytes. Sodium bentonite drilling muds become flocculated when salt water brines are present and drain into the drilling fluid. Sepiolite is the only clay mineral that is stable at high temperatures and for this reason it is also used in drilling muds for geothermal wells.

The colloidal or gel grades of palygorskite and sepiolite generally involve thickening or gelling and are used in paints, adhesives, sealants, fertilizer suspensions, and cosmetics. The largest growth market for the future is the fertilizer suspension application. Suspension fertilizers are fluid mixtures of solid materials suspended in concentrated fertilizer solutions, which are gel-like and stable over extended time periods of perhaps 1 or 2 months. These gels can be readily redispersed with mild agitation to be fluid enough to be pumped and applied uniformly to the soil. The premier suspending clay is palygorskite (attapulgite) because of its stability due largely to its elongate particle shape. This market is rapidly growing because of the ease of application using standard liquid fertilizer equipment and the higher concentrations of nutrients that can be carried in the suspension.

Palygorskite and sepiolite are excellent absorbents and are used in many traditional applications that utilize this particular physical property. The major markets are industrial floor absorbents, agricultural carriers, cat litter, anti-caking agents, and environmental absorbents (Murray, 1995). These applications, except for the use as an environmental absorbent, utilize granular material in the range from 20 to 50 mesh size. The cat litter market continues to grow, particularly in North America and Europe. A minor market that utilizes the good absorption property is as a natural decolorizing agent, particularly for mineral oils, because the colored components are simpler than those in vegetable oils (Galan, 1996).

The good absorbent properties and the elongate shape make palygorskite and sepiolite very useful for environmental applications as barrier clays. In landfills and toxic waste impoundments, a mixture of palygorskite and sodium montmorillonite works well to prevent movements of liquids through the barrier and to absorb heavy metals and toxic pollutants. Sodium montmorillonite flocculates easily and shrinks in the multiple drying and wetting cycles that the barrier undergoes. The palygorskite does not flocculate and so it maintains a constant volume that prevents permeability.

Another large and growing use for palygorskite is in tape joint compounds used to fill cracks and joints in wallboard. The tape joint compound must form a level and smooth surface that does not shrink on drying. The adhesive filled with palygorskite is the best for this application because it forms a smooth surface and does not shrink.

Other uses for palygorskite and sepiolite are reinforcing fillers in rubber and plastics, suspending agents in pharmaceutical products, animal feed bondants and supplements, catalyst supports, and as a coating material on no carbon required copy paper. In these applications, the elongate shape and/or the high absorbency are the physical properties that make palygorskite and sepiolite particularly functional. There have been studies reported in the literature that these absorbent clays, when used as an animal feed supplement, result in increased weight gains for chickens and farm animals (Galan, 1996).

5. New and increased applications resulting from improved processing

Over the past 30 years, many new and improved processes have become available, which has resulted in higher quality and more uniform clay products. This has expanded the traditional applications and has resulted in new applications. Another very important factor is that this new and improved process technology has allowed the use of marginal and sub-marginal crude clays, which has substantially increased the reserve bases of these traditional industrial clays. Also, improved mining techniques and equipment has resulted in the extraction and recovery of more useable clay from the mines.

As has been evidenced over and over again in the mining industry with the passage of time, improved mining and processing technology has permitted the recovery and use of lower grade ores. This is certainly true in the kaolin clay industry and also in the sodium bentonite industry. The process equipment manufacturers and the process engineers in the clay companies have made some outstanding innovations in process equipment and technology over the past 30 years in particular. Special and improved processes that are available to beneficiate clays are shown in Table 5.

Many of these processes have been described in the literature (Pickering and Murray, 1994; Prasad et al., 1991), so only air classification, calcination,

Table 5
Special and improved processes applicable to clay beneficiation

Acid activation	Dewatering	High intensity blunging
Air classification	Dispersion	Hydrocyclones
Blending	Drying	Magnetic separation
Calcination	Electrostatic separations	Organoclaying
Centrifuging	Extrusion	Oxidation
Chemical leaching	Flocculation	Pulverization
Computer controls	Flotation	Surface treatments
Delamination	Granular sizing	Wet and dry screening

flocculation, flotation, and magnetic separation will be described in this paper. Air classification is used in the dry processing of kaolin, bentonite, and palygorskite–sepiolite to remove quartz, mica, and other non-clay minerals and to produce various size fractions. This process has been significantly improved so that size classifications of -44 , 20 , 10 and $5 \mu\text{m}$ can be produced.

The calcination process is used in the kaolin industry to produce value added special grades for use in filling plastic for coating electrical wires, in paint to extend TiO_2 , in both paper coating and paper filling to extend TiO_2 and for improved brightness and opacity, and as a very fine abrasive for use in polishes. Calciners with very good temperature control have been developed for use in the kaolin industry and the kaolin companies have developed specially processed clays to feed the calciners to produce high brightness, good opacity, and low abrasion calcined grades.

Flocculation is an important process used in the wet processing of both kaolins and bentonites in order to improve filtration rates. The most common flocculants used are sulfuric acid and/or alum, and long chain polyacrylates. Special selective flocculation processes have been developed in the kaolin industry, (Attia, 1982) particularly for fine particle size crude clays. These processes normally flocculate the kaolinite and leave the iron and titanium contaminants in suspension. The kaolin products have a high brightness (90% to 93%) and a low *b*-value or yellowness factor.

Flotation is now a common process used by kaolin producers to make high brightness products. This process is particularly applicable to relatively coarse (60% to 75% finer than $2 \mu\text{m}$) clays. Again, the primary purpose of the flotation process is to remove titanium and iron impurities that affect the brightness of the final product (Prasad et al., 1991). Typically, if the kaolin feed to the flotation process contains 1.8% TiO_2 , the product will be reduced to 0.3% to 0.5% TiO_2 . Both column and flotation cells are used to produce the high brightness kaolin products.

High intensity wet magnetic separation is now a standard process used in the kaolin industry and will be used in the future in special white bentonite processing. Over the past 30 years, significant improvements have been made in

the design and field strength of the magnetic separators. Large cryogenic magnets with field strengths as high as 10 T have been developed and are available as process units. Also, the canisters through which the slurry passes have been improved both as to the flow distribution and the steel wool matrix used to fill the canister. The power requirements for the magnets have been very significantly reduced and some separators have been designed with two canisters, which permit operation on a continuous basis rather than using one canister, which must be cleaned periodically using a rinse cycle. Again, the purpose of wet magnetic separation is to remove iron, titanium, pyrite, mica, and other paramagnetic mineral particles, which are deleterious to making high brightness products.

New and improved process equipment for both wet and dry processing is continually being developed. This will enable clay producers to make both new and improved products. For example, a recent modification in the process used to produce organoclay is the use of homogenizers to significantly improve the quality and uniformity of the product. Innovative and new process developments will continue to be made in order to process kaolins, smectites, and palygorskite–sepiolite more effectively for both traditional and new applications (Murray, 1999a,b; Harvey and Murray, 1997).

6. Summary

The traditional applications for the industrially used clays kaolin, smectite and palygorskite–sepiolite will continue to grow at a rate equivalent to the growth of national products. In addition, because of improved processes and processing equipment that are now available to the clay industry, and because of active applied research and development, new products and applications will be developed. Clays are natural products so their cost effectiveness will continue to be lower than any synthetic competitive materials, which might be developed in the future. The future outlook well into the next century is very positive.

References

- Attia, Y.A., 1982. Fine particle separation by selective flocculation. *Sep. Sci. Technol.* 17, 485–493.
- Elzea, J.M., Murray, H.H., 1990. Variation in the mineralogical, chemical and physical properties of the cretaceous clay spur bentonite in Wyoming and Montana (USA). *Appl. Clay Sci.* 5, 229–248.
- Elzea, J.M., Murray, H.H., 1994. Bentonite. In: Carr, D.D. (Ed.), *Industrial Minerals and Rocks*. 6th edn. Society for Mining, Metallurgy and Exploration, Littleton, CO, pp. 233–246.
- Galan, E., 1996. Properties and applications of palygorskite–sepiolite clays. *Clay Miner.* 31, 443–445.

- Grim, R.E., 1962. *Applied Clay Mineralogy*. McGraw-Hill, New York.
- Grim, R.E., Guven, H., 1978. Bentonites — geology, mineralogy, properties and uses. *Developments in Sedimentology* 24, Elsevier, New York.
- Harvey, C.C., Murray, H.H., 1997. Industrial clays in the 21st century: A perspective of exploration, technology and utilization. *Appl. Clay Sci.* 11, 285–310.
- Heivilin, F.G., Murray, H.H., 1994. Hormites: palygorskite (attapulgite) and sepiolite. In: Carr, D.D. (Ed.), *Industrial Minerals and Rocks*. 6th edn. Society for Mining, Metallurgy and Exploration, Littleton, CO, pp. 249–254.
- Iannicelli, J., 1991. Polymer reinforcement with amino and mercaptosilane grafted kaolin. *Miner. Metall. Process.* 8, 135–138.
- Keith, K.S., Murray, H.H., 1994. Clay liners and barriers. In: Carr, D.D. (Ed.), *Industrial Minerals and Rocks*. 6th edn. Society for Mining, Metallurgy and Exploration, Littleton, CO, pp. 435–452.
- Lang, W.J., 1971. Bentonite: The Demand and Markets for the Future. Society of Mining Engineers of AIME, Preprint Number 71-H-29, Littleton, CO.
- Murray, H.H., 1986. Clays. *Ullmann's Encyclopedia of Industrial Chemistry* A7. 5th edn. VCH Verlagsgesellschaft, Weinheim, pp. 109–136.
- Murray, H.H., 1995. Clays in industry and the environment. *Proc. 10th International Clay Conference Adelaide, Australia*. pp. 49–55.
- Murray, H.H., 1999a. Applied clay mineralogy today and tomorrow. *Clay Miner.* 34, 39–49.
- Murray, H.H., 1999b. Clays for our future. *Proc. 11th International Clay Conference, Ottawa, Canada*, pp. 3–11.
- Murray, H.H., Keller, W.D., 1993. Kaolins, kaolins and kaolins. In: Murray, H.H., Bundy, W.M., Harvey, C.C. (Eds.), *Kaolin Genesis and Utilization*. The Clay Minerals Society, Boulder, CO.
- Odom, I.E., 1984. Smectite clay minerals: properties and uses. *Philos. Trans. R. Soc. London, Ser. A* 311, 391–409.
- Pickering, S.M. Jr., Murray, H.H., 1994. Kaolin. In: Carr, D.D. (Ed.), *Industrial Minerals and Rocks*. 6th edn. Society for Mining, Metallurgy and Exploration, Littleton, CO, pp. 255–277.
- Prasad, M.S., Reid, K.J., Murray, H.H., 1991. Kaolin: processing, properties and applications. *Appl. Clay Sci.* 6, 87–119.
- Rausell-Colom, J.A., Serratosa, J.M., 1987. Reactions of clays with organic substances. In: Newman, A.C.D. (Ed.), *Chemistry of Clays and Clay Minerals*. Mineralogical Society, London, pp. 371–422.
- Rupert, J.P., Granquist, W.T., Pinnavaia, T.J., 1987. Catalytic Properties of Clay Minerals. In: Newman, A.C.D. (Ed.), *Chemistry of Clays and Clay Minerals*. Mineralogical Society, London, pp. 275–318.