# CHARACTERIZATION OF BALL CLAYS FROM TABAS-IRAN FOR THE CERAMIC INDUSTRY

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**ABSTRACT** The characterization of clays from the mineralogical, chemical and technological viewpoints, in pre- and within-mining stages is a necessary step. This study is focused on the ball clays with ceramic application which are exploited from three mines in Tabas area-Yazd province. The chemical and mineralogical compositions of ball clays were determined by wet chemical analysis, XRD and SEM methods, respectively. Technological test samples have been prepared by pressing and then firing in an industrial kiln. Linear shrinkage, water absorption, fired color and fired bending strength were measured in order to characterize the ball clays after firing.

The mineralogical studies show that the ball clays are composed predominantly of kaolinite, illitic mica, and fine quartz, with different amounts of carbonaceous materials and minor amounts of pyrophillite, anatase, diaspore and gypsum. The chemical analysis results indicate that the studied ball clays are characterized by high $SiO_2$ contents ranging from about 62.5% to 72.6%, low to medium $Al_2O_3$ contents ranging from about 16% to 21.6%, low to high LOI contents ranging from about 5.7% to 7.5% and intermediate $SO_3$ contents between about 0.3% to 1%. The average values of $Na_2O$, $K_2O$, CaO, $Fe_2O_3$ and $TiO_2$ are around 0.5%, 2.3%, 0.4%, 1.1% and 1.4%, respectively. The technological tests clear that varicolored ball clays have different technological characteristics. Furthermore, almost all characteristics of the studied ball clays demonstrate the industrial suitability of Tabas ball clays as a potential ceramic raw material for the growing Iranian ceramic industry.

*Keywords: Characterization, Ball clay, Ceramic industry, Tabas, Iran*

## 1 INTRODUCTION

Ball clay has been defined technically as fine-grained sedimentary plastic clay in which the clay mineral kaolinite predominates. This clay is used as raw material in many industrial fields such as ceramics and refractory industry. Its application is dependent on mineralogical and chemical composition and physicomechanical properties (Baccour et al. 2008). In the ceramic industry, investigation of these properties is very important for indicating consumption amount of ball clay and optimization of ceramic production. Therefore, the characterization of ball clays from the mineralogical, chemical and technological viewpoints, in pre- and within-mining stages is a necessary step.

In the ceramic industry of Iran two production sectors, including tile and sanitaryware industries, are the main consumers of ball clay. According to the Iranian Ministry of Industries & Mines (IMIM) reports, ceramic industry of Iran presented a rapid growth since 1993. So that, in 2010, Iranian ceramic tile industry grew about 680% with production of 250 million square meters as compared with production in 1993. The production of Iranian sanitaryware industry was about 69000 tons in 2010. In addition, the nominal production capacity of tile and sanitaryware industries in the country was about 380 million square meters and 88000 tons per year respectively (IMIM 2010).

In Iran one of the most important locations in which ball clay deposits have been formed is Tabas area in the northeast of Yazd province, central Iran. The ball clays from Tabas area were studied for supplying refractory raw materials at the past years and then were neither tested for ceramics production nor characterized. Thus, to investigate the suitability of these ball clays for manufacturing ceramic bodies, especially ceramic tile bodies is of interest from an academic and technological viewpoint. The objective of this work is characterization of the Tabas ball clays by determining their mineralogical, chemical, physicomechanical and fired properties.

## 2 MATERIALS AND METHODS

The Tabas ball clay deposits are located about 115 km southwest of the town of Tabas, in the northeast of Yazd province, central Iran (Fig. 1). The studied ball clays come from three mines which have been locally known as Chahbid, Chahkular and Cheshmeh mines. The mines areas cover area of around 120 km$^2$ totally. Total reserves (proven and probable) are about 3 million tons as given exploration reports of Suravajin Aghigh Mining & Industrial Co. (SAMICO), owner of these mines. This company operates 15 quarries with production capacity about 100,000 tpy (SAMICO 2010).

Four bulk samples (weight of each one about 30 kg) were collected from the related stockpiles of mentioned mines, including ARK-10 from Chahbid mine, ARK-50 from Chahkular mine, ARK-20 and U1 from Cheshmeh mine. The samples were blended and homogenized thoroughly and then quartered into about 3 kg sub-samples for laboratory studies including characterization study and technological tests. The sub-samples were dried at 110 $^oC$ for 24 h, manually crushed, grounded, sieved and classified to required particles.


Figure 1. Location of Tabas ball clay deposits in Iran

The mineralogical analyses of the ball clay samples were carried out by X-ray diffraction method (XRD) using a Siemens D-5000 diffractometer, CuKα radiation, both on powder (bulk samples) and oriented specimens (air dried and treated with ethylene glycol for 1 h and heated to 550 $^oC$ for 2 h) of the clay(<2 μm) fraction (Moore and Reynolds 1997). The detailed mineralogical study of the ball clay samples and investigation of their microstructure or microtexture were examined by scanning electron microscopy (SEM, VEGA//TESCAN), and the compositions of minerals were determined qualitatively by this SEM instrument which was equipped with an energy dispersive X-ray spectrometer (EDS). The accelerating voltage was 15 kV for secondary electron imaging and elemental analysis. The SEM specimens were prepared by placing the separated samples on metallic sample holders and coating them with gold. The chemical analyses were obtained by wet-chemical analysis method.

To operate technological tests, the samples were ground to fine powders and then the fine powders were humidified (6 mass% moisture content), homogenized and pressed at 300 kg/cm$^2$ giving specimens of 100×50×5 $mm^3$ by using a laboratory press. The shaped green specimens were dried at 110 °C for 24 h until constant mass was achieved. The dried bodies were characterized by the measurement of drying shrinkage and bending strength. The firing step was carried out in commercially kiln at the tile plant within firing cycle of total 60 min (cold-to-cold). During firing, the heating and cooling rates were kept at 80 °C/min and at 90 °C/min, respectively. The specimens were maintained at about 1200 °C for 15 min. Firing characteristics including shrinkage, water absorption, and bending strength were measured. The bending strength was carried out using the three-point bending test and calculated by $3FL/2bh^2$ equation in which F=breaking load (kg), L=distance between supports (mm), b=sample with (mm) and h=sample thickness (mm). The dimensions of the pressed specimens were measured before and after firing to determine the firing shrinkage by $100(L_d-L_f)/L_d$ equation, where $L_d$=the length of the dried specimen and $L_f$=the length of the fired specimen. The water absorption values were determined by the routine procedure involving measuring mass differences between the as-fired and water saturated samples (immersed in boiling water for 2 h, cooling for 3 h and sweeping of their surface with a wet towel).

## 3 RESULTS AND DISCUSSION

### 3.1 Mineralogy

Table 1 and Figs. 2 show the XRD analysis results and X-ray diffraction patterns of the studied samples, respectively. The principal components of Tabas ball clays are disordered to ordered kaolinite, illitic mica (or illite/muscovite) and fine quartz. The main minor impurities or accessory minerals are carbonaceous material (probably lignite), pyrophillite, anatase, diaspore and gypsum. The most significant impurity, particularly in the black ball clay (such as U1) is lignite.
The reflections with d=7.21 Ǻ and 3.57 Ǻ for the <2 μm fraction disappeared after heating to 550 °C. This confirms the presence of kaolinite which is transformed into metakaolinite above 450 °C in samples (Brindley and Brown 1980). After glycol addition, there wasn't showed any changes in the XRD patterns of studied samples. It demonstrates that the samples don't contain expandable clay minerals, such as montmorillonite.

Table 1. Mineralogical composition of the studied ball clays

| Sample | Clay minerals | Associated minerals |
|---|---|---|
| U1 | Kaolinite, illite | Quartz, anatase |
| ARK-50 | Kaolinite, illite, pyrophillite | Quartz, gypsum, anatase |
| ARK-20 | Kaolinite, illite | Quartz, anatase |
| ARK-10 | Kaolinite, illite, pyrophillite | Quartz, gypsum, anatase, diaspore |

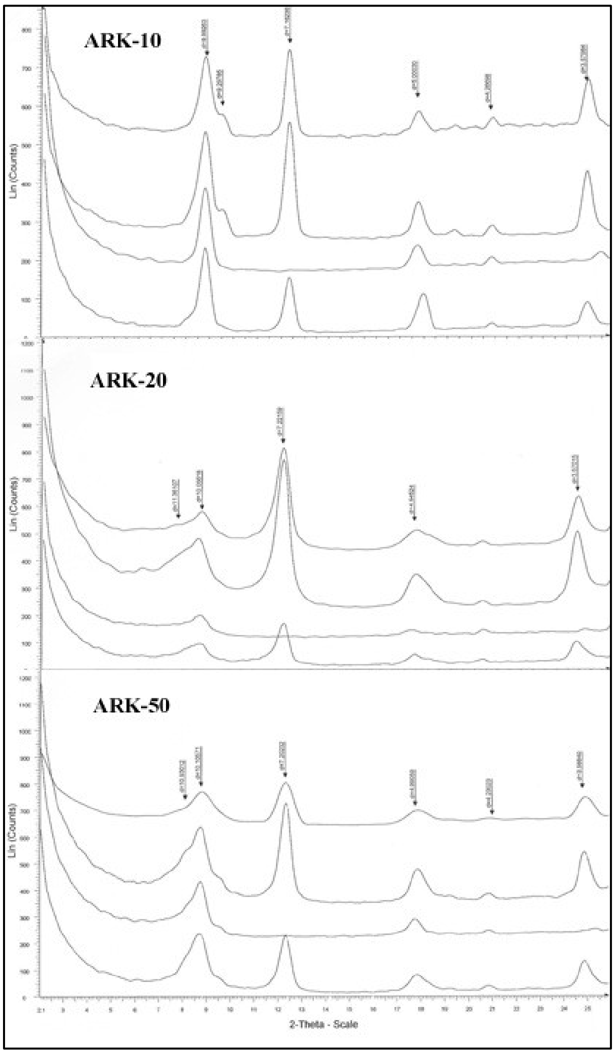


Figure 2. X-ray diffraction patterns of the studied ball clays

Selected samples (one black ball clay sample U1 and one light gray ball clay sample ARK-10) were analyzed by SEM for studying their detailed mineralogy, morphology (or microstructure) and size. SEM-EDS of selected samples/particles gave the microanalysis data on their qualitative and semi quantitative chemical composition. The studied ball clays have agglomerates of fine clay particles of ~2 μm size. The U1 (Fig. 3) and ARK-10 (Fig. 4) have stacks of very small kaolinite and illite platelet particles. Kaolinite particles are mostly observed as pseudo hexagonal irregular edged particles with ideal composition (Al/Si ratio ~1.0) as confirmed by the EDS analysis of particles (Fig. 5). These particles also possess a little K, Fe and Mg contents. The kaolinite predominantly possesses the Al/Si ratio comes close to 0.9:1 which is nearer to that of the ideal kaolinite 1:1. The K content in the kaolinite is very low, whereas the illite particles contain high K (Figs. 6). In addition to mentioned clay minerals, the submicron sized carbonaceous material and diaspore particles separated from the clay minerals are identified in the samples. Single crystals of diaspore are observed some of which are partly very fine granular.

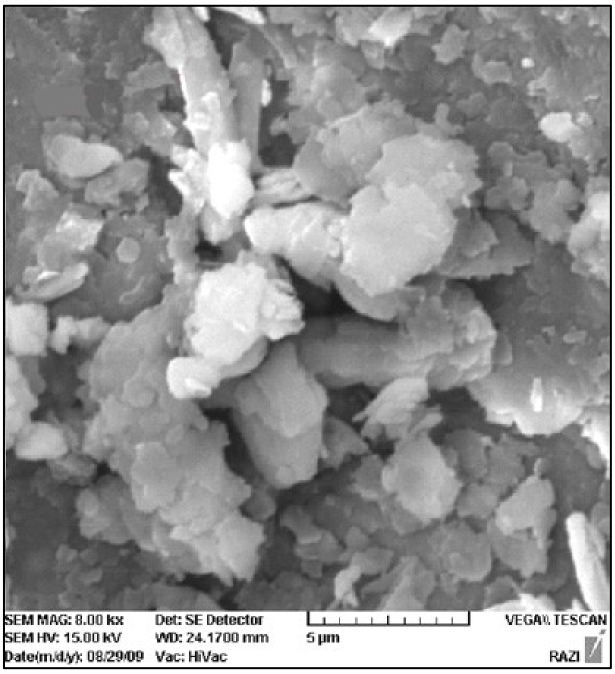


Figure 3. SEM photomicrograph of U1 ball clay sample which shows platelet particles of kaolinite and illite minerals

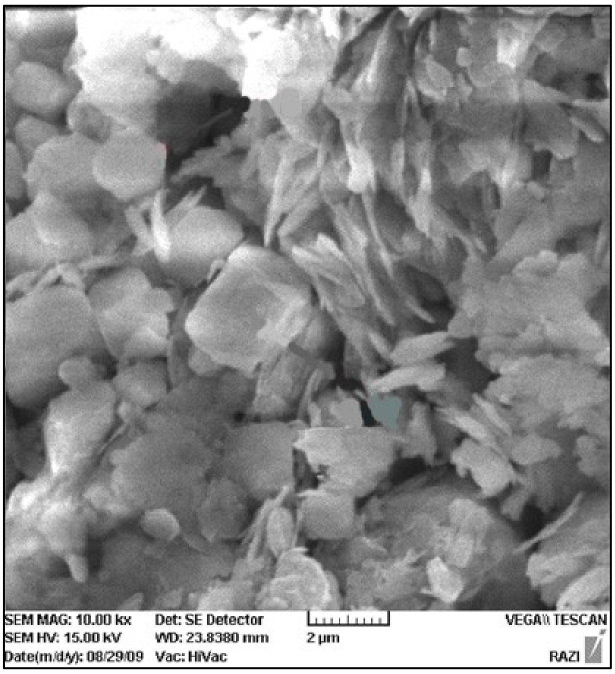


Figure 4. SEM photomicrograph of ARK-10 ball clay sample which shows platelet particles of kaolinite and illite minerals

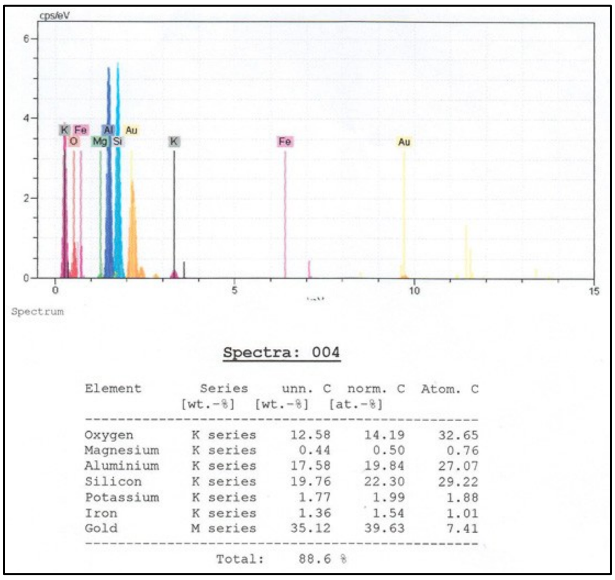


Fig. 5. EDS analysis of kaolinite

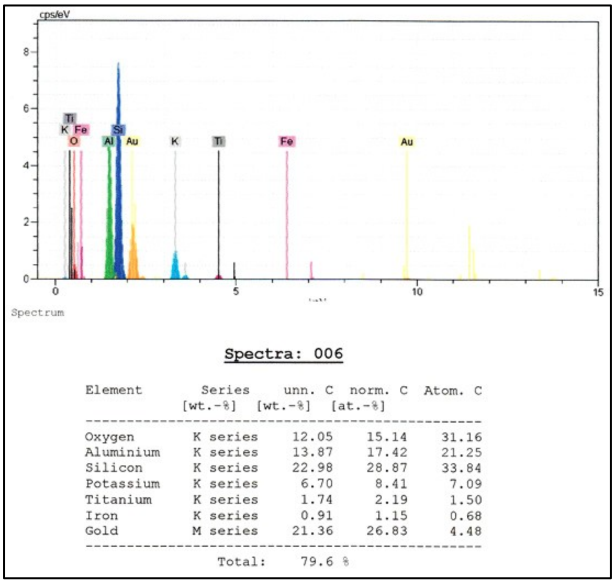


Fig. 6. EDS analysis of illite

The mineralogical differences in the ball clay have great influence on its technological characteristics and behavior of ceramic products, in respect to their rheological and thermal properties, as well as the porous structure of the fired products (Celik et al. 2009).

### 3.2 Chemical Composition

The chemical compositions of studied samples are showed in table 2. The Al2O3 and SiO2 contents in the samples range from about 16 to 21.6% and 62.5 to 72.6% respectively. The amount of alkaline oxides ($K_2O$+$Na_2O$) that acting as flux materials is about 2.75% cause to the amount of illite. The amount of CaO and MgO is low for all ball clays and indicate the absence of carbonates. The relatively high loss on ignition (average about 6.7%) associated with high $SiO_2$ and low $Al_2O_3$ contents are due to the significant content of quartz, low amount of clay minerals and high amount of carbonaceous material in the samples. The average of $Fe_2O_3$ and $TiO_2$ values are around 1.1% and 1.4% respectively. Besides their fluxing role, $Fe_2O_3$ and $TiO_2$ also provide the fired products the characteristic reddish color. However, these oxides are not the only factors responsible for the coloration of ceramicwares, as also other constituents such as CaO, MgO and MnO can appreciably modify the color of fired clays. Furthermore, the temperature of firing, the amount of $Al_2O_3$ relative to a range of other constituents, and the furnace atmosphere all play an important role in the development of color in the fired clay products.

Table 2. Chemical composition (wt %) of the studied ball clays

| Sample | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | $TiO_2$ | CaO | MgO | $Na_2O$ | $K_2O$ | $SO_3$ | LOI |
|---|---|---|---|---|---|---|---|---|---|---|
| U1 | 72.60 | 16.01 | 0.78 | 1.00 | 0.14 | 0.50 | 0.43 | 2.15 | 0.30 | 5.76 |
| ARK-50 | 66.76 | 19.05 | 0.75 | 1.47 | 0.44 | 0.70 | 0.65 | 2.50 | 0.60 | 6.27 |
| ARK-20 | 64.50 | 20.16 | 1.44 | 1.50 | 0.48 | 0.64 | 0.45 | 2.10 | 0.46 | 7.32 |
| ARK-10 | 62.50 | 21.65 | 1.58 | 1.52 | 0.49 | 0.60 | 0.44 | 2.30 | 0.90 | 7.55 |

### 3.3 Technological Tests

The studied ball clays show various drying and firing characteristics (Table 3). Their drying and firing strength values range from about 18 to 36 $kgf/cm^2$ and 460 to 780 $kgf/cm^2$ respectively. Three sample show high firing shrinkage around 10.5 to 12.5% and only one sample shows medium value about 5.5%. Two samples have high values of water absorption (5.5 & 6%) whereas other ones have low values (0.5 & 1.5%). The mineralogical and chemical characteristics of the ball clay samples were responsible for changing values of water absorption. The following characteristics can be highlighted: amount of $Al_2O_3$ and kaolinite clay mineral, amount of $K_2O$ and illite mineral, calcite and alkaline fluxes (Jordan et al. 2008). All samples have almost same fired color. The bony and creamy colors of samples can be attributed to amounts of iron and titanium oxide impurities.

Table 3. Technological tests results of studied ball clays

| Sample | Drying strength ($kgf/cm^2$) | Firing strength ($kgf/cm^2$) | Firing shrinkage (%) | Water absorption (%) | Fired color |
|---|---|---|---|---|---|
| U1 | 18.10 | 460 | 12.50 | 5.50 | Bony |
| ARK-50 | 23.50 | 470 | 5.5 | 6 | Bony |
| ARK-20 | 30.50 | 640 | 10.5 | 1.5 | Cream |
| ARK-10 | 36.05 | 780 | 10.7 | 0.5 | Cream |

## 4 CONCLUSIONS

Four ball clays from Tabas area, Iran, were characterized by chemical and mineralogical analysis. The ball clay contained mainly kaolinite, illite and fine quartz. The studied samples showed water absorption, firing shrinkage and bending strength values required for producing ceramic tile. Finally, Tabas ball clays have qualities necessary for the manufacture of ceramic floor tiles, and these clays are reliable alternative ceramic raw materials for the growing Iranian ceramic tile industry.

## REFERENCES


Baccour, H., Medhioub, M., Jamoussi, F., Mhiri, T., Daoud, A. (2008). Mineralogical evaluation and industrial applications of the Triassic clay deposits, Southern Tunisia. Mater. Charact. 59, pp.1613–1622.

Brindley, G.W., Brown, G. (1980). Crystal Structures of Clay Minerals and their X-ray Identification. Mineralogical Society.

Celik, H., Erturk, O., Day, N. (2009). Characterization of the clay in the region of Afyon and investigation of its utilization in ceramic floor tile bodies. Proceedings of the 7th Industrial Mineral Symposium and Exhibition. 25–27 February 2009. Kusadası, Izmir, Turkey, pp.1–7.

Iranian Ministry of Industries and Mining. (2010). Annual mining industries production report.

Jordan, M.M., Montero, M.A., Meseguer, S., Sanfeliu, T. (2008). Influence of firing temperature and mineralogical composition on bending strength and porosity of ceramic tile bodies. Applied Clay Science 42, pp.266–271.

Moore, D.M., Reynolds Jr., R.C. (1997). X-ray diffraction and the identification and analysis of clay minerals. Chapter 6. Sample preparation Techniques for clay minerals. Preparing the Oriented Clay Mineral Aggregate. Oxford University Press, p.214.

Suravajin Aghigh Mining and Industrial Company (SAMICO). (2010). R&D and exploration internal reports.