MINERALOGICAL AND CERAMIC INVESTIGATIONS ON A HIGH ALUMINA CLAY FROM SKESAR HILLS

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X-Ray, D.T.A. and other ceramic data are presented for a high alumina clay from Mianwali District. X-Ray studies revealed that the ore contains minerals boehmite, kaolinite and anatase. D.T.A. and other studies confirm the X-Ray findings. The mineral after calcination contains 72% Al_2O_3, thus having the highest percentage of alumina so far reported to occur in Pakistan. The mineral was found useful for ceramic purposes, such as for making high alumina refractories for lining in metallurgical, cement and glass furnaces. It could also be used for extracting alumina.

Introduction

The term 'high alumina clay' is used for those containing more than 47% of Al_2O_3, a larger portion than is contained in a calcined china clay, that is, 46.2%. Between this and the refractories made of almost pure alumina, a wide range of properties is possible. It is known that the pure grade of china clay has refractoriness equal to seger cone 34(1750), the high alumina clay should have refractoriness between this and the seger cone 42(2050°C.), the refractoriness of pure alumina.

The high alumina ores such as gibbsite, boehmite or diaspore are formed by weathering processes acting on alumina bearing igneous rocks, such as feldspar or clays. Usually these deposits occur in tropical or sub-tropical climates and are at or near the surface. They include not only the clay minerals but also a variety of impurities also ranging from discrete minerals to adsorbed ions, which, when present in excessive amounts, render the clay unsuitable for use as a refractory raw material. Fortunately, there appears to be at this time, in areas of Mianwali, adequate reserves of relatively pure and high alumina clays which are suitable for use without beneficiation.

Some information has been reported[1,2] on the properties of clays and their use in ceramics. This investigation was undertaken to determine the mineralogical nature and the ceramic characteristics that determine the refractory properties of the mineral.

Appreciable outcrops of clay favourable to the occurrence of high alumina clay, occur in Skesar Hills near Musakhel village, District Mianwali. The topography of the area is mostly hilly. The clay bearing strata are exposed in the shape of a vein with 10-12 miles in length, at some places mixed with iron and at others changing into a flint clay. Thickness varies from 5-20 feet. Idea of its width is not definite. It is believed that if surveyed thoroughly the deposits, with some variations, may continue throughout the salt range area. Three bags of clay from three different pits have been taken for study. The chemical analysis of all the three samples as shown in Table 1 are very similar. It was, therefore, decided to mix them together and to proceed further on a representative sample of the three.

Table 1.—Chemical Analysis of High Alumina Clay from Three Pits.

Clay No.	(1)	(2)	(3)
Loss on ignition	14.55	14.13	14.35
SiO_2	20.16	20.46	20.06
Al_2O_3	64.65	65.85	66.12
Fe_2O_3	0.18	0.39	0.33
CuO	0.46	0.32	0.16
MgO	0.47	0.28	0.09
TiO_2	2.91	2.98	3.11

Experimental

Some ceramic properties such as changes in colour, porosity, percent absorption, dimensions, specific gravity and cross breaking strength of the pieces fired to various temperatures, ranging from 1100°C. to 1500°C. have been investigated. Sintering vitrification and densification of the pieces have also been studied.

The chemical analysis and the softening temperature of the clay have been determined.

For the structural analysis of the mineral, a copper Kα radiation with Ni filter has been used in the X-Ray unit. The scan speed of 2% minute and a chart speed of 20 mm./minute has been maintained. The intensity has been obtained in arbitrary units from the chart Norelco scale-linear. Observed values and their relative intensities have been compared with the A.S.T.M.

Data. The fit of "d" values and their intensities with those of the A.S.T.M. values are very important for the identification of the mineral.

With the application of heat, materials undergo physical or chemical changes with accompanying heat effects. The differential thermal analysis technique is a mean of measuring the amount of heat evolved or absorbed and the temperature at which those changes take place within the material. This technique has been applied to the mineral under investigation.

Results and Discussion

Chemical Composition and the Softening Point.—Chemical analysis provides a basis for ore classification and indicates the range of alumina content in the sample. Data of these samples in Table 1 show the ore to be quite uniform in chemical composition and similar to one another. From the data it is obvious that the alumina content of the clay is around 62% which after calcination becomes 72%, silica about 23%, TiO_2 3.5% and all other impurities to about 1.5%. This composition when examined, resembles very much with to that of mullite except a 5.0% decrease in the SiO_2 content with 3.5% TiO_2 and 1.5% impurities in excess. The commercial mullite [3] refractories contain 72% Al_2O_3 and 22% SiO_2 with about 6% impurities. The P.E.C. of such refractories is given as cone 38(1835°C.). The clay under investigation seems to be superior when compared to the mullite because the softening point of this clay as determined is cone 39 (1865°C.). This is due to the fact that the clay contains about 3.5% anatase whose melting temperature itself is about 1855°C. Thus, there are only 1.5% low temperature fluxes in the clay as compared to the 60% in the above mullite. These fluxes, therefore, might have produced liquid at comparatively low temperature and resulted in lowering the softening point of the material mullite.

From the consideration of phase equilibrium diagram of alumina and silica [4] it is found that the more mullite in a mineral present, the less liquid is formed when high temperatures are reached and since the mullite content of a refractory is proportional to the alumina content, it follows that refractoriness increases with increasing alumina content. It has been established that all well burned refractories containing less than 72%. Alumina have lower refractoriness than those richer in alumina. The mineral under investigation with 72% Al_2O_3 may, therefore, be expected to have good refractoriness. This has been confirmed with its softening point (1865°C.) obtained earlier.

Ceramic Properties.—The specific gravities of imported china clay and high alumina clay calcined at 750°C. have been determined and found to be 2.59 and 2.75, respectively. This indicates that the alumina content in the clay is appreciably higher as compared to the imported china clay. It is known that the density of alumina is 3.7 to 4.0 and that of silica from 2.20 to 2.65. It is, therefore, expected that in a mixture of alumina-silica the specific gravity will increase with increasing alumina content, and this is exactly the case with the high alumina clay. The specific gravity of the high alumina clay fired to 1100°C. is 3.097 (Table 2). There is a clear difference

TABLE 2.—CERAMIC PROPERTIES OF HIGH ALUMINA CLAY.

Temperature °C.	Skrinkage %	Porosity %	Absorption %	Specific gravity	Crushing strength lb. 1 Sq."
1100	2	44.2	26.6	3.097	1792
1200	3	44.0	24.8	—	4626
1300	4	43.5	23.8	—	5397
1400	6	39.8	20.8	—	9059
1500	13	20.6	8.3	3.034	—

between the specific gravity of the material obtained at 750°C. and 1100°C. The explanation is that the clay might be a well crystallized type in which case it takes a higher temperature to decompose into amorphous silica and alumina. After the complete destruction of the lattice at 1100°C. a mixture of 72% alumina and 23% silica gives a specific gravity of 3.097, but when the same mixture is fired to 1500°C. the specific gravity decreased to 3.034. This is clearly due to the fact that at 1500°C. a larger proportion of amorphous alumina and silica has been changed to mullite which has a specific gravity of only 3.0. Thus the reaction between alumina and silica to form mullite (above 1200°C.) may be attributed to a decrease in specific gravity.[5] Refractory clays vary in colour; low grade clays due to the presence of iron are usually brown, tan, reddish yellow and cream. High grade refractory clays mostly range in colour from white through grey to black. Carbonaceous materials included in the clay often give them a dark colour. The iron content in the clay varies from .2–.4% with lime varying from .16–.46% and when fired to 1500°C., it gave a clear white colour. Thus based on relative plasticity and hardness it may be included in the "Flint Clays Group" having a compact structure without any lusture and smooth texture.

Pieces fired to various temperatures have been put to porosity, percentage absorption, shrinkage and crushing strength tests. From Table 2 it may be seen that with increase in temperature, the porosity and the percentage absorption decrease, resulting in the vitrification and densification of the pieces. Like-wise with increase in firing temperature, the crushing strength and the firing shrinkage increase. All these results show that at higher temperatures the clay is being sintered progressively but there is a rapid improvement in the properties of the pieces fired to 1500°C. This indicates that the clay could be workable only if fired to at least 1500°C., or above. Atth is temperature it seems the material has sintered properly. Another way of sintering the material at a lower temperature is to add same fluxing oxides, but this addition may decrease the refractoriness of the material.

Mineralogical Studies.—Differential thermal analysis has been found to be one of the most versatile techniques for the study of clay and other ceramic minerals. The method is not limited to clay and allied minerals only but it may be applied to any substance which undergoes exothermic and endothermic reaction on heating. It has been reported by Pask and Davies [6] that the thermal analysis curve of synthetically prepared boehmite is characterised by a single endothermic reaction with a peak at 550°C., whereas diaspore had a sharp endothermic peak at 530°C., mainly due to the evolution of chemically combined water. Later in 1948 others [7] found that a strong endothermic peak at 550°C. without any exothermic reaction is the characteristic of diaspore. They also reported that the endothermic peak of synthetic boehmite occurs at about 575°C. whereas that of the diaspore at 550°C.

In the light of the above studies it may be indicated, though not definitely, that the mineral is a mixture of Boehmite and Kaolinite. The D.T.A. work obtained is given in Fig. 1. It may be seen that the mineral has two major endothermic peaks at 580°C. and 620°C. The main peak

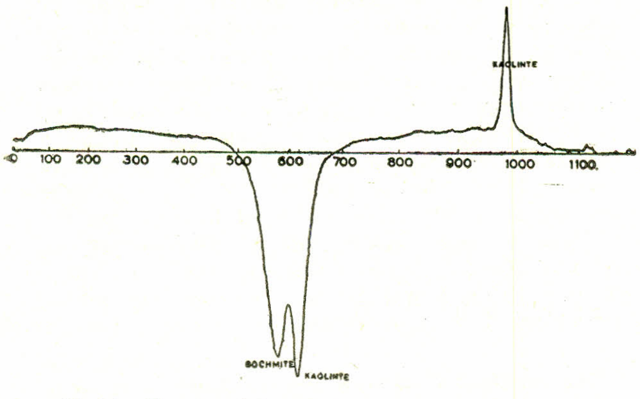

Fig. 1.—Showing differential thermal analysis of high aluminium clay.

starts at 450°C. and completes at 700°C. giving maximums at 580°C. and 620°C. This endothermic peak is followed by an exothermic peak which starts at 960°C. and completes at 1020°C. giving a maximum at 980°C. It is known that the major endothermic peak of the kaolinite occurs between 600°C. and 700°C. Kaolinite usually gives a symmetrical curve with a peak at about 610°C. All of the kaolin minerals show an exothermic peak at about 980°C., which is generally sharp. The endo-and exo-peaks at 620°C. and 980°C., respectively indicate clearly the presence of mineral kaolinite, and the endo-peak at 580°C. is that of high alumina mineral most probably boehmite. Both the endo-peaks are due to dehydration of water where the mineral-structure on heating loses (OH) ions. The sharp exo-peak at 980°C. is either due to recrystallization of the amorphous alumina[8] produced in the 600-700°C decomposition of the lattice to form gamma alumina or may be due to the formation of needle shaped crystals of mullite.[9] According to recent work,[10] this is due to the formation of an aluminium silicon spinel type of structure, developed at about 925°C., causes the 980°C. exo-peak. It is said that Mullite is formed by the decomposition of this spinel at a later stage. It may finally be concluded that the mineral contains a mixture of kaolinite and most probably boehmite.

The lattice spacings derived from the X-Ray powder diffraction together with the estimated intensities of the X-Ray reflections, provide the most convenient and the most generally used basis for comparing the results obtained by different techniques. Table 3 contains the 'd' values and their intensities obtained for the mineral under investigation. For comparison the standard 'd' values obtained for boehmite[11] and clay[12] are also included. It may be seen from Table 3 that there is no diaspore line in the mineral and that it contains boehmite and clay only. Lines 6,11, 3.51, 3.15 and 2.34 strongly represent the presence of boehmite whereas lines 7.08 and 3.56 indicate the presence of kaolin but to a lesser extent. The strongest reflection of all at 6.11 and the two second strongest reflections at 3.15 and 2.34 suggest the presence of a much larger quantity of boehmite. After studying the intensities of both boehmite and kaolinite it may be concluded that Kaolinite in the mineral is between 20-30%. The other diffraction lines having very low intensities indicate the presence of anatase, and traces of halloysite gibbsite, diaspore, goethite, hematite, cristobalite and rutile. Only anatase seems to be present in the proportion of about 1-5% where as the total of the remaining minerals is less than 3%. This is shown in the reproduction of Kα radiation diffraction patterns of Fig. 2.

TABLE 3.—'d' VALUES OF HIGH ALUMINA CLAY ALONG WITH STANDARD VALUES OF BOEHMITE AND CLAY

High alumina clay	Intensity	Boehmite	Clay
7.08	26	—	7.06
6.11	100	6.11	—
3.56	26	—	3.56
3.51	11	3.51	—
3.15	52	3.15	—
2.34	52	2.35	—

Conclusion

On the basis of the studies made and specially keeping in view the results of D.T.A. and X-Ray diffraction, the following conclusion about the mineralogy of the clay may be made.

(1). The clay appears to be lateritic in origin. (2). The chemical analysis shows that the calcined clay contains about 72% alumina, 23% SiO_2, 3.5% TiO_2 with a refractoriness of cone 39 (1865°C.) and, therefore, refractories made out of this material, could be used in furnaces operating upto 1750°C. (3). This could be a potential source of alumina for aluminium production. (4). The mineralogy of the clay as indicated by X-Ray shows that it contains boehmite, kaolinite (20-30%) and anatase and possibly halloysite with gibbsite, diaspore, goethite, hematite, cristobalite and rutite the first three having most abundant and in the order sited. (5). The D.T.A. results as far as interpretable, seem in accord with this mineralogy.

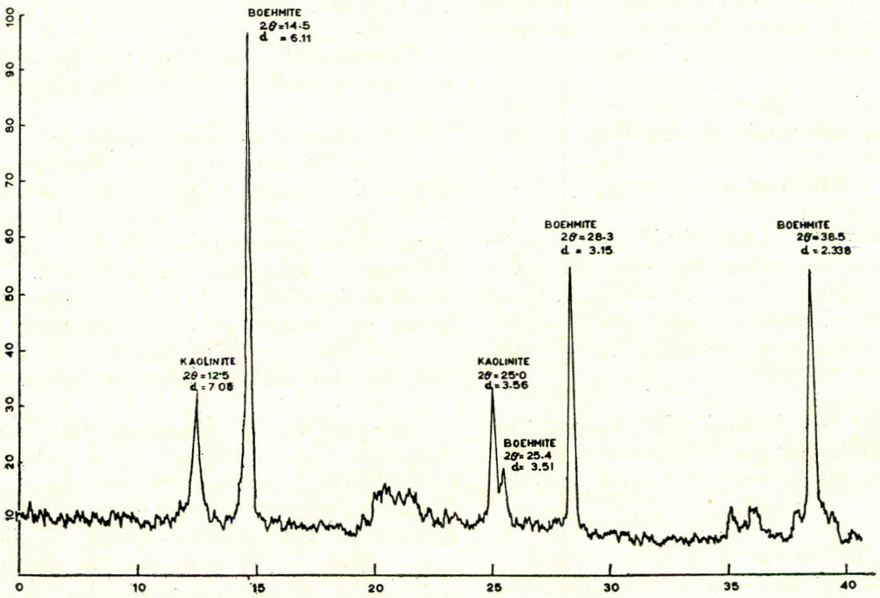

Fig. 2.—X-ray diffraction pattern of high aluminium clay.

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