

MINERALOGICAL STUDIES ON SOME HIGH ALUMINA BAUXITIC CLAYS FROM SALT RANGE AREA

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X-Ray, D.T.A., P.C.E. and other data are presented for three selected high alumina bauxitic clays from salt range area. A correlation between X-Ray data of the raw bauxites and the other properties obtained revealed that the materials contain a very high proportion of boehmite (70 to 75%). After calcination they contain Al_2O_3 70 to 80%. These bauxites may, therefore, be used for making mullite and other high alumina refractories to be used in high temperature furnaces and kilns for chemical glass, Cement, ceramic, iron and steel and other metallurgical and non-metallurgical industries.

The term "Bauxite" is usually applied to aluminium ores generally believed to consist of a mixture, in different proportions, of the trihydrate (gibbsite) and the monohydrates (Boehmite, diasporite, etc.) with certain impurities. The impurities are principally the iron minerals hematite, various hydrated ferric oxides, siderite, etc., Silica is usually found in the combined form of kaolinite and halloysite, and titanium present possibly as rutile, ilmenite or leucocoxene. Harder¹ indicates that all of the boehmite and diasporite deposits are of an early age, while all the more recent deposits are of the trihydrate, gibbsite type. It seems, therefore, that gibbsite forms first during the laterization of aluminium-silicates and that ageing, pressure and possibly heat, change the gibbsite to boehmite and eventually to diasporite.

Previously some information on the mineralogical nature and the ceramic properties of a high alumina clay has been reported.² The objective of the present study was to examine the three samples of Bauxitic clays quantitatively with respect to initial mineralogy through chemical analysis, Differential Analysis and finally through X-Ray studies and to correlate the data obtained and thus to establish the economic interest in these high alumina bauxitic clays by contributing information, providing a better understanding of their high temperature application in Industry. Three high alumina bauxitic clay samples were collected from the out crops of three different beds which are 3-4 miles away from each other. The general strike of the bauxitic beds is more or less East-West with a dip of about 30 to 35°, and lie at an altitude of about 2000 to 2500

feet above sea level, approachable from Katha, Pail and Sultan Mehdi etc. The deposits start from near village Kutha which is located some 18 miles north of Khushab Tehsil in Sargodha Distt. High alumina bauxitic clays seem to be scattered over most of the Central Salt Range area including the Sakser hills. Various veins having upto 30 feet thickness and over 10 miles length have been noticed and the probable reserves seem to be of several million tons. The predominant colour of the bauxites is cream, buff and white.

Experimental

Chemical analyses of the three samples as given in Table-1 have been made and their fusion temperatures have been measured to determine the maximum useful temperature to which they could be fired, and hence their suitability as refractory materials. The calculated mineralogical compositions of the clays are given in Table 2.

The procedure, method, and instrument used for the differential thermal analyses have been discussed previously.³ The clays were perfectly ground, passed through a 100 mesh sieve, dried at 110°C. They were then put into the apparatus for heat application, and the minerals present in this have been identified by the obtained endothermic and exothermic peaks. The differential thermal curves of the three samples are presented in Fig. 1.

X-Ray analyses have been made using wide range Norelco diffractometer and employing a

TABLE I.—CHEMICAL ANALYSIS OF THREE BAUXITIC CLAYS.

Sample No.	L/I %	SiO ₂ %	Al ₂ O ₃ %	Fe ₂ O ₃ %	TiO ₂ %	CaO%	MgO%
1	14.8	11.26	68.20	1.5	2.93	1.05	0.25
2	15.9	9.24	70.57	1.25	1.92	1.4	0.50
3	15.16	13.01	68.80	7.43	1.85	0.35	0.38

TABLE 2.—APPROXIMATE MINERALOGICAL COMPOSITION OF THREE BAUXITIC CLAYS.

Samples	No. 1		No. 2		No. 3	
	A	B	A	B	A	B
Mineral kaolinite	22.7	17.87	18.76	12.31	20.56	19.1
Alumina hydrate	69.67	69.67	74.27	73.94	71.33	71.33
Calcium silicates	—	5.19	—	6.95	—	1.72
Calcium carbonate	1.5	—	2.1	—	0.5	—
Iron compounds	1.8	—	—	1.5	—	9.1
Anatase	2.93	—	1.92	—	1.85	—

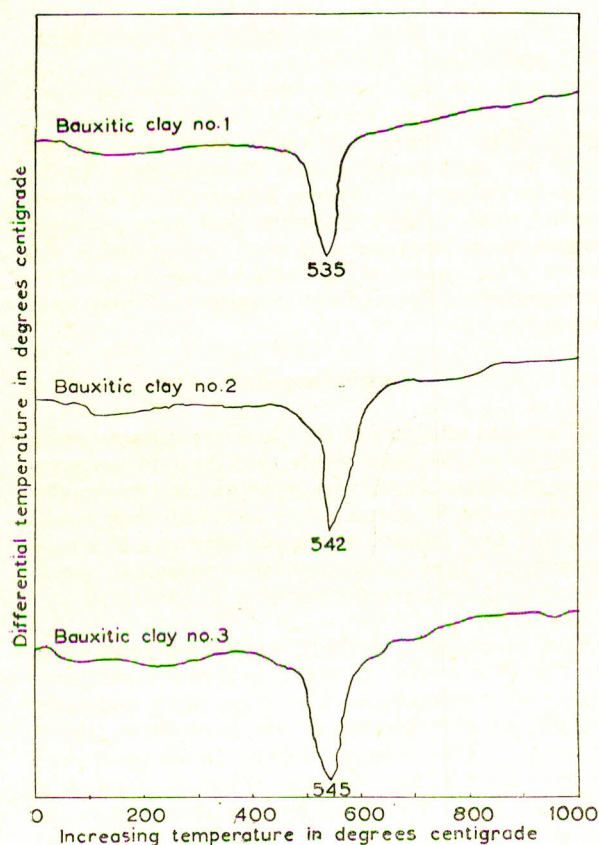


Fig. 1.—Differential thermal curves of Bauxitic clays No. 1, 2 and 3.

rotating type specimen holder. The diffractometer patterns have been obtained with filtered $\text{Cu K}\alpha$ radiation, 35 KV-10 ma excitation, with a full scale of 200 CPs, time constant 1 second, Scan speed 1 (2Q) minute and the chart speed 10 mm/min. The 'd' values obtained by the three X-Ray patterns alongwith their intensities are given in Table 3. Mineral identification has been performed by using the information contained in the X-Ray Powder Data File published by the ASTM. A search is first conducted on the

basis of the 'd' value for the strongest reflection in the diffraction pattern. An approximate percentage of the minerals present in the sample by comparing the intensities of the 'd' values have been determined. Samples have been passed through a 325 mesh sieve in order to obtain a reasonably statistical number of crystallinities contributing to the reflections when intensity measurements were made.

Results and Discussion

Chemical Composition and the Fusibility.—From the chemical analyses of three samples of high alumina bauxitic clays, as given in Table 1, it may be seen that the clays are essentially an admixture of bauxite and kaolinite with small amounts of calcium and iron compounds and anatase. The chemical composition has been expressed in terms of the oxides of the various elements, although they may be present in more complicated and some times unknown forms, whereas in the rational or mineralogical analysis the composition of the material is expressed in terms of various mineral compounds present.

Following the technique of Koenig⁴ the mineralogical composition of the three minerals have been calculated from their chemical analyses and presented in Table 2. The method is open to criticism due to the false assumption that kaolinite, feldspar and quartz are the dominant minerals. It may be seen that hydrated alumina forms the major portion of the raw minerals, varying between 70-74% of the total with 12-22% clay and some 2-7% calcium silicates or 0.5-1.5% calcium carbonate according to the methods used and a little anatase. As shown in Table 2 if calcium is calculated as some silicate the percentage of clays obtained is between 12 and 19% but if it is treated as lime stone, the clay increases to 22.7% in sample No. 1. Impurities included complex calcium and magnesium silicates, iron bearing minerals such as iron silicates, goethite and hematite etc. Iron bearing minerals in

TABLE 3.—'d' VALUES OF HIGH ALUMINA BAUXITIC CLAYS OBTAINED AND STANDARD VALUES OF BOEHMITE AND CLAY ALONGWITH THEIR INTENSITIES.

No. 1		No. 2		No. 3		Boehmite		Clay	
'd' values	Intensity	'd' values	Intensity	'd' values	Intensity	'd' values	Intensity	'd' values	Intensity
7.14	23	7.17	15	7.17	18	—	—	7.15	100
6.11	71	6.15	64	6.11	66	6.119	100	—	—
3.6	15	3.59	11	3.59	13	—	—	3.61	100
3.55	12	3.53	10	3.53	10	—	—	3.55	100
3.16	40	3.17	36	3.16	17	3.16	45	—	—
2.355	40	2.356	80	2.356	27	2.356	42	2.29	40
—	—	2.29	20	—	—	—	—	2.29	40
1.98	8	1.985	5	—	—	1.977	4	—	—
1.86	25	1.866	20	1.866	17	1.859	52	—	—
1.848	24	1.852	20	1.852	17	1.845	52	—	—
1.774	9	1.771	7	1.772	9	1.776	4	—	—
—	—	1.668	9	1.667	10	—	—	—	—
1.664	13	—	—	—	—	1.66	11	1.67	10
—	—	1.664	10	1.661	9	—	—	—	—

sample No. 3 are present in appreciable amounts (9%), more than the calcium compounds in sample No. 1 and 2. It is known⁵ that commercial Mullite refractories contain 72% Al₂O₃ 22% SiO₂ and about 6% impurities with a refractoriness of pyrometric cone equivalent to 38(1835°C). The three minerals under investigation contain Al₂O₃ 68–70% which after calcination becomes 80–84%. Thus all the three calcined clays apparently seem to be superior to Mullite. This is true in case of clays No. 1 and 2 whose refractoriness has been obtained as cone 39(1865°C), whereas clay No. 3 gave a refractoriness of cone 35(1785°C). The explanation lies in the fact that it contains about 12% impurities almost double than are found in other two clays. Moreover iron is the main impurity in this clay which might be forming low temperature iron silicates and other low melting fluxes, all responsible for lowering the refractoriness of the clay.

Mineralogical Studies.—Since it is unlikely that any two minerals have chemical bonds of identical strength, they under heat treatment will decompose, oxidise or change phase at different temperatures. The temperature at which a peak occurs, therefore, often indicates which mineral is present. The DTA. curve on the dehydration of the three bauxitic clays is given in figure 1.

It may be seen that clay No. 1 has a major endothermic reaction which starts at 450°C and completes at 620°C giving a maximum at 636°C. In case of clay No. 2 the main peak starts at the same temperature of 450°C but completes at a slightly higher temperature of 650°C giving a maximum at 542°C. In clay No. 3 the only endothermic peak may be seen occurring between 450°C and 650°C with a maximum at 545°C. There seems to be a slight endothermic dip in

all the three samples between 110–150°C. The small amount of water adsorbed at the edges of the kaolinite plates is perhaps too small to produce any noticeable effect on the thermal curves. Irregularities in the thermal curves of these clays in the 100–150°C range are generally caused by associated impurities. This may also be due to the poorly crystallized kaolinite present in the sample in small quantities. In any case the effect is very small and therefore, negligible. Kaolinite gives generally symmetrical curve with a peak at about 580°C. As the total kaolinite is less than 15–20% it seems that 580°C peaks have been superimposed or depressed, by the large peaks of Boehmite/diaspore which give a maximum between 510°C and 600°C. All the kaolinite minerals show an exothermic peak which occurs between 950°C and 980°C. The reason and the nature of this reaction has been the subject of speculation for a number of years. In 1959 however, Brindley and Nakahira⁶ established that some kind of spinel phase was formed, with the composition Si₃Al₄O₁₂. The formation of this silicon spined phase at 925°C gives the strong exothermic peak between 950°C and 980°C. This peak in the bauxitic clays is absent, instead an endothermic dip may be seen in clay No. 3. This clearly indicates that the small quantity of kaolinite present in the samples (10–20%) has not been able to produce an exo-peak and has been suppressed by the boehmite/diaspore present in larger quantities (70–80%). Bauxitic clay No. 3 which in the chemical analysis shows 7% iron oxide, seems containing a portion of it as pyrite. This reflected in the endothermic dip in the thermal curve No. 3 at 450°C. The slight irregularities found in the curve at 450°C and 700°C may thus be attributed to pyrite. Now coming to the main endothermic peaks, it may be observed that the three varieties No. 1, 2 and 3 give the maximum at

535°C, 542°C and 545°C respectively. As the structures of gibbsite, boehmite and diasporite differ, it is hoped that they will lose ions at different temperatures, thus indicating the presence of a particular mineral, but in practice it has been found difficult to differentiate between boehmite and diasporite. This might be due to the presence of kaolinite and other mineral impurities and may also be due to the fact that there is very little difference between the structures of the two. According to Norton⁷ and others⁸ the endothermic peak for diasporite is between 550 and 575°C and for gibbsite around 360°C whereas a synthetic boehmite gives a strong endothermic peak at 555°C⁹ though a peak temperature of 575°C has also been reported.⁸ D.T.A. index data by Mackenzie¹⁰ gives the range for boehmite between 510°C and 600°C whereas for diasporite it is between 510°C and 570°C. In the light of the above discussion, the presence of gibbsite may easily be discarded, but it is difficult to decide between boehmite and diasporite, as the endothermic peaks overlap each other and vary according to the impurities present. It is, therefore, at this stage concluded that the minerals are either boehmite or diasporite or a mixture of the two.

The calculated 'd' values obtained from the X-Ray diffraction patterns with their intensities are given in Table 3. These 'd' values and their peak intensities roughly give the quantities of the minerals present in the samples. For comparison the standard 'd' values obtained for boehmite¹¹ and Clay¹² are also included. It is confirmed from the Table that minerals under investigation have in common boehmite as their major constituent and that diasporite may be discarded completely. X-Ray lines of kaolinite in each sample 7.15, 3.61/3.59 and 3.55 are also present which indicate that the mineral kaolinite is the second largest mineral present in the samples. The strongest reflection of all at 6.11 Å and the second largest reflections at 3.15 Å/3.17 Å and 2.355 Å suggest the presence of a large quantity of boehmite; a mineral very difficult to identify by other methods, and is therefore, always mistaken as diasporite. Bohm¹³ for the first time in 1925, through X-Ray techniques, discovered the presence of this mineral in bauxite and, therefore, it was named after him. The intensities of the diffraction peaks suggest that mineral kaolinite in the samples ranges between 15 and 20% and boehmite between 70 and 75%.

Conclusions

On the basis of the results obtained by X-Ray and other techniques, and the discussions made, the following conclusions may be drawn.

1. The Clay appears to be lateritic in origin.
2. The calcined clays No. 1, 2 and 3 contain Al₂O₃, 68.2%, 70.57% and 68.8% respectively with a refractoriness of cones 39(1865°C) 39(1865°C) and 35(1785°C) respectively, and therefore, Mullite and other high alumina refractories made out of these minerals could be used in furnaces operating upto 1750°C, and 1650°C respectively.
3. The D.T.A. results indicate the presence of large amount of diasporite or boehmite or a mixture of the two alongwith a little kaolinite mineral.
4. The X-Ray studies finally confirmed that boehmite is the only main constituent present and that there is no diasporite. It also confirmed that boehmite is between 70 and 75% and that kaolinite is between 15 and 20%. In minor amounts are found calcium and iron compounds and anatase.

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