EVALUATION OF SOME WEST PAKISTAN CLAYS

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Twenty-seven clay samples from different regions of West Pakistan have been studied. The tests include chemical analysis, infrared absorption analysis, plasticity, water of plasticity, drying and firing behaviour including shrinkage, water absorption and colour. The majority of these clays have been found suitable for different uses in the ceramic industry.

Introduction

Clay deposits have been reported[1] to occur all over West Pakistan; very little is, however, known about the extent and quality of these deposits. The scanty and scattered information hitherto available of West Pakistan clay deposits was recently reported by Kazmi and Safdar.[2] The present work was, therefore, undertaken to provide relevant information on the physico-chemical characteristics of West Pakistan clays, and to determine their suitability for different uses in the ceramic industry.

Twenty-seven clay samples were collected from the various ceramic raw material suppliers and lease-owners. Insufficient information is available regarding the geology and the magnitude of these clay deposits. Since most of these samples were obtained from suppliers, it is assumed that in all cases the deposits are commercially exploitable. They were subjected to a number of physical and chemical determinations including chemical analysis, infra-red absorption analysis, plasticity, water of plasticity, slaking nature and drying and firing behaviour. These tests are of considerable importance to a clay worker. However, further work on differential thermal analysis, X-ray studies, particle size analysis and dehydroxylation studies is in progress and the results will be communicated later.

Experimental

Methods.—The *raw colour* of clays and the visible impurities like quartz, sand and other gritty materials present therein, were observed by visual examination.

Slaking Nature of clays was determined by immersing an approximately one-inch cube of crude clay lump in distilled water in a beaker. The slaking behaviour was recorded as quick, slow or non-slaking. The raw colour, visible impurities and the slaking nature of these clays are given in Table 1.

Chemical Analysis was carried out, on duplicate samples using the ASTM[3] methods for clay analysis. Presence of free lime (calcium carbonate) was detected by dropping dilute hydrochloric acid on several representative pieces of the dried material. Any effervescence was taken as an indication of the presence of calcium carbonate. The absence of any effervescence was indicative of the absence of free lime.

The Pyrometric Cone Equivalent (PCE) was calculated from the chemical analysis according to the Schuens,[4,7] formula:

$$\text{Seger Cone} = \frac{113 + Al_2O_3 - RO}{4.48}$$

This method is reported to have an accuracy of ± one cone for clays containing 20-50 percent alumina. The results of chemical analyses, along-with the alumina: silica ratio and the PCE for each clay are presented in Table 2.

Infra-Red Absorption Analysis was conducted with a double-beam Beckman Spectrophotometer, Model IR5A. The samples, for infra-red absorption analysis, having particle diameters smaller than 5 microns, were prepared according to the Hunt and Turner method.[5]

Plasticity was noted by the hand-feel method by mixing 120 mesh clay sample with an adequate amount of distilled water to form a mass suitable for plastic pressing between the fingers; it was recorded as good, fair, moderate or poor.

The test pieces for the determination of other physical properties were prepared by hand-pressing the same plastic clay mass used for noting plasticity, in a steel mould to form straight and smooth rectangular bars of $7'' \times 1'' \times 1''$ size, free from air bubbles and voids. The test pieces were marked with two parallel crossed lines 14 cm. apart for shrinkage measurements.

Drying Linear Shrinkage was calculated in the usual way by measuring the difference of the shrinkage marks after drying at 110°C. *Fired linear shrinkage* at 1000°, 1100°, 1150°, 1200°, 1250°, 1300°, and 1350°C. was similarly measured and calculated on the dry-length basis of the test pieces.

TABLE 1.—PRELIMINARY EXAMINATION.

Clay No.	Location	Original colour and visible impurities	Slaking nature
1.	Village Musakhel, District Mianwali	Lumps; pale white with occasional yellow specks	Quick
2.	,,	,, ; dark grey	,,
3.	,,	,, ; greyish white	,,
4.	,,	,, ; ,,	,,
5.	,,	,, ; greyish black	,,
6.	,,	,, ; greyish white with reddish yellow streaks and specks on the surface	,,
7.	,,	,, ; light grey	,,
8.	,,	,, ; greyish white	,,
9.	,,	,, ; greyish black	,,
10.	Chakwal, District Jhelum	,, ; ,,	,,
11.	,,	,, ; greyish white	,,
12.	,,	,, ; ,,	,,
13.	Karuli	,, ; greyish black	,,
14.	,,	,, ; white with reddish yellow streaks on the surface and deep inside	,,
15.	,,	,, ; white	,,
16.	,,	,, ; greyish black	,,
17.	Kutki	,, ; greyish white	,,
18.	,,	,, ; ,,	,,
19.	Village Kalri	,, ; light grey	,,
20.	,,	Powder; grey *	*
21.	,,	,, ; greyish white *	*
22.	Daudkhel	Lumps; light grey	Quick
23.	,,	,, ; pinkish white	,,
24.	Kohat	,, ; ,,	,,
25.	Kohat (Ghari Chandan)	,, ; greyish black *	,,
26.	Dandot	Powder; greyish white with pinkish tinge	*
27.	Dulmial	Lumps; pale white with occasional reddish streak on the surface and deep inside	Very slow

* Slaking nature in case of the samples received in powdered form was not determined.

TABLE 2.—CHEMICAL ANALYSIS.

Clay No.	Loss on Ignition	SiO_2	R_2O_3	Al_2O_3	Fe_2O_3	CaO	MgO	Al_2O_3 : SiO_2 (molecular)	Pyrometric cone equivalent
1.	11.30	51.21	36.70	36.43	0.27	0.43	Traces	1:1.39	34
2.	12.02	51.72	36.30	35.82	0.47	—	—	1:2.24	34
3.	9.20	61.13	29.50	28.72	0.78	—	—	1:3.62	32
4.	14.03	56.35	30.00	29.40	0.60	—	—	1:3.25	above 32
5.	7.40	66.40	22.00	21.19	0.81	Traces	—	1:5.34	29
6.	6.18	69.80	20.75	19.84	0.91	—	Traces	1:5.96	—
7.	11.30	60.90	26.50	25.63	0.87	Traces	—	1:4.03	31
8.	6.20	70.40	24.45	23.18	1.28	—	—	1:5.14	31
9.	11.83	54.48	34.00	31.60	2.40	Traces	—	1:2.80	above 32
10.	7.40	63.51	29.00	28.08	0.93	—	Traces	1:4.17	32
11.	7.82	67.55	25.59	24.59	1.00	—	—	1:4.69	31
12.	11.70	50.09	38.13	37.50	0.63	Traces	Traces	1:2.18	above 34
13.	9.90	62.10	28.42	27.30	1.12	—	—	1:3.88	32
14.	15.17	44.58	40.00	39.28	0.73	0.40	—	1:1.94	35
15.	14.40	44.90	40.26	38.96	1.30	0.50	—	1:1.96	35
16.	11.73	55.38	32.96	30.46	2.50	—	—	1:3.06	above 32
17.	7.60	64.70	25.13	23.88	1.25	Traces	—	1:4.59	30
18.	5.36	76.55	17.38	16.61	0.78	0.35	—	1:7.82	—
19.	7.45	51.10	40.75	40.00	0.75	—	—	1:2.17	35
20.	12.30	56.90	28.80	28.33	0.47	2.50	—	1:3.42	32
21.	5.10	63.70	30.10	29.29	0.81	0.62	—	1:3.70	32
22.	4.90	78.05	15.96	15.69	0.28	0.76	—	1:8.45	—
23.	8.83	65.69	25.28	24.03	1.25	0.25	—	1:4.84	31
24.	12.58	49.99	36.33	35.55	0.78	Traces	Traces	1:2.39	34
25.	11.51	50.98	37.33	35.13	2.20	—	—	1:2.46	33
26.	11.35	53.50	34.95	33.39	1.56	—	—	1:2.72	33
27.	10.20	55.00	35.00	34.82	0.19	—	—	1:2.69	34

Water of Plasticity was determined as percentage loss in weight of the green test piece dried at 110°C, in an electric oven for 5 hours.

Water Absorption was determined according to the ASTM method.[6] Fired linear shrinkage and water absorption was, however, not calculated for samples which warped, bloated and/or deformed and showed distinct cracks at the firing temperature.

Results and Discussion

The data of the various physical properties of clays is presented in Table 3. The total linear shrinkage and the water absorption, at different temperatures are given in Figs. 1,2 and 3,4 respectively.

Chemical Analysis, Alumina : Silica Ratio and Pyrometric Cone Equivalent.—Table 1 shows the results of chemical analysis, alumina to silica ratio and calculated pyrometric cone equivalent (PCE).

It will be seen from this table that three clays (Nos. 14,15 and 24) have a silica content ranging between 44.58 to 49.99%, in eleven clays (Nos. 1,2,4,9,12,16,19,20,25,26 and 27) it varies between 50.1 to 56.9%; ten clays (Nos. 3,5,6,7, 10,11,13,17 21 and 23) have a silica content of 60.9 to 69.8% whereas three clays (Nos. 8,18 and 22) show a silica content varying between 70.40 to 78.05%.

As mentioned elsewhere, the clay mineral in all the samples was identified as kaolinite. It was, therefore, reasonable to assume that the excess silica in all cases exists in the free state. Excepting three clays (Nos. 6, 18 and 22) the alumina content of the clays studied ranges from 20.0 to 40.0%.

Loss on ignition (at 1000°C.) of the clay samples studied ranges between 4.90 and 12.58% except for clay No. 4 where the ignition loss is 14.03%. The higher ignition loss in the latter case is presumably due to the presence of a larger amount of organic matter.

The alumina: silica ratio (molecular) of these clays varies between rather wide limits of 1:1.94 to 1:8.45. Four clays (Nos. 12, 14, 15 and 19) show a ratio of 1:1.94 to 1:2.18 which lies close to the theoretical ratio for kaolinite (1:2). The alumina: silica ratio of another seven clays (Nos. 1,2,9,24, 25, 26 and 27) lies between 1:2.39 and 1:2.8. This group may also be considered fairly close to the theoretical value of kaolinite. Of the remaining clays, six (Nos. 3,4,13,16,20 and 21) have a ratio of 1:3 to 1:4; in five clays (Nos. 7, 10,11, 17 and 23) it lies between the range 1:4 to 1:5 and three clays (Nos. 5,6 and 8) have a ratio ranging from 1:5 to 1:6 whereas two clays (Nos. 18 and 22) have a ratio of 1:7.82 and 1:8.45, respectively.

Eight clays (Nos. 1,14, 15, 18, 20, 21, 22 and 23) have a CaO content varying from 0.25 to 2.50%. However, in all these clays no free lime is present and as such the CaO content is not objectionable.

The Fe_2O_3 content also varies between 0.185 to 2.5%. Only in clay Nos. 6, 25 and 26 containing 0.91, 2.20 and 1.56% Fe_2O_3, respectively, the fired colour is objectionable. In all other cases where the iron content is above the normally permissible limit, the fired colour is creamish or at the most off-white.

As mentioned previously, the PCE of these clays was calculated from the chemical analysis. In the present study, only three clays (Nos. 6, 18 and 22) possess less than 20% alumina. As the calculations of PCE are valid only for clays containing 20-50% alumina, the PCE values of these three clays have not been calculated.

The calculated PCE for clay No. 25 does not appear to be correct as this clay fused at 1200°C. In all other cases, the calculated PCE appears generally reliable and the same conclusion can be drawn from the alumina to silica ratio and the low total flux content. In view of high PCE value, these clays are all suitable for making medium and heavy duty fire-bricks. It may also be mentioned that the total amount of fluxes in all these clays is well below the maximum permissible value of 6% for refractory clays.[7]

Ignition Loss and Composition.—It is interesting to note that the ignition loss at 1000°C. appears to be inversely proportional to the silica content and directly proportional to the alumina content of the clays as shown in Figs. 5 and 6. In the case of ignition loss versus silica plot, it is assumed that pure silica would show no ignition loss and a theoretical line is drawn between this value and the theoretical ignition loss for kaolinite. In the case of ignition loss versus alumina plot, it is assumed that the mineral with no alumina content would show no ignition loss and this value is connected with the theoretical ignition loss for kaolinite. The extrapolated value, from this plot for pure alumina is identical with the theoretical ignition loss of Gibbsite.

The relationship of ignition loss with silica content would appear rather obvious as the free silica content in a clay would be expected to function merely as a diluent. The ignition loss versus

TABLE 3.—PHYSICAL PROPERTIES.

Clay No.	Plasticity	Water of plasticity %	* Drying behaviour	Dry linear shrinkage (plastic length basis) %	* Firing behaviour	Fired linear shrinkage (dry length basis) at 1000°C. %	Water absorption after firing at 1000°C.%	Fired colour at 1000°C.
1.	Fair	24.8	Good	2.50	Good	1.2	18.0	White
2.	,,	26.0	,,	1.30	,,	2.5	15.0	Dull white
3.	,,	17.4	,,	2.70	,,	1.3	15.3	White
4.	Poor	18.8	,,	3.49	Bad	2.6 +	—	White with pinkish hue
5.	Fair	26.3	,,	5.44	Good	1.5	11.3	,, ,,
6.	,,	20.7	,,	5.72	,,	3.7	12.2	Creamish yellow
7.	,,	32.5	,,	6.81	,,	4.51	8.5	Creamish yellow
8.	Good	22.4	,,	5.00	,,	Nil	13.5	White
9.	,,	25.2	,,	4.60	,,	2.7	16.0	,,
10.	,,	25.0	,,	5.00	,,	1.7	14.3	Pale white
11.	,,	16.3	,,	1.40	,,	3.0	17.3	White
12.	,,	28.0	,,	3.40	,,	2.1	17.3	,,
13.	,,	24.1	,,	5.00	,,	4.3	17.3	Creamish white
14.	Poor	26.2	Bad	1.45 +	Bad	3.7 +	—	Buff
15.	Good	27.6	,,	3.69 +	,,	—	—	Yellowish white
16.	Fair	24.1	Good	5.30	,,	4.15 +	—	Dirty white
17.	Good	16.4	,,	5.60	Good	3.8	9.3	Creamish brown
18.	Fair	18.3	,,	3.20	,,	0.4	16.0	White
19.	,,	19.0	,,	2.20	,,	1.3	15.0	,,
20.	,,	25.8	,,	2.80	,,	1.5	19.8	,,
21.	Fair	20.5	,,	5.00	,,	1.3	15.8	,,
22.	Poor	21.1	,,	4.20	,,	Nil	17.0	,,
23.	Good	20.2	,,	3.70	,,	1.3	17.2	White with reddish hue
24.	,,	18.0	,,	2.10	,,	5.8	15.0	Dirty white
25.	,,	37.8	,,	5.00	,,	Nil	28.7	Chocolate
26.	Moderate	21.7	,,	5.30	,,	1.8	17.0	Pinkish red
27.	Poor	29.0	,,	2.50	Bad	—	—	White

*Drying and firing behaviour was recorded as good if the clay test pieces did not warp and crack during drying and firing, respectively; and bad if otherwise.

+ The values are approximate as the test pieces either cracked or warped.

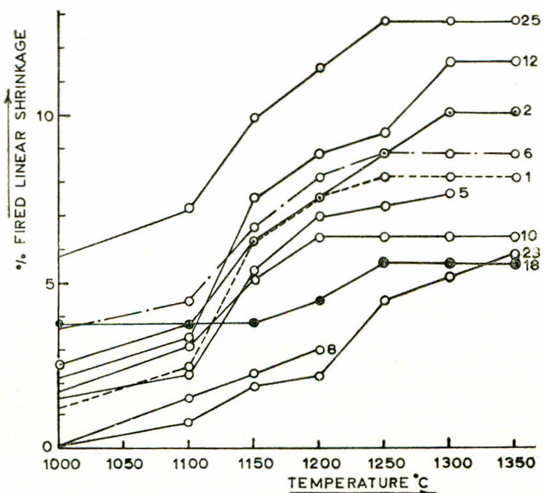

Fig 1.—Percent fired linear shrinkage vs. temperature.

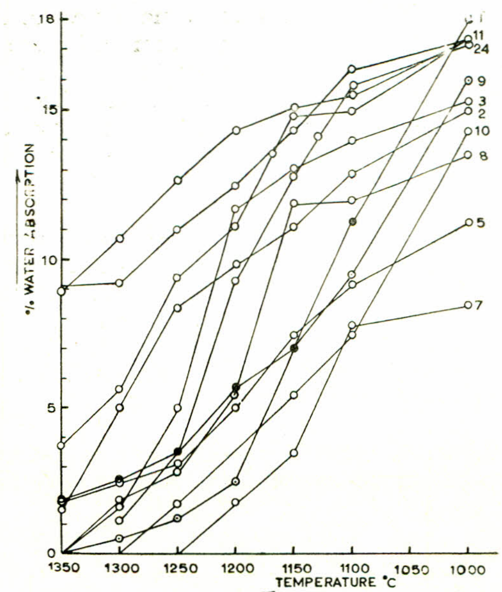

Fig. 3.—Percent water absorption vs. temperature.

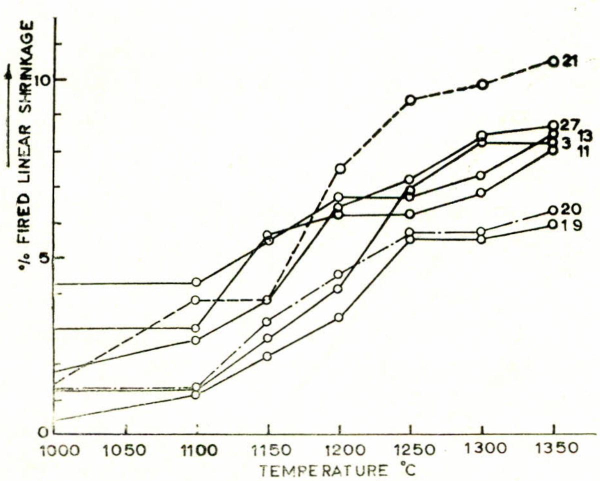

Fig. 2.—Percent fired linear shrinkage vs. temperature.

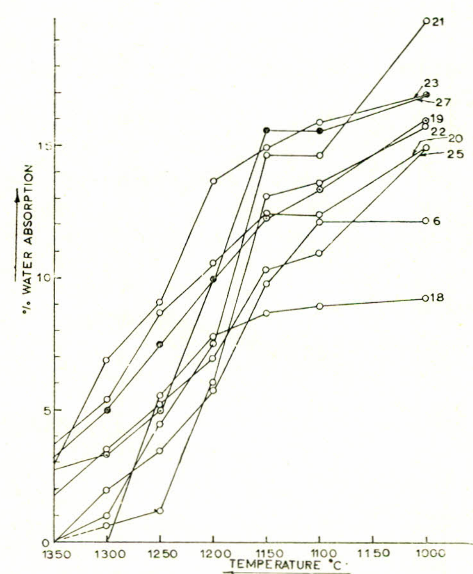

Fig. 4.—Percent water absorption vs. temperature.

alumina content, however, may indicate that alumina in these clays exists mainly as kaolinite. This plot thus holds some promise for use as a simple method for predicting the kaolinite content in a clay sample. It is, therefore, being investigated in greater details alongwith the dehydroxylation of clays and the results will be presented later.

Infra-Red Absorption Analysis.—The infra-red absorption characteristics in all cases were found to be identical to the standard kaolinite spectrograph.[8] For the sake of brevity, a typical absorption spectrograph of one sample is shown in Fig. 7. Another spectrograph of a standard kaolinite sample is shown in Fig. 8 for comparison

Physical Characteristics.—An examination of the physical properties of these clays reveals that a fairly large number of clays fire white at 1000°C. and as such can be recommended for use in the manufacture of pottery and porcelain.

The plasticity of these clays varies from fair to good excepting in case of clay Nos. 4,14,27 and 22. Of these, the first three show an unsatisfactory firing behaviour and as such cannot be generally recommended. Clay No. 22, however, shows good drying and firing behaviour. Of the other clays, sample No. 15 and 16 show bad firing behaviour. The plasticity of both these clays is satisfactory but they have a rather high drying shrinkage. These clays may be used after blending with other clays and under controlled drying and firing conditions.

Behaviour on Firing.—The fired linear shrinkage and water absorption of the fired samples in the

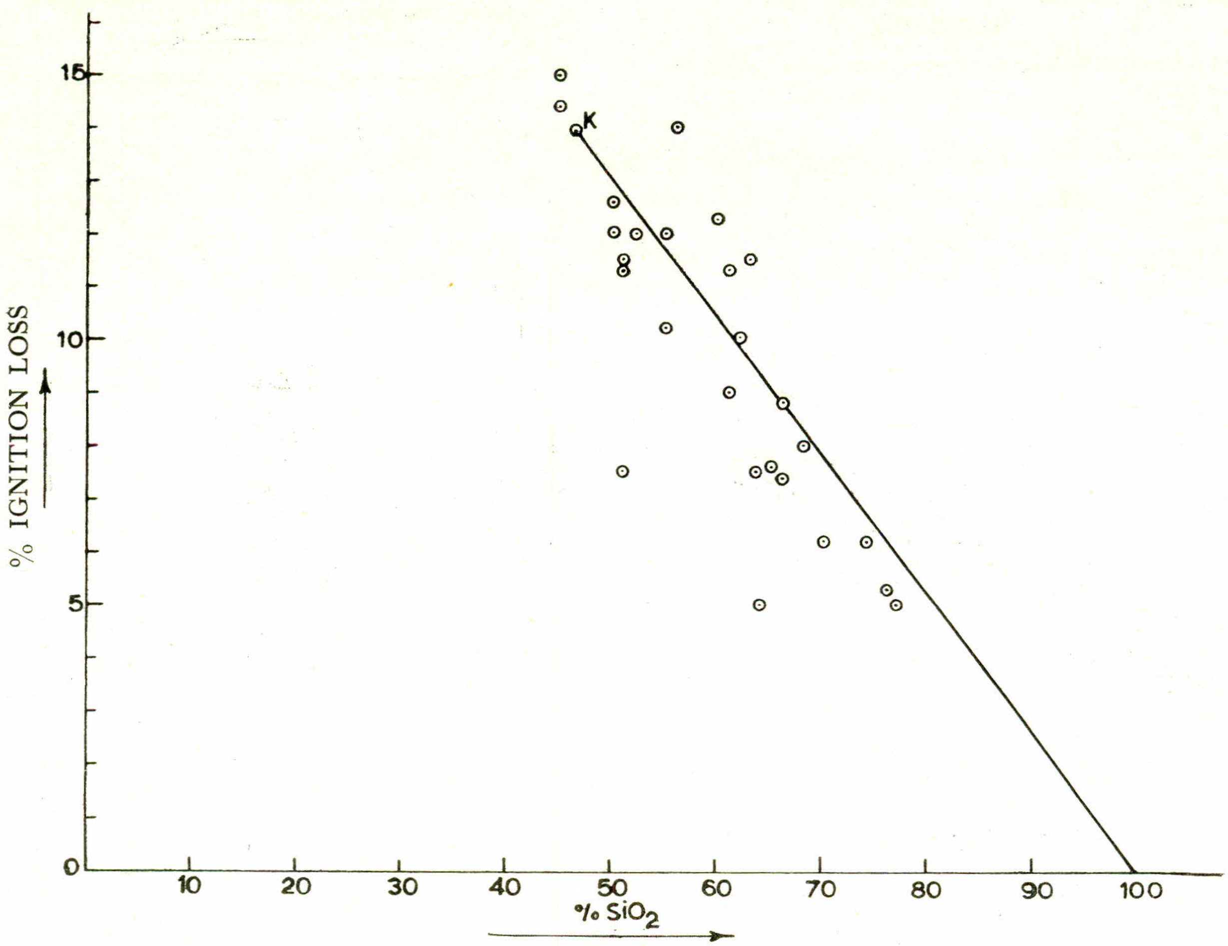

Fig.5—Percent Ignition Loss vs. Silica.

temperature range 1000° to 1350°C. is shown in Figs. 1,2 & 3,4. An examination of fired linear shrinkage and temperature curves shows that although the shrinkage is measurable in most cases at 1000°C. the shrinkage rate shows an increase above 1100°C., and this increased rate continues till about 1250°C. where it levels off to a considerably lower value. This behaviour is in agreement with the characteristics of kaolinitic clays.[9]

The water absorption versus temperature curves show, that in the majority of the clays, the water absorption decreases sharply after 1100°C. although nine clays achieve zero water absorption when heated to a maximum of 1350°C. Figs. 7 and 8 show that most of the clays studied possess a large vitrification range and thus recommend themselves for industrial use.

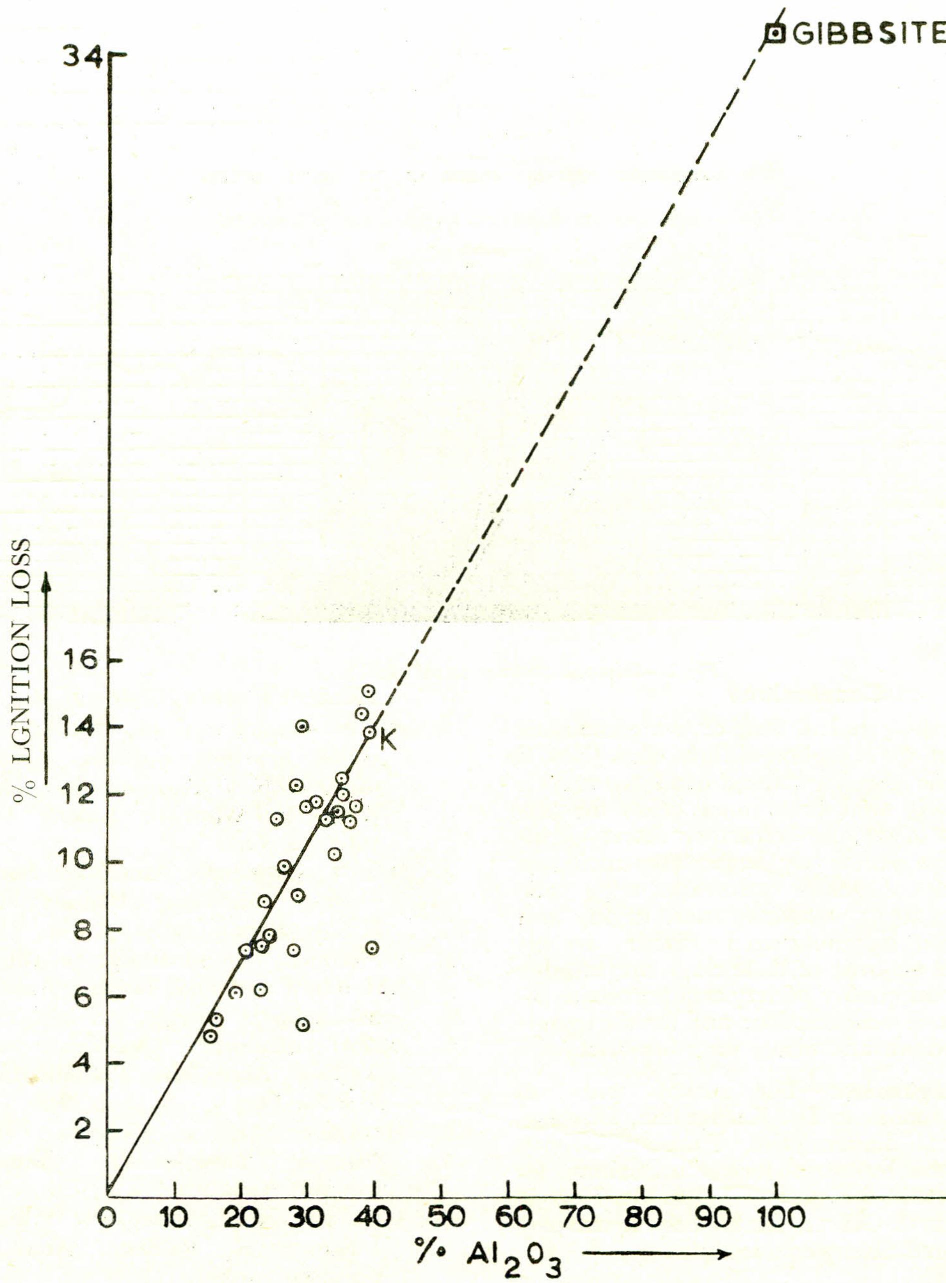

Fig. 6—Percent Ignition Loss Vs. Alumina.

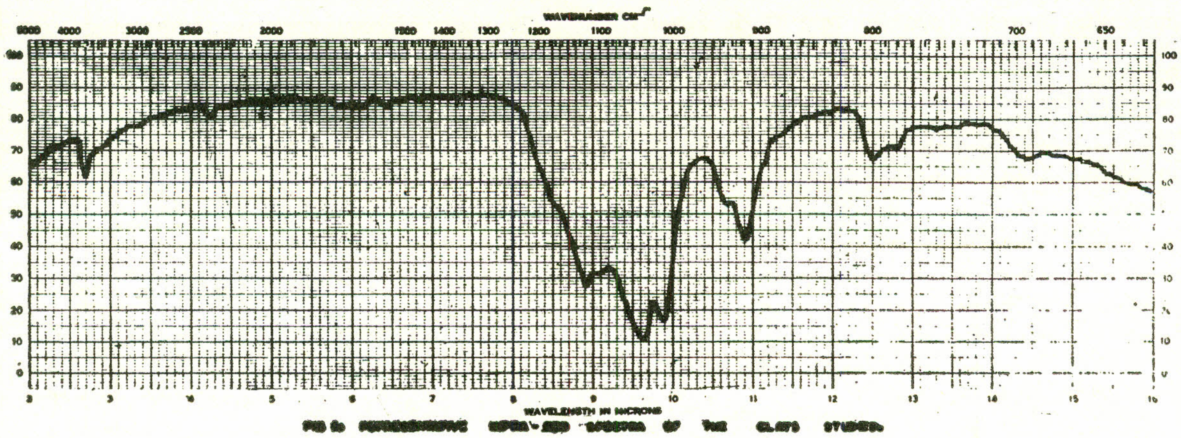

Fig 7.—Representative of Infra-red spectra of the clays studied.

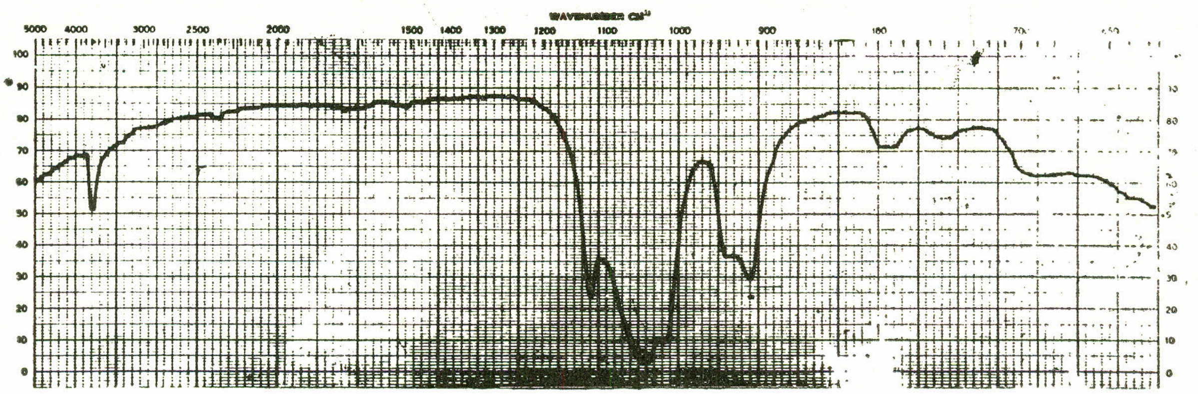

Fig 8.—Infra-red spectra of Ward's kaolin.

Conclusions

The results show that all these clays are kaolinitic in nature. With the exception of three clays (Nos. 6, 18 and 22), the alumina content in all the clays is 20% and above; total fluxes much below the permissible limit of 6% for refractory clays; vitrification range is sufficiently large; the calculated PCE range of these clays varies from seger cone 30 to seger cone 35. Plasticity and drying and firing behaviour including fired colour are satisfactory. The majority of these clays are suitable for making good quality pottery and porcelain after washing and beneficiation; and for the manufacture of medium and heavy duty fire-bricks.

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