

## A STUDY OF A SWAT KAOLINITE

RIAZ ALI SHAH

*Central Laboratories, Pakistan Council of Scientific and Industrial Research, Karachi*

MUSHTAQ AHMAD NAZ, ARSHAD ALI NAQVI AND M. SAFDAR

*West Regional Laboratories, Pakistan Council of Scientific and Industrial Research, Lahore*

(Received March 30, 1964)

A recently discovered Swat clay has been studied with a view to determine the physical properties like plasticity, water of plasticity, drying and firing shrinkage, water absorption and reflectance; and chemical analysis, differential thermal analysis, infra-red absorption analysis, spectrographic analysis and pyrometric cone equivalent. Results indicate it to be a kaolinite of an excellent quality suitable for making high grade ceramics and porcelain, paper making and various miscellaneous industries.

In view of the scanty and scattered information hitherto available on Pakistani glass and ceramics raw materials, the West Regional Laboratories, P.C.S.I.R., Lahore, in collaboration with other Laboratories, have undertaken a comprehensive programme of evaluating indigenous raw materials. Previous work on the clay resources of West Pakistan has already been reported.<sup>1,2</sup>

This communication is in continuation of this project and is based on the study of a Swat clay. The clay deposit occurs in villages Shah Deri and Shalhan, P.O. Bewlay, approximately 13 miles north-west of Mingora (Swat State), and is at a distance of about 8 miles from the Swat river. The samples have been taken from surface outcrops in this area. It is believed that the deposits are fairly extensive and occur in various stages of weathering from the parent rock. Geological information is not at present available and the Minerals Division of the North Regional Laboratories, P.C.S.I.R., Peshawar, are shortly undertaking a geological survey of this deposit.

### Experimental

Physical properties namely, plasticity, water of plasticity, specific gravity, drying and firing shrinkage at different temperatures and chemical compositions were determined by methods previously described.<sup>2</sup> The particle size distribution in the sub-sieve range was determined by the Andreasen pipette method, pH was determined after agitating a 1:4 clay water suspension for 30 minutes and using a Cambridge pH meter, brightness of the -300 mesh fraction of washed clay was measured on a photo volt Reflection Meter, Model 610, samples for infra-red absorption analysis were prepared by the Hunt and Turner method,<sup>3</sup> pyrometric cone equivalent was determined according to ASTM methods 4 and differential Thermal Analysis was carried out by using

calcined alumina as inert material. Before making the D.T.A. run of the raw clay, larger pieces of quartz and feldspar were removed by hand picking. PCE in °C. was also calculated from the chemical analysis according to the equation:<sup>5</sup>

$$\text{PCE} = \frac{360 + \text{Al}_2\text{O}_3 - \text{RO}}{0.228} \text{ } ^\circ\text{C.}$$

Washing of the raw clay was carried out in the following way:—

500 g. of -60 mesh B.S. clay was mixed with 1.5 litre of tap water in an enamel bucket. The clay-water mixture was thoroughly hand-blunged for 30 minutes and then stirred mechanically to ensure the thorough dispersion of clay particles. The mixture was allowed to stand for about 15 minutes to permit coarse impurities to settle down. The top suspension was then passed through a 200 mesh B.S. sieve into another basin and allowed to settle down. The supernatant water was decanted and the sedimented clay was oven-dried at 110°C. The washed clay thus obtained was weighed and the percent yield was calculated.

### Results and Discussion

*Chemical Composition and PCE.*—From Table 1, it may be seen that the alumina/silica ratio of both raw and washed clay is nearly the same as for theoretical kaolinite.

The only colour imparting oxide present in raw clay is Fe<sub>2</sub>O<sub>3</sub> to the extent of 0.525%. Most of this is associated with the quartz and feldspar and is reduced to 0.093% by beneficiation. Both the raw and the washed clay are white-firing.

The raw clay has a total flux content of about 10%, including 9.15% of CaO, which contributes to its low PCE value (Orton Cone 23-, 1595°C.),



in spite of the high alumina content. However, these fluxes are reduced to a total of 6% in the washed clay which results in the higher PCE value (Orton Cone 30+, 1680°C.). The observed PCE of the washed clay is also lower than the calculated value, presumably due to the high calcium oxide and P<sub>2</sub>O<sub>5</sub> content. The calcium oxide content of the washed clay is unusually high (5.4%), as compared to that of a Cornish china clay<sup>6</sup> (0.28%). It, however, does not exist in the free state and does not undermine the firing behaviour although the refractoriness is reduced by about 70°C.

TABLE I.—CHEMICAL ANALYSIS AND PYROMETRIC CONE EQUIVALENT.

	Raw Clay%	Washed Clay%
Ignition loss	11.470	12.880
SiO <sub>2</sub>	43.9700	45.470
Al <sub>2</sub> O <sub>3</sub>	34.70	35.490
Fe <sub>2</sub> O <sub>3</sub>	0.525	0.093
TiO <sub>2</sub>	Traces	Traces
CaO	9.150	5.400
MgO	Traces	Traces
P <sub>2</sub> O <sub>5</sub>	0.270	0.600
Al <sub>2</sub> O <sub>3</sub> /SiO <sub>2</sub> (Molecular)	2.150	2.160
PCE (Observed) Orton Cone 23- (1585°C.)		Orton Cone 30+ (1680°C.)
PCE (Calculated)	1687°C.	1751°C.

Grim<sup>7</sup> states that the nature of the exchangeable cations in a clay is indicated frequently by its pH. A pH value of about 9 suggests sodium, of 7.5, calcium, and of less than 7, hydrogen. The pH of the raw and washed clay is 7.82 and 8.23, respectively. It may be reasonable to assume, in view of the high CaO content and the pH values, that the exchangeable cation in the present case is calcium. The presence of calcium as the exchangeable cation usually results in high plasticity.<sup>8</sup>

This effect is likely to have been negated by the presence of a larger percentage of coarser particles in the clay. As can be seen in Fig. 3, the washed clay contains only 45% particles smaller than 1 micron as compared to 57% in a Georgia kaolin.<sup>9</sup>

The phosphate (P<sub>2</sub>O<sub>5</sub>) content of the raw and washed clay is 0.27% and 0.60%, respectively. Phosphates are usually found in the allophane series of clay minerals but there has been no indication of the presence of allophane in the DTA, and IRA results. It, therefore, appears that the phosphates are present in the clay in a finely divided insoluble condition. This view is supported by the observation that the P<sub>2</sub>O<sub>5</sub> content of the washed clay is much higher than that of the raw clay.

*Spectrographic Analysis* of this clay qualitatively showing the presence of the various elements is given in Table 2. In addition to indicating the trace impurities, the spectrographic analysis is in agreement with the chemical analysis.

*Differential Thermal Analysis*.—The DTA curves given in Fig. 1 show that the low temperature endothermic peaks for the raw and washed clay occur at 130° and 135°C., respectively. However, another DTA run on the washed clay sample dried at 100°C. showed no endothermic reaction at 135°C. It may, therefore, be concluded that the low temperature endothermic reaction is caused by absorbed water. This rules out the presence of halloysite (Al<sub>2</sub>O<sub>3</sub>.2SiO<sub>2</sub>.4H<sub>2</sub>O), which gives an endothermic reaction at 145–150°C.

The main endothermic and exothermic peaks in the raw and washed clay appear at 610°, 995°C. and 615°, 1005°C., respectively and are characteristic of the clay mineral kaolinite.

In the case of the washed clay, the peaks are comparatively more pronounced and larger in size indicating, as might be expected, a greater kaolinite content. The lower peak temperature for raw clay can be attributed to the presence of non-reactive impurities in the clay.

TABLE—2. SPECTROGRAPHIC ANALYSIS OF SWAT CLAY.

Elements	Al	B	Ca	Cu	Fe	Ga	Mg	Mn	Na	P	Si	Ti
Raw Clay	.. A+	F+	A+	E	C+	D+	B	D	C+	D+	A+	E
Washed Clay	.. A+	E+	B+	E+	D+	D+	B	E+	C+	C	A+	D

A+ = 10 to 100%, B= .3 to 3%, B+ = 1 to 10%, C = .03 to 3%, C+ = 1 to 1%, D = .003 to .03%, D+ = .01 to 1%,

E = .0003 to .003%, E+ = .001 to .01%, F+ = .0001 to .001%.



*Infra-red Absorption Analysis.*—The infra-red absorption spectrogram of the clays (Fig. 2) shows that, between 2 to 7 micron, the absorption peaks are located at 2.7, 3.0 and 6.1 micron. Between 8 to 11 micron, there is a singlet at about 8.95 micron and a doublet in the region 9.6 to 9.9 micron; a shoulder-like formation at 10.6 micron and a singlet at about 10.95 micron. Three feeble humps are also observed at 12.5, 13.2 and 14.5 micron.

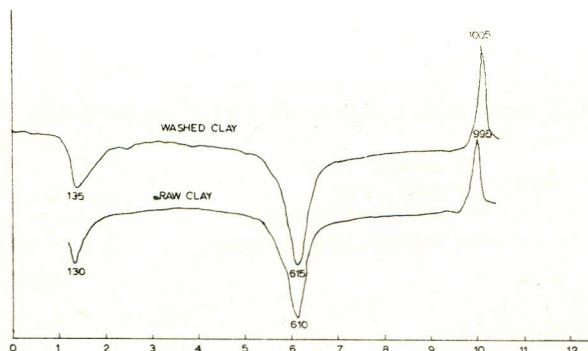


Fig. 1.—DTA curves of Swat clay.

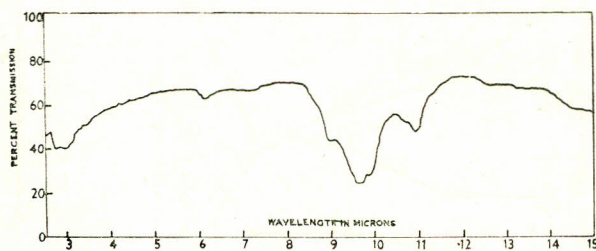


Fig. 2.—Infra-red spectra of Swat clay.

A comparison of the infra-red spectrogram and the position of absorption bands with that of a standard kaolinite<sup>10</sup> (Table 3) reveals a very close similarity. Hence it can be concluded that the clay mineral in this clay is kaolinitic in nature. This conclusion is also supported by DTA results. The minor departure in the absorption features of this clay with that of standard kaolinite may be attributed to the variation of kaolinite content, difference in particle size and degree of crystallinity.

*Physical Characteristics.*—Table 4 shows that both the raw and the washed clay burn pure white and possess good drying and firing behaviour; plasticity of the raw clay is poor and is slightly improved by washing. Poor plasticity and low firing shrinkage of the raw clay is caused by coarse grained impurities; petrological examination revealed the presence of quartz, feldspar, epidote

and corundum. The beneficiated clay has a brightness of 85% and only 0.015% of the material is coarser than 325 mesh.

*Grain Size Distribution.*—The grain size distribution curves (Fig. 3) show that 64.0% of the raw clay is of a diameter less than 74 micron (-200 mesh); and 21.0% of its particles have a diameter less than 1 micron; the washed clay, however, contains 45.0% of particles of this size. This increase of finer particles in the washed clay slightly improves its plasticity and enhances its shrinkage. The particle size distribution curve

TABLE 3.—POSITIONS OF INFRA-RED ABSORPTION BANDS OF SWAT CLAY AND STANDARD KAOLINITE (WAVE LENGTH IN MICRONS).

Swat Clay	Standard Kaolinite
* 2.70 (w)	* 2.73 (s)
3.00 (vww)	—
6.00 (s)	6.00 (w)
8.95 (s)	8.93 (s)
9.60 (s)	9.65 (s)
9.90 (w)	9.90 (s)
10.60 (w)	10.68 (w)
10.95 (s)	10.95 (s)
12.50 (vw)	12.50 (vw)
13.20 (vww)	13.30 (vww)
14.50 (vww)	14.50 (vw)

\*The symbols (s), (w), (vw) and (vww) correspond to the relative intensities of strong, weak, very weak and very very weak bands, respectively.

TABLE 4.—PHYSICAL CHARACTERISTICS.

	Raw Clay	Washed Clay
Original Colour	White	White
Plasticity	Poor	Moderte
Water of Plasticity	29.6%	36.7%
Drying Behaviour	Good	Good
Drying Shrinkage	4.64%	5.3%
Firing Behaviour	Good	Good
Firing Shrinkage (at 1000°C.)	1.12%	5.3%
Fired Colour (at 1000°C.)	White with tiny dirty brown specks	White
pH	7.82	8.23
Specific Gravity	2.73	2.59
Reflectance (-300 B.S.S.) mesh	—	85%



for the raw clay shows that it contains 64% particles of less than 74 micron size (-200 mesh), which favourably compares with the 60% of washed clay on beneficiation.

**Firing Characteristics.**—The fired linear shrinkage and water absorption of the fired samples of the raw and washed clay in the temperature range 1000 to 1400°C. are shown in Fig. 4. The fired linear shrinkage of the raw clay at 1000°C. is negligible (1.12%) which increases sharply upto 1100°C. presumably due to vitrification. Between 1100° and 1300°C., the shrinkage levels off and again shows a sharp increase between 1300° and 1400°C. The firing shrinkage of the washed sample at 1000°C, is considerably more than that of the raw clay. This increase is due to the re-

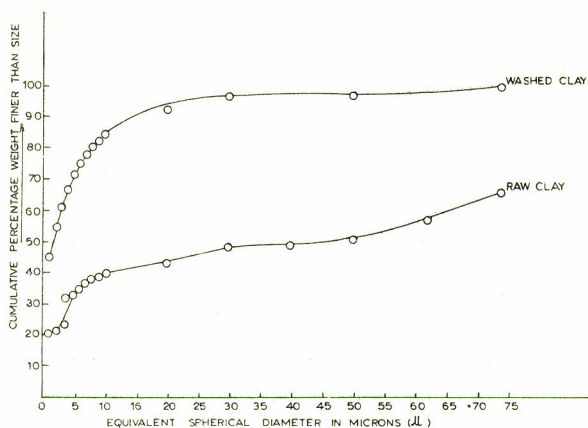


Fig. 3.— Grain size distribution in Swat clay.

moval of the coarser particles and also due to the elimination of quartz and felspar during beneficiation. Because of the removal of impurities, there is little evidence of further vitrification upto 1300°C. The fired shrinkage increases sharply between 1300°C and 1400°C, due to final vitrification. The firing behaviour of both the samples is typical of kaolinitic clays.<sup>11</sup>

The water absorption of the raw clay shows a fairly sharp decrease between 1000 and 1100°C. and is in agreement with increased shrinkage in this temperature range. The water absorption of the washed clay between 1100° and 1300°C. shows only a gradual decrease. A sharp decrease in both cases, however, is observed between 1300° and 1400°C. The above mentioned behaviour shows that the clay possesses a large vitrification range.

### Suitability for Various Industries

As already discussed, the clay possesses a large vitrification range, and a sufficiently high refractoriness; an extremely low iron content and gives a pure white colour on firing. The drying and firing behaviour is excellent and the clay is thus considered suitable for making high grade pottery and porcelain. It may be mentioned that an excellent porcelain body has been obtained from the beneficiated Swat clay in laboratory scale experiments. The casting properties of the slip and the firing behaviour of the body are satisfactory and the pure white body thus obtained is far superior in quality to a similar body made with a high quality English china clay.

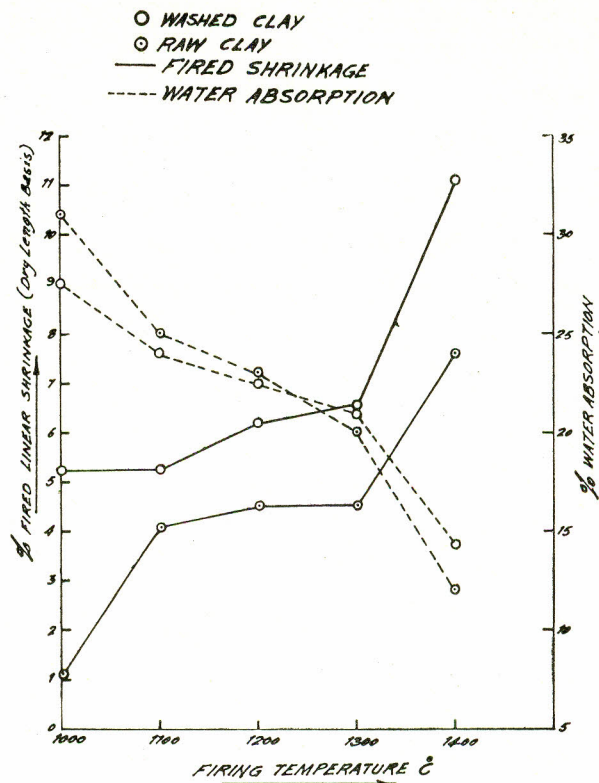


Fig. 4.— Firing characteristics of Swat clay.

The raw clay, although containing 10% fluxes has a satisfactory refractoriness (Orton Cone 23-) and is suitable for use as such for making medium duty fire bricks.

The beneficiated clay with a considerably improved refractoriness (Orton Cone 30+) is also expected to give satisfactory heavy duty fire bricks. In view of the pure white fired colour of the clay, the deposit is considered to be



valuable for making fire bricks. The extremely low  $\text{Fe}_2\text{O}_3$  content also recommends its use in making glass melting pots and tank blocks.

The properties of widely used kaolins in the paper industry<sup>12</sup> and of the washed Swat clay are given in Table 5. It is evident that the clay can be used as a paper filler although its pH needs to be adjusted. The sample studied contains only 55% particles finer than 2 micron, as compared to 75.95% particles of the similar size in

**Acknowledgement.**—The authors wish to thank Mr. M.A.S. Khan, Deputy Director, PITAC, Karachi for information regarding the clay deposit, Dr. S.A. Warsi, Director, North Regional Laboratories, Peshawar for supplying the clay samples and Mr. Hal J. Kelly of the U.S. Bureau of Mines for carrying out DTA, PCE and spectrographic analysis of the samples. The authors also are grateful to Dr. Karimullah, Director, West Regional Laboratories, Lahore for his keen interest in this project.

### References

TABLE 5.—PROPERTIES OF SWAT CLAY AND SOME KAOLINS USED IN PAPER MAKING.

Grain size distribution, equivalent spherical diameter, % by weight	Filler clays <sup>8</sup>	Coating clays <sup>8</sup>	Washed Swat clay
0—1 micron ..	10—41	55—72	45
1—2 micron ..	10—17	20—23	10
2—5 micron ..	13—31	8—20	16
5—10 micron ..	12—30	0—7	14
10—30 micron ..	7—19	0—0	12
Maximum Screen residue, wet, 325 mesh ..	0.15	0.01	0.015
Brightness ..	80.5—84	85—88	85
pH ..	3.8—5.0	4.2—7.0	8.23

the reported coating clays. Coating clays are usually 'predispersed' and Swat clay can be subjected to the treatment to enable its use for a similar purpose.

1. Ali H. Kazmi and M. Safdar, "Clay Resources of West Pakistan", Proceedings of the CENTO Symposium on Industrial Rocks and Minerals, December (1962), pp. 120.
2. Mushtaq A. Naz, Arshad Ali Naqvi and M. Safdar, Pakistan J. Sci. Ind. Res., **7**, 174 (1964).
3. J.M. Hunt and D.S. Turner, Anal. Chem., **25**, 1169-74 (1953).
4. ASTM standards, American Society of Testing Materials, Philadelphia, Pa, U.S.A. Part 3, (1955), p. 711.
5. W. Schuen, Tonindustrztg, **50**, 1623 (1926).
6. A.B. Searle and R.W. Grimshaw, The Chemistry and Physics of Clays (Ernest Benn Ltd., London, 1959), third edition, pp. 294.
7. Ralph E. Grim., *Applied Clay Mineralogy*, (Mcgraw Hill Book Co. Inc., New York, 1962), pp. 32.
8. R.W. Grimshaw, Trans. Brit. Ceram. Soc., **57**, (6) 343 (1958).
9. George A. Loomis, J. Am. Ceram. Soc., **21**, 1395 (1938).
10. John M. Hunt, Mary P. Wisherd, and Lawrence C. Bonhan, Anal. Chem., **22**, 1486 (1950).
11. *-ibid-* pp. 123.
12. *-ibid-* pp. 194.