

CERAMIC PROPERTIES OF SWAT CLAY

Part II.—Chemical Characteristics

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Chemical characteristics of Swat clay were studied by determining its water soluble content, pH value and cation exchange capacity. For comparison, the characteristics of an English china PCI clay were also studied. Results indicate that the Swat clay has a high initial pH and a high exchange capacity than the imported china clay. Further the exchange capacity of the finer fraction of Swat clay was higher than the coarser fractions, suggesting that the ion exchange in Swat clay is partly a surface phenomenon. The high exchange capacity of Swat clay is believed to be due to the poor crystallinity of the clay crystals and the presence of such impurities as halloysite and montmorillonite.

Introduction

Kaolin clays or china clays are an integral part of all whiteware ceramics such as dinnerware, artware, wall tile, sanitary ware, chemical stoneware, electrical porcelain, etc. Along with ball clays, kaolin clays impart plastic properties to the ceramic body and provide necessary strength to the formed article. A ceramic body may contain anywhere between 10-60% of china clay. Beside ceramics, china clay is also employed in considerable quantities by such industries as paper, paint, rubber, adhesive, insecticides, etc. As a matter of fact in the industrially developed countries, tonnage of kaolin employed in the paper and rubber industries exceeds the amount used in the manufacture of pottery products.

Presently no china clay deposit is being exploited in Pakistan. The only huge clayey deposit containing china-clay discovered so far in West Pakistan is that of Swat area. The deposits lie mainly in Shah Dheri, Shalhan and Tagma areas of Swat basin located at a distance of about 18 miles north-west of Saidu Sharif, the capital of Swat State. The clay deposits develop roughly in the direction from east to west in the Shah Dheri Area and from west to north-east in the areas of Shalhan and Tagma.¹ According to one preliminary report the total reserves of Swat clay deposits are around 1,700,000 tons;² another report estimates the amount at around 2,500,000 tons.¹ It is believed that on a thorough survey, even this estimate may well prove to be considerably conservative. Under the circumstances, therefore, the importance of Swat clay deposit is obvious.

Swat clay was first tested in the P.C.S.I.R. Laboratories, Lahore in early 1962,³ and later in a somewhat detailed manner in 1964.⁴ The results obtained during these studies indicated

that the Swat clay sample contained kaolinite of excellent quality and could be used in the manufacture of high grade ceramics and porcelain, paper-making and for various other industrial purposes after proper beneficiation. Realizing the importance of the deposit, the Geological Survey of Pakistan undertook the task of through surveying and prospecting of the area and sent to our Laboratories, in early 1965, some 79 representative samples. Accordingly, a more exhaustive research project was initiated with a view to fully investigating the clay from the Swat deposit. In this connection, two extensive studies have already been made, one dealing with the chemical and mineralogical composition of the various constituents present in the clay samples, and the other with its physical properties. The chemical and mineralogical studies revealed that the Swat clay was a semi-weathered felspathic material, comprising anorthite, albite, kaolinite, free quartz and mica; the amount of kaolinite in the raw sample being only up to 20% which may be raised to 45-50% after proper washing.⁵ The study of the physical characteristics of the clay sample indicated that the water-washed, -200 mesh Swat clay can be successfully used to replace imported china clays as well as a part of the fluxes in the production of high quality pottery and porcelains. Unlike the earlier conclusions, however, it was suspected that the presence of plagioclase feldspars in the water-washed sample may produce a tendency of excessive warpage in body compositions containing Swat clay which may create production problems.

The present investigation is concerned with the chemical characteristics of Swat clay which have been studied primarily by determining the water-soluble content, the pH value and the cation exchange capacity of the clay. All the above three properties are interlinked with each other, for example, higher pH value of a clay may partial-

ly be due to the higher percentage of soluble salts and partially to the presence of large amount of exchangeable cations. However, during the course of investigation an attempt to explain the high CEC value of Swat clay also led to the fortunate discovery of the presence of Halloysite and Monmorillonite in the finer fractions (below 5 micron) of the clay sample. Incidentally, the presence of these important impurities is being cited for the first time in the entire course of research work associated with Swat clay—the previous mineralogical study included. It has therefore, been decided to lay particular emphasis on the below 5-micron fraction. The presence of the above impurities has come to light while explaining the high CEC value of Swat clay. The effect of these impurities in slip casting of potteries cannot be overlooked. Similarly, the importance of pH as far as its use in various grades of paper and rubbers concerned, is well known.

Experimental

As the -200 mesh china clay is required by the ceramic and other industries, the soluble salt content was determined only on -200 mesh Swat clay and PC I samples. The pH determinations

on the other hand were made on raw, -120 mesh, -120+200 mesh and -200 mesh Swat clay, and PC I samples. The cation exchange capacity, was determined on raw, -200 mesh and -5 microns Swat clay, and on PC I samples. The -120 mesh, -120+200 mesh and -200 mesh Swat clay samples were prepared by routine B.S. sieve screening procedures. The finer Swat clay fraction containing particles below 5 microns was, however, obtained by filtering through a special filter paper, violently shaken, partially settled suspension of -200 mesh Swat clay. Chemical analysis and particle size distribution of this fine fraction is given in Table 1. The x-ray and D.T.A. results are shown in Figs. 1 and 2 respectively.

The characteristics of the other fraction of Swat clay and of PC I have already been presented in previous publications.^{5,6}

(a) *Soluble Salt Content.*—The soluble salts present in -200 mesh Swat clay and PC I were determined on 50-g portions of the undried clay samples. These were shaken for 24 hr in a shaker with 1 litre of distilled water and then filtered. The Swat clay filtrate was centrifuged to get a clear solution.

TABLE 1.—CHEMICAL AND MECHANICAL ANALYSES OF -5 MICRON SWAT CLAY.

% Constituents	L/I %	SiO ₂ %	Al ₂ O ₃ %	Fe ₂ O ₃ %	CaO %	MgO %	(Na ₂ O + K ₂ O)	Total %
	12.39	46.14	36.46	0.60	3.22	0.48	0.61	99.90
<i>Particle size distribution</i>								
Equivalent spherical radius in microns	0.1	0.2	0.4	0.6	0.8	1	2	3 4 5
% by w. finer than	23.97	27.00	36.01	44.88	53.65	86.45	95.32	98.01 99.52 100

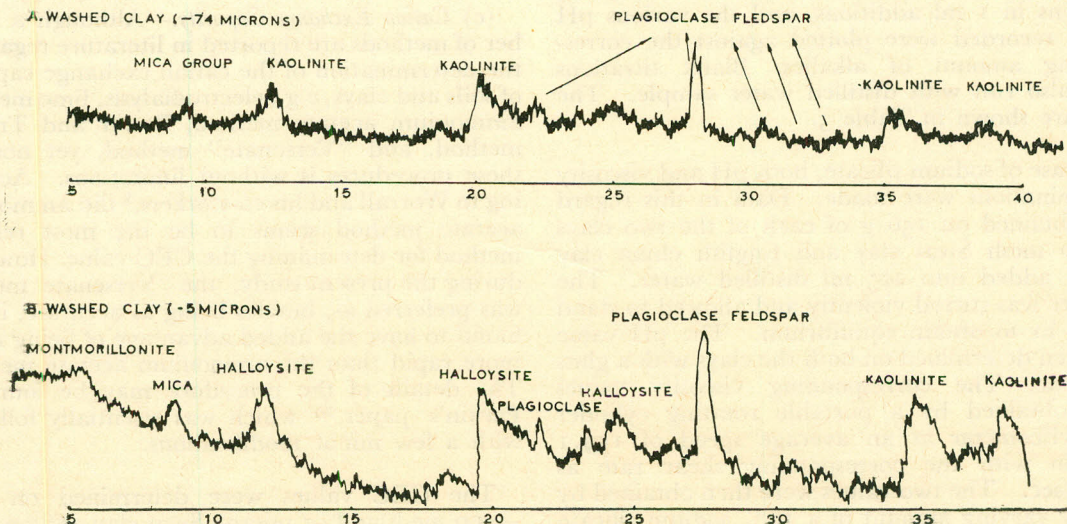


Fig. 1.—X-Ray diffraction of Swat clay.

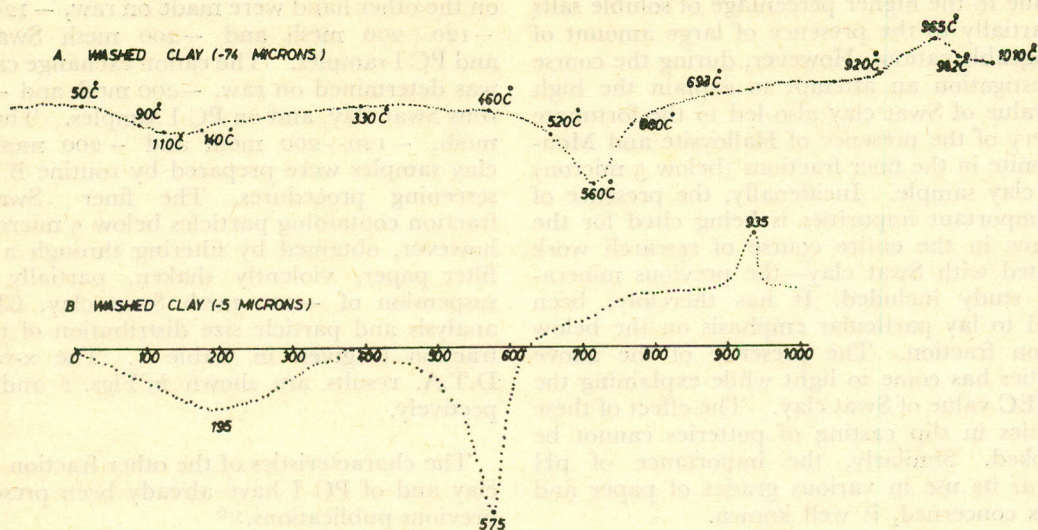


Fig. 2.—DTA curves of Swat clay.

The extract was examined for the following items by standard analytical procedure:⁸ (1) Total dissolved solids; (2) Loss on ignition (organic material, water of crystallization etc.); and (3) CaO, MgO, Na₂O, K₂O and SiO₂+R₂O₃ (by difference) The results are presented in Table 2.

(b) *pH Determination.*—The pH values of raw, -120 mesh, -120+200 mesh, and -200 mesh Swat clay and of PC I English China clay were determined with a glass electrode. pH meter, on suspensions containing 20% of dry clay; the clay standing in water overnight at room temperature to attain equilibrium. The suspensions were titrated against 0.1 N NaOH and 0.1 N Na₂CO₃ solutions in 1 ml additions, and the various pH values recorded were plotted against the corresponding amount of alkalis. Blank titrations were also run with distilled water sample. The data are shown in Table 3.

In case of sodium silicate, both pH and viscosity determinations were made. Data in this regard was obtained on 150 g of each of the two clays (-200 mesh Swat clay and English china clay PCI) added into 225 ml distilled water. The mixture was stirred violently and allowed to stand for 24 hr to obtain equilibrium. The pH value was then determined on both the clays with a glass electrode. The corresponding viscosity values were obtained by a portable rotating cylinder type viscometer at an average speed of 159.1 rev/min with the corresponding shear rate as 258.4/sec. The two values were then obtained by adding varying amount of a 10% sodium silicate solution. The data is presented in Table 4.

TABLE 2.—SOLUBLE SALTS.

Soluble salts contents	-200 mesh Swat clay mg/100 g of clay	PCI mg/100 g of clay
Total dissolved solids	310.0	82.0
Loss on ignition	113.0	22.0
CaO	78.0	11.2
MgO	16.2	4.0
Na ₂ O	80.0	18.8
K ₂ O	8.2	7.2
SiO ₂ +R ₂ O ₃ etc. (by difference)	15.0	18.8

(c) *Cation Exchange Capacity.*—Although a number of methods are reported in literature regarding the determination of the cation exchange capacity of soils and clays, e.g., electro dialysis, lime method, ammonium acetate method, Bower and Troug's method, and "Versenate" method, yet none of these procedures is without limitations. According to Worrall and his co-workers,⁸ the ammonium acetate method seems to be the most reliable method for determining the CEC value. However, during the present study, the 'Versenate' method was preferred as, besides being as accurate, it was found to have the added advantage of being much more rapid than the ammonium acetate method. The details of the procedure may be found in Parkin's paper,¹⁰ which was essentially followed with a few minor modifications.

The CEC values were determined on raw, -200 mesh and -5 micron Swat clay and on PC I English china-clay samples. The samples were

TABLE 3.—pH DATA NaOH AND Na₂CO₃.

Electrolyte added (ml)	0.1 N NaOH			0.1 N Na ₂ CO ₃			Raw Swat clay	-120 mesh Swat clay	-120-200 mesh Swat clay
	Water	-200 mesh	PC I	Water	-200 mesh	PC I			
0	6.70	7.50	5.20	6.70	7.50	5.20	7.4	7.45	7.40
1	9.35	7.80	6.85	8.95	7.80	6.85			
2	9.60	8.10	8.00	9.40	8.05	7.40			
3	9.80	8.38	8.60	9.45	8.20	7.90			
4	9.98	8.50	9.00	9.55	8.30	8.25			
5	10.10	8.75	9.35	9.65	8.45	8.45			
6	10.15	8.85	9.45	9.70	8.55	8.55			
8	—	9.05	9.67	9.76	8.65	8.75			
10	—	9.20	9.80	—	8.70	8.90			
15	—	9.50	10.00	—	8.85	9.05			

 TABLE 4.—pH AND VISCOSITY DATA (SODIUM SILICATE P).
Amount of Sodium Silicate Based on Dry Wt of Clay.

Samples	0.0		0.1		0.2		0.21		0.3		0.4	
	V*	pH	V*	pH	V*	pH	V*	pH	V*	pH	V*	pH
-200 mesh Swat clay	4.55	7.35	3.0	8.0	2.40	8.4	2.35	8.43	2.45	8.35	2.65	8.40
PC I	503.1	5.20	70.24	7.2	16.6	8.0	16.20	8.1	16.7	8.40	21.7	8.65

* Apparent viscosity expressed in centipoise.

saturated with calcium acetate, an excess of 'Versenate' was added and the unreacted 'Versenate' back titrated with magnesium acetate. Blank experiments were also run with these samples without saturating them with calcium acetate with a view to determining the nature of the exchangeable cations. Results are presented in Table 5.

Results and Discussion

The pH value of Swat clay suspension is higher than that of PC I. This initially higher pH value of the Swat clay-water system may be attributed partially to the higher percentage of soluble salts in Swat clay and partially to the presence of the large amount of exchangeable cations, especially Ca⁺⁺. This latter explanation would be in agreement with Worrall's⁸ opinion that the pH of a clay is largely dependent on the percentage saturation with metallic cations.

The pH value of English China clay PC I-water system is very sensitive to a change in the amount of various electrolytes; Swat clay-water system, on the other hand, does not respond so drastically. Accordingly, a greater variation in the amount of electrolyte may be tolerated in slips made of Swat clay.

Amongst the conventional electrolytes employed for the preparation of ceramic slips, sodium silicate appears to be the best in imparting ideal properties to suspensions containing Swat

TABLE 5.—CATION EXCHANGE CAPACITY.

Samples	Cation exchange capacity* (total)	Cation exchange capacity* (blank)
Raw Swat clay	9.12	6.57
-200 mesh Swat clay	14.77	13.21
-5 micron Swat clay (fraction)	19.4	18.15
PC I	2.25	1.70

*Expressed in milliequivalent/100g. of clay

clay. Also, because of the high initial pH of the Swat clay suspension, the amount of electrolyte needed to make an ideal Swat clay slip is much less than the amount required for slips of PC I clay. It is possible to get a good workable slip of Swat clay without any electrolytic addition whatsoever.

From the study of the comparative CEC values of the various fractions of Swat clay and of PC I presented in Table 5, the following two significant observations may be made: (a) the finer the Swat clay fraction, the higher is its CEC value, and (b) the cation exchange capacity of Swat clay is much higher than that of PC I. As a matter of fact, the CEC value of washed Swat clay is much higher than the average value of standard china clay; kaolinite itself has a value of only about 6 me./100 g.⁹

The increase in the CEC value of Swat clay fractions with decreasing particle size may be explained partially by assuming that some of the cation exchange is taking place at broken edges. As Grim states, 'In the kaolinite and halloysite minerals, broken bonds are the major cause of exchange capacity'.¹⁰ Results obtained by Johnson and Lawrence¹¹ also appear to support the view that CEC is proportional to surface area. On the other hand, part of the explanation may lie in the fact that the finer fractions are more enriched in clayey constituents than the coarser ones. As has been indicated during the mineralogical study of various Swat clay samples, raw Swat clay contains a maximum of only 15–20% kaolinite. On washing some enrichment takes place in the kaolinite content of the sample, which may rise to a maximum of 45–50%. Since the main impurities are plagioclase feldspars which would not contribute towards the cation exchange characteristic, it is reasonable to conclude that the elimination of the same would result in an increase in the CEC value of the sample.

However, the fact of the high absolute value of the CEC of the finer Swat clay fractions is still to be explained. The cation exchange capacity of the fraction containing particles below 5 micron is 19.4 me/100g. While the poor crystallinity of the kaolinite crystals, may help in increasing the CEC value, the figure of 19.4 me/100g is too high to be completely explained by this factor alone.

It was at this juncture that some scepticism was shown by the authors towards the previous mineralogical results, and the possibility of some minerals like livesite, halloysite and montmorillonite as impurities was entertained. Accordingly DTA and x-ray analysis were performed on the clay fraction containing particles below 5 micron size. As may be seen from the results obtained in this connection appreciable traces of halloysite and montmorillonite do seem to be present in the sample. In the light of these lately discovered facts from the DTA and x-ray analyses of the finest fractions and the reinterpretation made of the electron micrograph, the presence of halloysite and monmontmorillonite may be regarded as the major factor in increasing the CEC value of the Swat clay samples.

Conclusion

(1) The soluble salt content of Swat clay is comparatively higher than that of PC I; the most

significant cations in Swat clay leach being Ca^{++} and Na^+ . (2) Swat clay suspension has a high initial pH than the English China-clay suspension, Accordingly the amount of electrolyte required to make an ideal Swat clay slip is comparatively much lower than the slips containing PC I clay. (3) The CEC value of Swat clay is significantly higher than that of the English China-clay. The high exchange capacity of Swat clay is due to the poor crystallinity of the clay paraticles, on the one hand and the presence of such significant impurities as halloysite and montmorillonite, on the other.

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