Technology Section

Pak. j. sci. ind. res., vol. 34, no.12, December 1991

A STUDY OF MINERALOGY AND PHYSICO-CHEMICAL PROPERTIES OF SWAT CLAY REJECT (FINE SLIP)

MUSHTAQ AHMAD AND MUHAMMAD IBRAHIM

PCSIR Laboratories Complex, Lahore-54600, Pakistan

(Received April 29, 1989)

Mineralogy, chemical and physical investigations of "Fine slip" - a by-product of Swat clay reject, have been carried out in order to evaluate and find out the areas of its utilization. The results indicate that it can be utilized in the manufacture of pressed ceramic wares and tiles in particular.

Key words: Fine slip, Plagioclasefeldspars, Deflocculation.

Introduction

China clays are amongst the most important raw materials used in the ceramic industries. Their large amounts are consumed annually for producing the bone china, hard porcelain, electrical porcelain, earthenware, fine stone-ware, tiles and sanitary wares etc. The major demand of china clay for the country is met through imports. The principal deposits of china clay in Pakistan are those of Swat and Nagar Parker areas. Swat clay deposits are located between the villages Thagma and Shah Dheri in Swat. The contents of China clay are 15-20% in the material of this deposit. This clay, in fact, is a semi-weathered feldspathic material which occurs with large sizes of un-weathered pieces of feldspars, alongwith quartz and other minor impurities. An elutriation plant has, therefore, been installed at Mingora (Swat) to extract the 20% portion of the clayey material. During the elutriation of Swat clay a 10% material component of the reject is obtained as a by- product, termed "Fine slip" by the Factory Management. Fine slip has accumulated in huge heaps around the factory. It has created a great problem to accommodate the huge amount of this waste material at site. Its disposal is an extra un-economical burden on the factory. The factory management, therefore, requested the G&C Research Centre of PCSIR, Lahore, to help and advise for its disposal on economical basis and to find out the areas of its commercial exploitation. A project has, therefore, been under- taken for this purpose and it has been planned to determine its properties prior to assessing the areas of its proper utilisation and beneficial disposal.

Earlier [1] some ceramic body compositions were prepared by utilizing 30-70% of coarse fraction (-72 + 100 mesh) obtained by washing the raw swat clay sample in the Laboratories and their fired properties were determined. The sample of Fine slip under the present study has been furnished directly from the Eluteriation Plant Mingora (Swat). The plant is producing this waste material as a by-product at the rate of about 10 tonnes/day. Earlier no studies have been carried out on this by-product, which is available in huge quantities and causing hinderances for the running of plant efficiently.

Experimental

The sample of "Fine slip' was supplied in bulk and it was subjected to the following evaluation studies:

Chemical analysis: The Fine slip sample was further fractionated into two parts of +200 and -200 mesh sizes by washing with water through 200 mesh sieve. The chemical analyses of the original sample and its fractions were carried out by using the Standard methods [2]. The results have been presented in Table 1.

Rational analysis. The mineralogical composition of Fine slip was calculated from the results of the chemical analysis by Koening method [3]. The results have been recorded in Table 2.

TABLE 1. CHEMICAL ANALYSIS (FINE SLIP SAMPLES).

Percent chemical composition	Original	Fraction +200 mesh	Fraction -200 mesh
L/I	8.44	7.01	9.05
SiO_2	45.20	47.20	42.70
Al_2O_3	30.00	29.30	33.65
Fe_2O_3	0.90	0.95	0.85
CaO	12.90	12.90	11.80
MgO	0.40	0.41	0.36
Na_2O	1.80	1.80	1.20
K_2O	0.24	0.24	0.17

TABLE 2.

1.	Rational analysis (calculated)	
	Percent mineralogical composition	
	Sodium feldspar (albite)	15.20
	Calcium feldspar (anorthite)	63.81
	Potassium feldspar (orthoclase)	1.42
	Kaolinite	8.54
	Quartz	2.33
	H_2O	7.24
2.	Specific gravity	2.69
3.	Refractories (pyrometric cone equivalent).	1400°

(a). *Differential thermal analysis (DTA).* DTA determination was made using the technique of Mackenzie [4] and raising the temperature to 1100° at the rate of 10°/ min. The curves obtained are shown in Fig. 1.

(b). *X-Ray diffraction (XRD).* X-Ray diffraction pattern of the powder mount was obtained by using 10 cm camera, Ni-filtered Cu-K alpha radiation, from 30 MA/40 Kv generation. The XRD pattern is presented in Fig. 2 and the "d" values in Table 3.

prepared and dried at 60°. The slip was formed by adding gradually the dried material into the distilled water contained in one litre beaker and stirring it with the glass rod. The viscosity of the slip was measured by using the Brookfield viscometer with spindle 3, at a speed of 20 rev/min. Additions of 2 mls of the defflocculant solution were made at 5 mins intervals and the viscosity measured after each addition, till the viscosity no longer falls and then begins to rise. The results are presented in the form of a curve shown in Fig. 4.

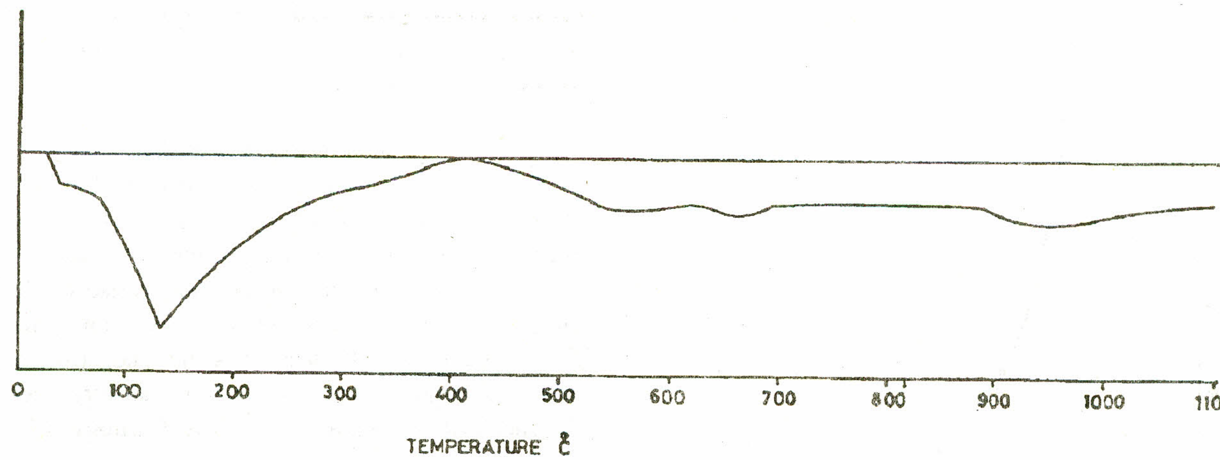

Fig. 1. Differential thermal analysis cure of "Fine slip".

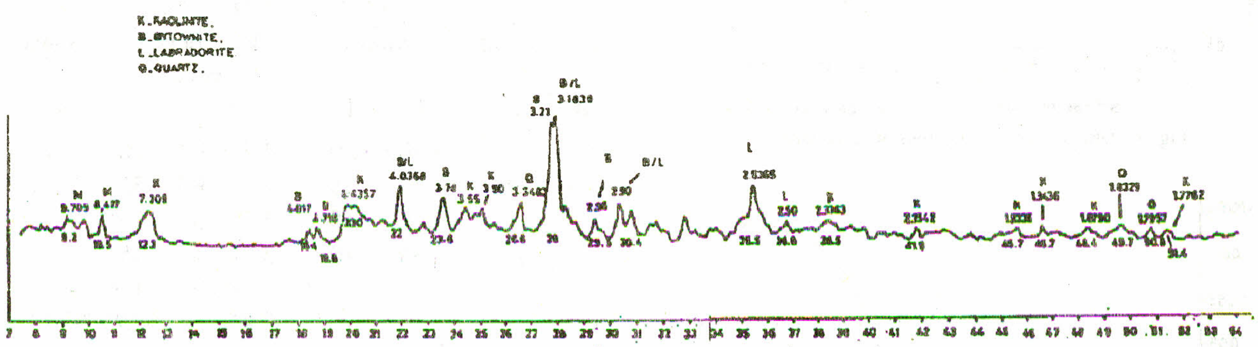

Fig. 2. X-ray diffraction pattern of "Fine slip".

Specific gravity. The specific gravity was determined by using the standard pycnometer method. The results are recorded in Table 2.

Particle size analysis. Particle size distribution data was obtained by means of Bouyocos Hydrometer in accordance with H-152 ASTM method [5], and it has been presented in the form of a curve shown in Fig. 3.

Pyrometric cone equivalent. Test cones were prepared in the form of a trigonal pyramide from the moist material with the help of a standard metal mould. The cone specimens were dried and fired to determine the pyrometric cone equivalent in accordance with ASTM method [6]. The results are included in Table 2.

Deflocculation behaviour. A sample of -25 mesh size was

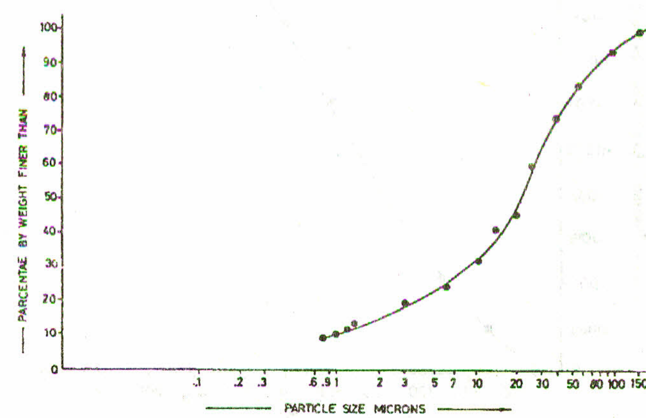

Fig. 3. "Fine slip" sizing analysis (cumulative plot).

Reversible thermal change. Test specimens of 2.5 inches length and 0.75 inch diameter were prepared by extrusion through de-airing pug mill. The specimens were dried at 110° and fired at 1200°. The thermal expansion was determined with the help of a dilatometer, and a heating rate of 3°/min. was maintained upto 1000°. The data for percent thermal expansion has been represented by the curve of Fig. 5.

Pyroplastic deformation. Test specimens of 10 cm length and 1.5 cm dia. were extruded in a de-airing pug mill. They were dried at 110° and subjected to deformation test by placing horizontally accross the refractory V-Block in the furnace and firing at 1000, 1100, 1200 and 1300° in different crops. A standard schedule of firing was followed and pyroplastic index values were determined according to McDowall and Vose [7]. The results have been registered in Table 4.

Dry and firing shrinkage. Test specimens of 6 inch length and 1 inch diameter were prepared by extruding through a de-airing pug mill. The specimens were dried at 110° and fired to 1000, 1100 and 1200° The dried and firing shrinkage were estimated in accordance to the ASTM method [9]. The results are included in Table 4.

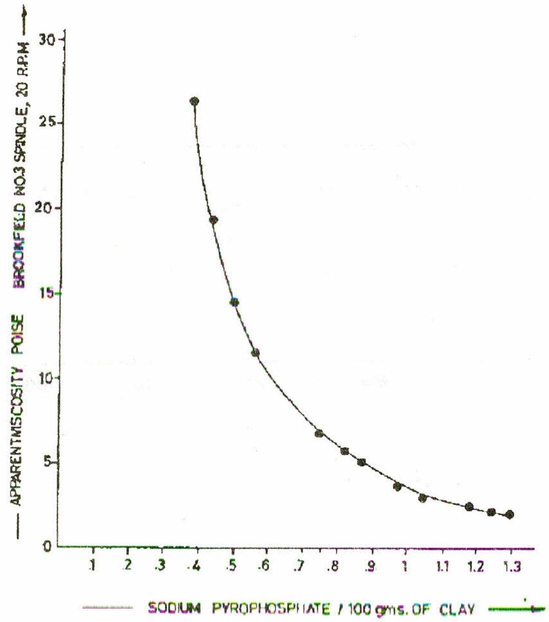

Fig. 4. Deflocculation behaviour of "Fine slip".

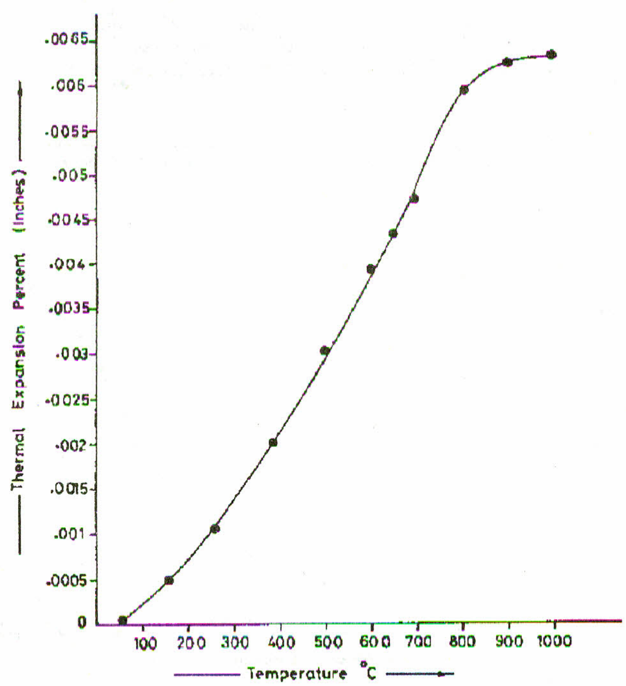

Fig. 5. Reversible linear thermal expansion of "Fine slip".

Results and Discussion

The chemical constituents of the Fine slip and its two fractions have been recorded in Table 1. The alumina and silica contents of Fine slip are present in the ratio of 1:1.5, which is a common factor in the composition of clays and feldspars etc. The presence of 8.44% loss on ignition and 12.85% (CaO), when the test for calcite is negative, makes it slightly difficult to understand, as to what form they exist. The chemical composition of the two fractions of Fine slip

TABLE 3. X-RAY ANALYSIS "d" VALUES AND INTENSITIES OF THE MINERALS DETECTED.

Mica group		Kaolinite		Plagioclase series		Quartz	
'd'	I	'd'	I	'd'	I	'd'	I
9.7	5	7.309	20	4.716 B*	10	3.348	25
8.41	20	4.43	25	4.036 B/L	35	1.795	7
–	–	3.50	15	3.78 B	25	–	–
–	–	3.55	10	3.21 B	95	–	–
–	–	–	–	3.183 B/L	100	–	–
–	–	–	–	2.95 B	20	–	–
–	–	–	–	2.90 B/L	25	–	–
–	–	–	–	2.53 L	40	–	–
–	–	–	–	2.50 L	15	–	–

* B,L represent Bytownite, Labradorite respectively.

TABLE 4. MODULUS OF RUPTURE, SHRINKAGE AND PYROPLASTIC INDEX.

	Firing temperature				
Properties	110°	1000°	1100°	1200°	1300°
1. Modulus of rupture	215.00	836.86	974.85	1229.24	.–
2. Percent linear shrinkage	2.50	0.65	1.53	3.29	–
3. Pyroplastic index (cms.)	-	11.5×10^{-6}	22.3×10^{-6}	29.8×10^{-6}	150.6×10^{-6}
4. Colour	White	Off white	Buff	Light brown	Brown

reveals simply that the SiO_2 contents has increased in the coarser (+200 mesh) and decreased to the equal amount in the finer portion, while Al_2O_3 contents has decreased in the coarser and increased in the finer part of the washed material. The chemical composition further reveals that the mineral causing excessive loss on ignition has increased in the finer fraction of the material.

The mineralogical composition derived by calculation from the chemical analysis data, is also included in Table 2. It is apparent from the Table that Fine slip is mainly an admixture of anorhite and albite associated with 8.54% kaolinite, 2.33% quartz and 1.41% ortholase as minor constituents of the material. The contents of albite and anorthite are as 15.20 and 63.83% respectively, in the ratio of 1:4.2. Another factor identified during the calculations of the mineralogical composition is the residual 7.24% contents of the loss on ignition (or H_2O content) which remained uncombined with the mineral constituents. Its presence in association with the feldspars could not be explained at this stage.

The mineralogical composition data obtained from the Differential Thermal Analysis has been represented in the form of a curve shown in Fig. 1. There is a very distinct and large endothermic peak at 130°. The only peak given by the clays below 500° is due to the presence of the adsorbed water and the associated impurities. This peak indicated the presence of the large amount of adsorbed water which liberates at about 130° and a large peak is produced. This idea relates to the above thought of 7.24% residual water which remained un-adjusted during the calculation of the rational analysis. The presence of this much amount of the adsorbed water may account for the poor crystalinity of the material. The view that only the crystal imperfection of 8.54% kaolinite mineral alone can accommodate 7.24% of water, while the material is mainly composed of feldspars, does not seem genuine. The elaboration of this point needs further studies which are beyond the scope of this paper.

Two endothermic small depressions in the curve may be observed at 550 and 650°. These are presumably due to the break- down of the structure of the kaolinite mineral brought about by the removal of the chemically bonded water in the clay lattice. There is another small endothermic depression at 910–1010°, which is a range of temperature, where an exothermic peak- a characteristic of Kaolinite mineral, occures. The nature of the thermal curve in this range of temperature indicates that the exothermic peak due to the presence of the smaller amount of the kaolinite mineral has been subdude by the large amount of the non- reactive, innert material of the feldspars.

The XRD pattern has been presented in Fig. 2 and the "d" values have been given in Table 3. The "d" values and their intensities show that a large amount of anorthite and albite alongwith small amounts of kaolinite and quartz are present in this by-product. It is well known that anorthite and albite form extensive series of the solid solutions. The ratio of albite to anorthite is 1-4.2 calculated in the rational analysis, and thus the Bytownite is the expected plagioclase to be present in large quantity. The lines 3.17 and 3.21 are very strong, while other lines for these minerals as shown in the table are of medium values. The amount of the feldspars interpretted from these lines also conform to the results calculated in the rational analysis. Since "d" values of Bytowite and Labradorite are similar so the presence of labradorite in combination with Bytownite can not be ignored. The lines 4.34, 1.83 and 4.43, 3.55 show the presence of quartz and kaolinite minerals respectively and 1.4869 indicates the presence of Montmorillonite in small amounts as well.

The specific gravity of Fine slip is 2.69 as shown in Table 2. This value is higher than English and Barfab (Swat) China clays, which are 2.6 [10] and 2.66 [11] respectively. The plagioclase which forms the major component of Fine slip, is composed of albite and anorthite. Their specific gravities are 2.61 and 2.76 [10] respectively. Obviously, it can be presumed that the high value of Sp. gravity of "Fine slip" is due to the presence of these denser feldspathic minerals which are predominating in the by-product material.

The colour of the specimens made of "Fine slip" is off-white when fired at 1000° and it became buff at 1100°, light brown at 1200° and at 1300° it turned brown with conspicous dots, scattered scarcely on the surface of their bodies.

The data of the grain size distribution and its graphic representation have been shown in Fig. 3. It can be ascertained from these results that Fine slip is a coarser material than china clays; as it contains 65% particles finer than 50 micron, 28% finer than 10 micron and 10% finer than 2 micron size. Generally, good quality china clays consist of particles over 90% less than 10 microns and over 50% less than 2 micron size. It is obvious from the data of the size distribution and the slope of the curve, that Fine slip is a well graded material, so far as the size distribution is concerned; and this character will induce a good compacting property which consequently will account for its good strength properties; inspite of its being coarser in size.

The deflocculation behaviour of Fine slip has been plotted in a graph shown in Fig. 4. It reveals the viscosity in poise against the deflocculant concentration in terms of gramms per 100 gm. of clay. Sodium pyrophosphate was used as a suitable deflocculant for this material. The rhelogical investigation was designed to establish the minimum apparent viscosity using the lesser amount of the deflocculant. Generally 5 poises is the minimum viscosity of a slip when it is considered to be at the ideal casting concentration and 0.4 to 0.5% of deflocculant per 100 gm of clay is required to achieve the above viscosity value. On the contrary the deflocculation curve of Fine slip shows that about 0.9% deflocculant is required to attain the minimum viscosity of 5 poises, which is almost double the amount required for a typical china clay. It is also obvious from the curve that Fine slip does not seem sensitive towards the addition of the electrolyte rather it shows less response and indifferent attitude for the deflocculant with the result that the viscosity falls slowly. This behaviour of Fine slip may be attributed to the presence for the inactive, feldspathic material in large quantity. It can be ascertained in the light of the above that Fine slip may not show a normal deflocculation behaviour and as thus may create difficulty for the casting wares.

The values of linear thermal expansion have been represented graphically in Fig. 5. The test specimens were fired at 1200° before measuring their thermal expansion, it is therefore, reversible. The thermal expansion of "Fine slip" increases with the rise of temperature but its magnitude is considerably lower than the standard China clays. Normally the kaolin clays expand to about 0.2% at 750° and 0.35% at 1000°, on the other hand Fine slip registered 0.0053% expansion at 750°, and 0.0063 at 1000°, these values are almost negligible as compared with the China clays. The low values of expansion of Fine slip may be attributed to the presence of an innert, non-reactive plagioclase feldspars which when fired to high temperature, react to produce material having a low expansion, and vitrify comparatively at lower temperature. The low thermal expansion of Fine slip is a valuable property for producing the ceramic wares.

The fusion point of Fine slip has been determined as 1400° and is recorded in Table 2. Pure kaolin clays have higher fusion points ranging between 1750 and 1770° [12]. Fine slip on the contrary deforms at low temperature, because of the presence of the plagioclase feldspars which act as fluxes and thus melt at lower temperature. The softening points of albite and anorthite are 1200 and 1550°respectively [13]. Fine slip contains about 80% albite and anorthite, and its refractoriness is approximately the average value of both the major constituents.

The dry strength of ceramic materials is very important for making the articles such as, tiles etc. The modulus of rupture of clays depends mostly upon chemical, mineralogical composition, and physical properties of the material. Fine slip is comparatively a coarser material than pure china clays, but its transverse breaking strength (Modulus of rupture) is greater than these clays. The values of modulus of rupture at 110, 1000 and 1200° are presented in Table 4. These values go on increasing as the firing temperature is increased. It is interesting to note that its dry strength is 215 PSI, which is more than English ball clays, whose strength when determined under the same conditions; has been found as 172 PSI. The fundamental cause of this high value of dry strength is not known with certainty. Undoubtedly, the "Fine slip" is a well graded material and there should be more points of contact within the mass, it may result in the reduction of the void spaces with increase in the strength. Other possibility for its greater dry strength may be due to the attractive forces between the particles or due to the union of the ionic fields of the surface layers. Anyhow, this high value of its dry strength is very important for producing ceramic articles like tiles.

The fired strength values of Fine slip are considerably higher and comparable, with quality ball clays. Here the main factor influencing the fired strength of the material is the presence of the fine grained feldspars in large quantity, which acts as fluxes and thus are capable of imparting greater strength at comparatively low temperatures than the pure kaoline.

The values of dry and firing shrinkages have been included in Table 4. It is evident from these figures that the wet to dry shrinkage is low; which is due to the removal of water from the surfaces of the grains. Fine slip is comparatively coarse grained, non-kaolinitic material and containing non-plastic feldspars, therefore, its drying shrinkage is accordingly low. The firing 'shrinkage values are also comparatively lower than the china clays. The firing shrinkage mainly depends upon the reactions occuring between the minerals, and the resulting crystalization liquid formation. The low values of the firing shrinkage from 1000 to 1200° are probably due to the non-plastic and non- kaolinitic character of the Fine slip. It has smaller void space which imparts lesser contraction when fired to 1200°. This quality of the "Fine slip" can be considered favourable for its application in the manufacturing of the ceramics, specially wall tiles.

Pyroplastic deformation is a property to investigate and quantify the deformation due to gravity on a ceramic body when it is rendered plastic during firing. The values of the pyroplastic index at various firing temperatures are quoted in Table 4. These values are expressed as a figure x 10^6 and these are usually in the range of 0-50. The pyroplastic index values of Fine slip are well within this range upto 1200°. After this temperature, this value increases abruptly and reaches at high level at 1300°, which indicates the fact that the body made of this material becomes very plastic at 1300° and its severe deformation range starts.

Conclusion

The following conclusions may be drawn from the foregoing discussions:

1. Fine slip is a by-product obtained in large quantity from the elutriation process and it is composed of mainly an admixture of anorthite and albite, with 8.5% kaolinite and a small amount of quartz as a minor impurity.

2. Its grain size distribution is well graded which accounts for its high values of modulus of rupture particularly in the dried state.

3. It is a low melting material as compared to china clays and its response towards electrolytes is poor. Its low value of the thermal expansion is also a significant property.

4. Its dry and firing shrinkage is lower as compared to china clays and pyroplastic deformation character is quite normal upto 1200°which is a creditable quality for Fine slip because anorthite when present in large quantity in a material, usually exhibits excessive warpage during firing.

Thus, it can be ascertained from the above properties that Fine slip is a valuable byproduct and it shows the possibility of being used as a raw material for making the pressed ceramic products particularly the tiles and other low grade ceramicwares. Further R&D work may perhaps lead to the discovery of some new scope of use for this byproduct.

Acknowledgement .The authors wish to thank Mr. F.A. Gill, Mr. M.D. Saadi, Mr. Javed Amjad and Mr. Muhammad Riaz of Glass and Ceramics Research Centre, PCSIR Laboratories Complex, Lahore, for their valuable assistance in carrying out these studies.

References

1. I.H. Shah, *et. al.,* Pak. j. sci. ind. res., **17,** 236 (1974).
2. H. Bennett and W.G. Hawlely, *Methods of Silicate Analysis* (Academic Press, London and New York, 1965).
3. E.W. Koening, J. Am. Ceram. Soc., **25,** 420 (1942).
4. R.C. Mackenzie, The Differential Thermal Investigations of Clays, Min. Soc., London, (1957).
5. *ASTM Standards* (1961), Part 4, pp. 1280.
6. *A Book of ASTM Standards* (1964), Part 13, C, 24-56 pp. 39-42.
7. I.C. McDowall and W. Vose, Trans. Brit. Ceram. Soc., **50,** 507 (1951).
8. *ASTM* (1961), Part 5, p. 530.
9. *ASTM* (1964), Part 13, pp. 296-97.
10. H.H. R utleys, *Elements of Mineralogy* (Thomas Murby, London, 1957), pp. 374 and 412.
11. F.A. Faruqi, M. Ahmad *et. al.,* Pak. j. sci. ind. res., **12,** 467 (1970).
12. F. Singer and S.S. Singer, *Industrial Ceramics* (Chapman and Hall Ltd., London, 1963), pp. 27.
13. F.A. Faruqi and Mushtaq Ahmad, Pak. j. sci. ind. res., **10** 58 (1967).