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CERAMIC PROPERTIES OF SWAT CLAY

Part I.—Physical Characteristics

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A comparative study has been made of the physical characteristics of the china clay of Swat State with those of an imported china clay. The results indicate that the indigenous clay is quite suitable as a ceramic material after simple water-washing and can successfully replace the imported china clay in pottery and porcelain manufacture.

Introduction

Chemical analyses of various samples of the clay deposits of Swat State obtained through the Geological Survey of Pakistan have been presented in an earlier publication.[1] where a detailed study of the mineralogical composition of the various constituents present in the clay samples has also been made. The present investigation is essentially confined to the study of physical properties of water-washed Swat clay sample with a view to finding its suitability as a ceramic material to replace the imported china clays. Complimentary study of the chemical characteristics of the clay has also been completed and follows the present study.[2] The possible non-ceramic uses will be presented in later communications.

It may be noted that the −200 mesh, water-washed Swat clay sample contains only about 50–60% kaolinite, the rest being mainly plagioclase felspars. Attempts are being made under a separate research project to further upgrade the clay, since very pure china clay is needed for non-ceramic applications. However, it was felt that the water-washed clay–felspar mixture may be profitably incorporated in ceramic compositions without further processing. That the assumption was justified was proved during the course of the investigation, as may be clearly seen in the concluding part of this communication.

Experimental

While some experiments were made on the raw, −120+200 mesh, and −120 mesh Swat clay samples, most determinations were made on −200 mesh, water-washed sample used by ceramic and other industries. For comparison, a representative sample of a typical English china clay, called PCI clay, was used. The plasticity and workability behaviour and the transverse strength were also compared with a typical English ball clay.

The representative raw Swat clay sample was prepared by blending some 79 samples received through the Geological Survey of Pakistan. The other samples were obtained from the sample by normal screening with B.S.S. and washing procedures.

Pertinent chemical and mineralogical data regarding Swat clay has been presented elswhere.[1] The chemical analysis of PC I clay is as follows: Ignition loss 12.52%, SiO_2 46.32%, Al_2O_3 37.74%, Fe_2O_3 0.32%, TiO_2 0.14%, CaO 0.78%, MgO 0.11%, Na_2O 0.74% and K_2O 0.86%

The following determinations were made on the −200 mesh, water-washed Swat clay sample and on the PC I clay. (1) Specific gravity; (2) colour and brightness; (3) particle size distribution; (4) dry and fired shrinkages; (5) reversible thermal change; (6) transverse strength; (7) viscosity and casting rate and; (8) plasticity and workability.

Determinations (2), (4), (5), and (6) were also made on the raw and −120 mesh Swat clay samples while determination (6) included the English ball clay as well, whose plasticity and workability characteristics were also determined under (8).

(1) *Specific Gravity.*—The specific gravities were determined in accordance with the British specifications using picnometer and water. Results were also verified with kerosene as the liquid.

(2) *Colour and Brightness.*—Colour was observed visually of the raw, −120 mesh and −200 mesh Swat clay samples as well as the PC I sample in the green state and after firing at 1050°C and 1150°C respectively. Brightness was determined by the "EEL" reflection spectro photometer on the −200 mesh Swat clay and the PC I samples fired at 110°C, 1150°C, 1250°C and 1250°C.

(3) *Particle Size Distribution.*—The particle size distribution data was obtained up to 0.1 micron size by the Andreasen pipette method.[3]

(4) *Dry and Fired Shrinkages.*—Rectangular bars were prepared by hand pressing the plastic clay in steel moulds. The specimens were marked for the drying shrinkage and dried at 110°C in an electric oven. The same were fired to 1050°C and 1250°C respectively and their linear shrinkages determined.

(5) *Reversible Thermal Change.*—Test bars of 2.5 in length and 0.75 in dia were prepared by the extrusion method and dried at 110°C. They were then fired to 1250°C in an electric kiln in 11½ hr including 2 hr of soaking and were cooled overnight. The expansion data was obtained on a dilatometer designed by the British Ceramic Research Association. A heating rate of 3°C per 6 min was maintained from room temperature to 1000°C.

(6) *Transverse Strength.*—Extruded specimens 7-in long with 1-in dia were dried at 110°C and fired to 1250°C and 1350°C separately in two crops. About eight specimens of each sample were used to determine the transverse strength at each firing temperature, i.e., 110°C, 1250°C and 1350°C in accordance with the standard ASTM method.[4]

(7) *Viscosity and Casting Rate.*—Four batches of clay suspensions containing 60% water with varying amounts of electrolyte were prepared for each clay. Sodium silicate was used as the electrolyte, its varying amounts being 0.1%, 0.15%, 0.2% and 0.25%, based on the dry wt of the clays. Each batch was ball-milled for 24 hr and its viscosity determined 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 slip of each of the above batches was cast in plaster moulds. The level of the slip was maintained constant for 5 min by intermittent addition of the slip after which time the slip was drained out and the cast piece allowed to dry. The released sample was dried at 110°C and weighed. The rate of casting was calculated as cast /50.44 cm^2 for 5 min. Casting rate by volume was calculated by taking into account the specific gravities of the two clays.

(8) *Plasticity and Workability.*—The plasticity and workability of the two clays were determined by the Linseis's plasticity apparatus. Shearing and tensile strengths were measured on the apparatus at a definite percentage of water content. The shearing strength was plotted against the transmitted tensile strength and the plasticity of the clays assessed according to Norton's suggestions.[5]

Results and Discussion

The specific gravity of the water-washed Swat clay sample is higher than the PC I, the values as shown in Table 1 for the two clays being 2.66 and 2.40 respectively. The higher specific gravity of the Swat clay sample may be attributed to the comparatively denser nonkaolinitic minerals present in the water-washed samples. As is known, the water-washed Swat clay sample contains not more than 50% kaolin, the rest being predominantly plagioclase felspars like bytownite and labradorite.[1] The specific gravities of the two minerals are 2.72 and 2.67 respectively; specific gravity of kaolin clays being around 2.58–2.60.[6]

The colour and brightness data is included in Table 1. The raw Swat clay sample burnt red while the −120 mesh and the −200 mesh samples burnt white at 1150°C. The red colour of the raw sample may be attributed to the high percentage of Fe_2O_3 present.

As may be observed from Table 1 the brightness of both the −200 mesh Swat clay and the PC I clay samples decreased with an increase in temperature from 1150°C to 1350°C. However the increase in the value of Swat clay was of, greater order than the PC I. As a result while the brightness was 79.50 vs 77.50 at 1150°C, it became 67.50 vs 71.00 at 1350°C. In other words, the Swat clay sample fired brighter at lower tem-

TABLE 1.—SPECIFIC GRAVITY, COLOUR, BRIGHTNESS AND PERCENTAGE LINEAR SHRINKAGE.

	Sp. gr.	Colour			Brightness				% Linear shrinkage			
		Green state	1050°C	1150°C	Dried at 110°C	1150°C	1250°C	1350°C	Wet to dry	1050°C	1150°C	1250°C
Raw Swat clay	—	Dirty white	Red	Red	—	—	—	—	1.13	1.60	1.90	2.60
−120 mesh clay	—	,,	Dirty white	White	—	—	—	—	2.00	6.00	6.10	8.00
−200 mesh clay	2.66	,,	White	,,	73.50	79.50	71.50	67.50	4.00	8.00	8.25	10.00
PC I	2.40	,,	,,	,,	72.50	77.50	76.56	71.00	3.00	4.00	4.40	11.00

Table 2.—Mechanical Analysis (Particle Size).

Equivalent spherical radius in microns	50	30	10	8	6	4	2	0.9	0.6	0.5	0.4	0.2	0.1
	Percentage by weight finer than size												
—200 mesh Swat clay	96.25	93.00	78.00	71.75	65.60	52.75	36.30	22.55	18.00	17.25	15.65	12.55	10.96
PC I	100.00	99.95	98.90	97.05	91.15	80.00	52.90	28.80	20.55	19.85	10.25	8.65	2.55

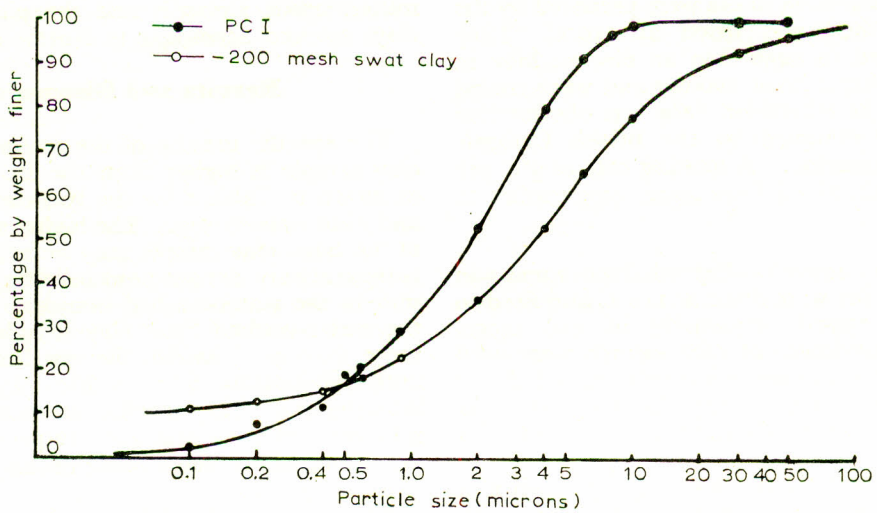

Fig. 1.—Sizing analysis (cumulative plot), logarithmic scale.

perature than the PC I sample while at higher temperatures the case was reversed. Thus while for high temperature ceramics, PC I has advantage over Swat clay, for lower temperature whiteware compositions, however, the indigenous clay has a decided edge over the imported china clay.

The physical and chemical properties of clays are profoundly influenced by their absolute particle size as well as their particle size distributions. The absolute particle size strongly influence such important ceramic characteristics as plasticity, rate of dewatering, dry shrinkage, dry strength and rate of vitrification, while on the particle size distribution depends the particle packing and thus the porosity of the formed article as well as its casting rate.

In general, the standard china clays consist of particles over 50% less than 2 microns and over 90% less than 10 microns, while 100% of their particles are less than 50 microns and thus pass through a 300 mesh sieve. While the PC I clay shows such a distribution, the washed Swat clay sample has only 36% particles finer than 2 microns, only 78% finer than 10 microns and total of only 96% less than 50 microns size. Thus the washed Swat clay sample appears to be comparatively coarser than PC I. This fact is clearly observable in Table 2. Fig. 1

However, from ceramic point of view, the colloid content of a clay is more important. The upper limit for colloidal range, as suggested by Freundlick,[7] is 0.25 micron equivalent spherical radius (e.s.r) size. Lower values have been suggested and 0.1 micron e.s.r. may be a better estimate. Accordingly, taking 0.25 micron e.s.r. as the upper limit the approximate colloid contents for PC I and Swat clay are 9% and 13% respectively. If, on the other hand, we assume 0.1 micron e.s.r. as the upper limit the amounts of colloid materials in the two clays come to 3% and 11% instead. This difference in the particle size distribution in the colloidal range of the two clays will have marked influence on their physical properties, in particular the strength characteristics.

It may also be observed from Fig. 1 that over a large range above 0.5 micron e.s.r. size, the distribution coefficient (represented inversely by the slope of the curve) of Swat clay is higher than that

of PC I. In other words Swat clay is more graded than the PC I clay. This characteristic as we shall see later has a decided effect on the casting rate of the two clays.

Both wet-to-dry and dry-to-fired shrinkages of the raw Swat clay samples are considerably lower than those of the washed clay. On the other hand, the values for PC I clay fall between those of the raw and the washed Swat clay samples.

The lower shrinkages of the raw clay may be conveniently explained by regarding the sample as essentially a plagioclase felspar with china clay as impurity, rather than a clay sample with large amount of fluxes. As is revealed by its chemical and mineralogical analysis, the raw Swat clay contains some 80% of non-clayey material a lager proportion of which is plagioclase felspars.[1]

Comparing the dry-to-fired shrinkage values of thewashed Swat clay sample with those of the PC I clay, it may be observed that while the washed Swat clay sample registers a higher shrinkage at lower temperatures, at 1250°C, PC I gives a higher value instead, there being a sharp increase in shrinkage in the case of PC I between 1150° and 1250°C. It may be concluded from this latter fact that while the vitrification of Swat clay starts at much lower temperatures, in the case of PC I, it becomes prevalent only after 1150°C, which is the expected behaviour in the light of the respective chemical and mineralogical compositions.

The lower wet-to-dry contraction of the PC I clay may be attributed to the difference in the ultimate particle size and the particle size distribution of the two clays.

Figure 2 is a graphic representation of the data obtained on the raw, −120 mesh, and −200 mesh Swat clay, and the PC I clay samples. Since the samples were fired to 1250°C, their thermalexpansions may be regarded as completely reversible.

In general, kaolin clays show a rather uniform reversible expansion, reaching a total of about 0.2% at 750°C and 0.35% at 1000°C. The PC I clay appears to correspond to this generalization: its expansion being 0.24% at 750°C and 0.38% at 1000°C. The Swat clay samples on the other hand, registered higher expansions all along the experimental temperature range of 0 to 1000°C, their respective expansions being in the following order: −200 mesh < −120 mesh < raw clay. Further, the expansion of −200 mesh Swat clay is appreciably different from that of PC I only after 750°C; at 750°C its expansion being about 0.26% (as compared with 0.24% for PC I) while at 1000°C it rises to 0.46%, the corresponding figure for PC I being only 0.38%. In contrast, the expansion of the raw Swat clay sample is approximately 0.6% at 1000°C. The high expansions of the Swat clay samples may be attributed to the presence of plagioclase felspars. When fired to higher temperatures the kaolin content of Swat clay would react with these fluxes, producing minerals of higher expansions than pure kaolin. Also being comparatively more vitrified, the expansion of Swat clay samples would in principle be higher than the less vitrified PC I clay sample.

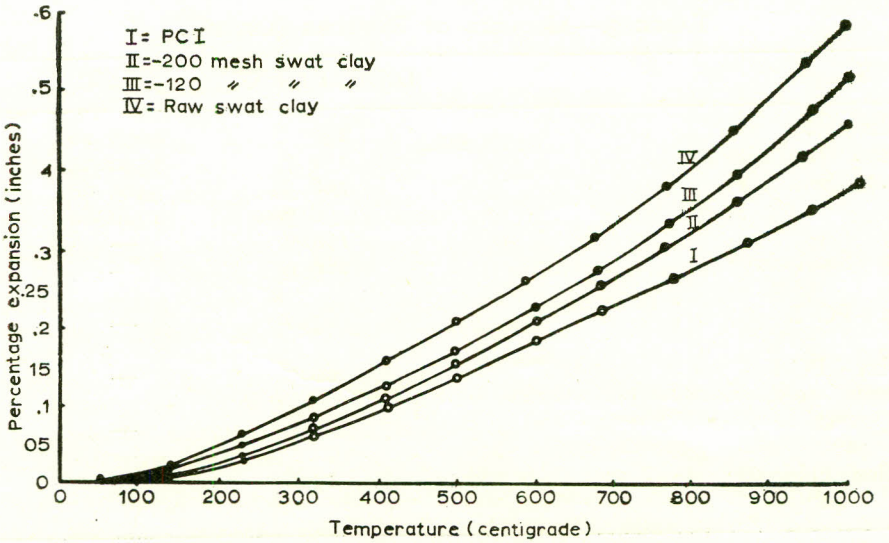

Fig. 2.—Reversible linear thermal expansion,

Dry strength refers to the ability of the dried article to withstand handling before firing without distortion of shape. This strengthening property is imparted by clays to widely different degrees, and appears to depend upon the cation exchange capacity of the clay, on the one hand, and the amount of colloidal material present, on the other.[8,9]

Table 3 shows that the dry strength of raw Swat clay is greater than −120 mesh and −200 mesh washed clay samples; these in turn have much greater strength than PC I clay. Further, the strength of −120 mesh Swat clay approaches that of English ball clay. As a matter of fact, their strength imparting capacities also seem to be equal. Samples of PC I clay containing 50% ball clay gave an average modulus of rupture value of 63.0 p.s.i. while pieces containing 50% Swat clay recorded the corresponding value of 60.7 p.s.i.

These results are in accord with the cation exchange capacities[2] as well as the colloid content values of two clays. In addition, the shape and size distribution of the particles in the non-colloidal range may also have played their part in providing more strength to the Swat clay pieces. As is known from the electron microscopic study,[2] the Swat clay particles have broken edges and are irregular in shape, which should facilitate a more thorough interlocking of the particles and thus should contribute towards increasing the dry strength. Similarly, the high distribution coefficient of the Swat clay particles should result in a better packed piece with higher strength. That the Swat clay pieces are better packed than those of PC I clay has also been empirically confirmed during the study of the casting rate characteristics of the two clays.

The fired strength of the Swat clay samples is much higher than that of the PC I piece. The strength of the raw clay piece fired at 1250°C being more than 300% of the PC I sample. In general, the fired strength of a ceramic ware depends upon the amount of fluxes and the degree of fineness of the particles present. It appears that in the present case, the amount of fluxes is the deciding factor as the modulus of rupture has increased exactly in the same order as the increase in the amount of fluxes in the various samples, i.e. raw > −120 mesh > −200 mesh > PC I.

The apparent viscosities and casting rates of PC I and −200 mesh. Swat clay samples are graphically represented in Fig. 3 and the pertinent data pertaining to the same is given in Table 4.

As is apparent from the graph, all along the experimental range, PC I proves to be more viscous than the Swat clay sample. Also, the minimum viscosity is attained for both the clays at 0.20% of sodium silicate, based on the dry wt of the materials. Further, the minimum viscosity of Swat clay is much less than that of PC I, being 5.70 centipoises as compared with 20.5 centipoises for PC I at 0.20% of sodium silicate. However, the PC I clay is much more sensitive to the introduction of the electrolyte. Its viscosity decreased almost cubically as compared with Swat clay which approximated a linear decline. All these observations fit well with the fact that the

Table 3.—Modulus of Rupture (lbs/in^2).

Sample	Dried at 110°C	1250°C	1350°C
Raw Swat clay	230	4039.26	—
−120 mesh Swat clay	171.7	3540.34	5896.72
−200 mesh Swat clay	168.5	3409.08	5479.50
PC I	38.3	1326.60	2002.30
Ball clay	172.3	—	—
Ball clay + Swat clay* 50% 50%	169.9	—	—
Ball clay + PC I 50% 50%	63.0	—	—
*Swat clay + PC I 50% 50%	60.7	—	—
PC I + Quartz 60% 40%	12.0	—	—
PC I + Sod. Feldspar 60% 40%	14.6	—	—

* Swat clay — 200 mesh Swat clay.

TABLE 4.—VISCOSITY AND CASTING RATE.

% Electrolyte*	Swat clay			PC I clay		
	Apparent viscosity (centipoises)	Casting rate by weight†	Casting rate by volume**	Apparent viscosity (centipoises)	Casting rate by weight†	Casting rate by volume*
0.10	21.3	23.50	8.83	77.9	25.01	10.40
0.15	11.0	21.01	7.9	45.1	21.98	9.1
0.20	5.7	18.75	7.04	20.5	19.11	7.96
0.25	9.8	20.50	7.70	21.0	23.50	9.79

Note.—Percentage of water added in each clay was 60%.

*Based on dry weight of clay: electrolyte being sodium silicate † Weighed /50.44 sq cm/5 mins: **Calculated from specific gravity data.

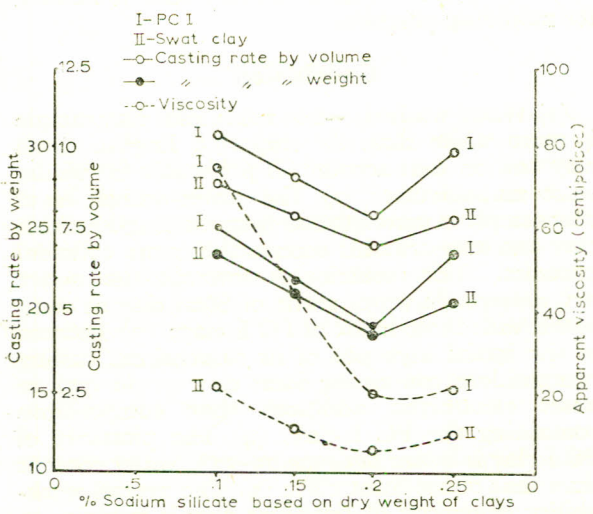

Fig. 3.—Viscosity and casting rate vs. amount of electrolyte.

PC I clay is a pure china clay with little nonclayey impurities while the −200 mesh Swat clay contains some 50% of nonplastic plagioclase felspars.

Coming to the casting rates it may be seen from Fig. 3 that the casting rates of the two clays, as well as their change with the change in the amount of electrolyte, show similarity to their viscosity behaviour. Like viscosity, the casting rate of the PC I clay is higher at any given electrolytic addition, than that of Swat clay. Also like viscosity, the minimum rate of casting for the two clays is registered at 0.2% of electrolytic addition: the casting rate of PC I at this addition being 19.11 g/50.44 sq cm/5 min as compared with 18.75 g for Swat clay. Calculated in terms of volume the two amounts come to 7.96 and 7.04 respectively. Further, like the rate of change of viscosity, the casting rate of PC I is influenced to a greater degree than Swat clay. It is known, that, other factors being equal, the casting rate of a slip shall be influenced by the packing arrangement of the clay particles in the cast layers. A more compact initial packing would resist filtration and thus result in a slower rate of casting than loose packing. It is also known that the packing arrangement of an aggregate depends upon the shape and size distribution of the particles. The more angular and the more distributed the particles, the more compact the system would tend to be. We know from Fig. 1 that the distribution coefficient of Swat clay is higher than that of PC I. Cast walls of Swat clay would, accordingly be more compact and the rate of casting of Swat clay suspension be comparatively slower. The experimental results correspond with these conclusions.

As has been suggested by Norton,[5] the workability characteristics of a clay may be defined by taking into consideration the following three factors: (a) yield value, (b) total strain, and (c) maximum stress. The yield value of a clay defines the onset of plastic deformation and is of importance in connection with the ability of a formed clay article to retain its shape under gravitational forces and handling conditions. The total strain, or maximum deformation, is a measure of the degree with which the plastic clay can be formed without rupture. Maximum stress on the other hand, indicates the amount of power required to work the clay and is thus of crucial importance only in extrusion processes. In the case of casting, it may not be of much significance. In general, a good plastic clay should have a high yield value and a high extensibility range; especially the latter. Clay of good workability characteristics should possess a low maximum stress value as well. For casting purposes, however, the workability and the plastic behaviour of clays may be taken to be identical.

From Fig. 4 it may be observed that the yield value (represented by point A in the graph) for PC I clay is higher than Swat clay but slightly lower than the English ball clay. On the other hand, the extensibility range (the range between

Table 5.—Plasticity and Workability Data.

	Swat clay				PC I clay				Ball clay			
	1	2	3	4	1	2	3	4	1	2	3	4
%Water contents	28.30	27.30	24.90	22.7	31.90	30.50	27.50	24.8	32.30	30.13	27.70	26.36
Shearing strength	1.50	5.00	15.00	29.00	2.00	5.00	11.80	20.00	7.00	9.50	19.50	30.00
Tensile strength	0.40	0.48	0.63	0.85	0.54	0.69	0.79	0.70	0.61	0.75	1.30	1.85

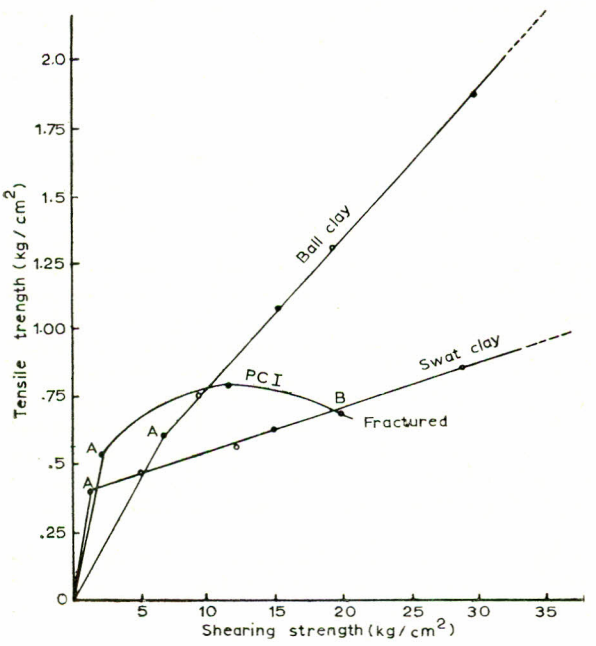

Fig. 4.—Plasticity curves.

point A, the yield point, and point B, the breaking point) of PC I clay is much shorter than the other two clays. As a matter of fact, the breaking point could not be reached under the experimental conditions both for the Swat clay and the ball clay. Their tensile strength vs shearing strength curves is still linearly ascending in the range of the observed shearing strengths. It may also be seen that the tensile strength of PC I is higher than that of Swat clay for any shearing strength value up to about 20 kg/cm², at which point the PC I sample broke. However, it continues to rise, reaching the maximum recorded value of 0.85 kg/cm² at 22.7% water content, beyond which value the trend could not be traced on account of experimental limitations.

From these facts it may be concluded that: (a) The plasticity of PC I is better between 25–32% water content than that of Swat clay. (b) The overall workability behaviour of the Swat clay is superior to that of PC I. (c) Wares made of PC I clay would be somewhat tougher in the green state than those of the Swat clay, and thus it may be advantageous to add a small quantity of ball clay or bentonite to the Swat clay body to be used for moulding purposes.

Conclusion

(1) Water-washed, −200 mesh Swat clay sample is more white than the imported English china clay and on that account, is preferable for whiteware manufacture; (2) The water-washed Swat clay sample is more graded than the English china clay and also contains comparably more colloidal particles. This contributes towards the better dry strength of wares made of Swat clay as compared with those made of PC I clay; (3) Because of the initial high pH of its suspensions, casting compositions containing Swat clay would require lesser electrolytic additions than compositions containing the PC I clay; (4) The plasticity of PC I clay is better between 25–32% water content than that of the Swat clay; (5) The overall workability behaviour of the Swat clay is superior to that of the PC I clay; (6) Wares made of the PC I clay would be somewhat toughter in the green state than those of the Swat clay. Accordingly, it would be advisable to add a small quantity of ball clay or bentonitic clay to the Swat clay composition to be used for moulding purposes; (7) The water-washed −200 mesh Swat clay sample can be successfully used to replace the imported china clays as well as a part of the fluxes in the production of high quality pottery and porcelains. However, plagioclase felspars present in the water-washed Swat clay due to their short vitrification range may produce in body compositions containing this clay, a tendency to excessive warpage which may create production problems.

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