PHYSICO-CHEMICAL INVESTIGATIONS OF SOME MYSORE CLAY SAMPLES

Part II. Particle Size Distribution, Plasticity and Dye Adsorption

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Received May 6, 1954

The mineralogical composition of the clay samples determined by chemical analysis, differential thermal analysis and base exchange capacity reported in Part I indicated that Gullahalli, Bageshpur, Tirthahalli and Czechoslovakian samples were kaolins while Gollahalli sample was halloysite. The Hebbur sample, on the other hand, was a mixture of kaolinite and montmorillonite. Although the clay mineral composition of the first four has been found to be the same, yet, it has been noticed both in industry and in the laboratory that these clays behave differently. With a view to understanding these differences, studies of particle size, plasticity and dye adsorption of these samples were undertaken.

Particle Size Distribution

The principle of the methods that are commonly employed for the determination of the particle size depends upon the application of the Stoke's law for the rate of settling of particles of different dimensions. Martin[1] has developed a method for the automatic recording of the weights of the solid settling down in an aqueous suspension by employing a granulometric balance. Bouyoucos and McCool[2] employed a hydrometer to determine the density of the suspension at different intervals of time, the amount of material settled being read from a predetermined concentration-density curve, for the substance concerned. Anderson[3] measured the concentrations by measurement of the refractive indices of the suspensions.

Von Hahn and Ostwald[4] in 1923 developed a method for the determination of rate of settling by keeping the clay suspension (20%) in one arm of a U-tube and the medium in the other. The rate of settling could then be ascertained by noting the densities of the suspension at different intervals as revealed by the heights of the liquid column in the two limbs. Kelly[5] has modified von Hahn's method whereby suspensions containing only 0·5–1·0% clay can be used. He increased the sensitivity of the apparatus by using a capillary for one arm of the U-tube and by having it at a small angle

(1° 30′). This method has been employed in the present work to determine the particle size of the clays.

APPARATUS

The apparatus employed consists essentially of a glass test tube 32 cm. in length and 2 cm. in diameter, with a capillary stop-cock fused to it at about 7 cm. from the closed end. The capillary tubing on the other side of the stop-cock was bent upwards to remain parallel to the above test tube for a length of 25 cm. and then bent practically at right angles with an inclination of about 1·5° to the horizontal.

A 1% suspension of clay in water was prepared using solutions of sodium silicate (0·001%) and gelatin (0·001%) to function as the peptising and the stabilising agents respectively. The apparatus was fixed vertically in an air thermostat maintained at 30° C. and filled with distilled water (containing the gelatin and scdium silicate as above) up to the upper bend of the capillary tube. The stop-cock was then closed and the water in the test tube was replaced by the clay suspension to the same height. The stop-cock was then opened and the equilibrium position of the water meniscus in the capillary was noted by means of a travelling microscope. The position of the meniscus was noted at intervals of 5 minutes during the first 30 minutes and then at intervals of 30 minutes. Suitable covers were employed to prevent the evaporation of water from the suspension. At the end of the experiment, the angle of inclination of the capillary to the horizontal was determined by the travelling microscope which could be used to measure both the horizontal and vertical distances.

The following relationship[5] was employed to calculate the weight of the solid that was settling down:

$$W = \frac{d.V.S.l \sin b}{h(S - d)}$$

where, W = weight of solid that settles; d = density of the water; V = volume of clay suspended in the large tube above the side tube, S = specific gravity of the suspension; l = length of the water column in the horizontal position of the capillary; $\sin b$ = sine of the angle which the side tube makes with the horizontal; h = height of the suspension in the large tube above the side tube.

Using this relationship, the weight of the material that settles at different intervals of time has been calculated. In Fig. 1, the percentage of clay that has settled, has been plotted as a function of time for the different samples.

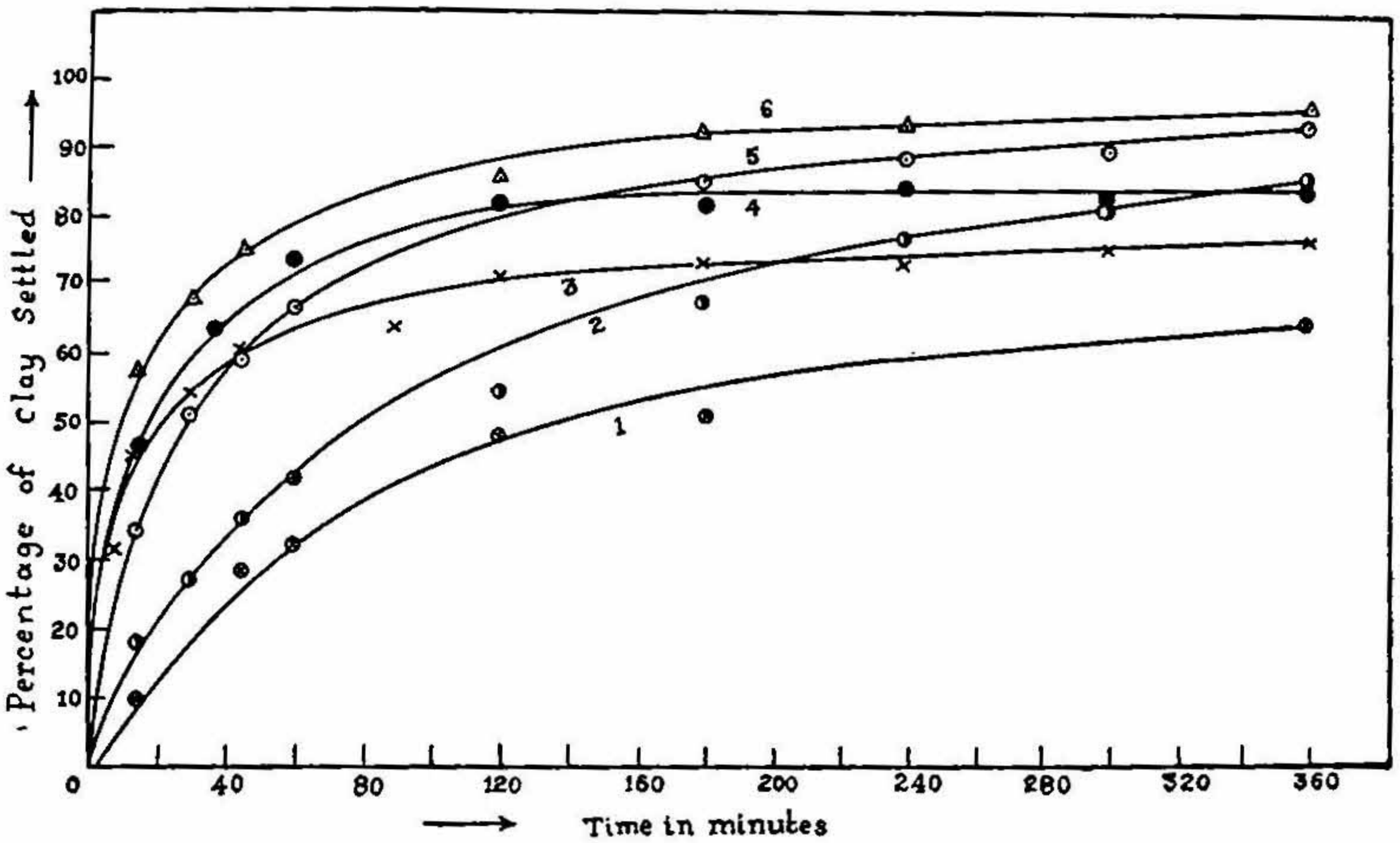

FIG. 1. 1. Czechoslovakian. 2. Gullahalli. 3. Gollahalli. 4. Hebbur. 5. Bageshpur. 6. Tirthahalli.

By the application of the Stoke's law at any particular interval, the average size of the particles remaining in suspension at any desired interval can be calculated. A knowledge of the amount of unsettled matter in the suspension can give a comparative idea of the particle size in the various suspensions. Table I gives the percentages of particles of various size ranges

TABLE I

Particle Size of the Clay Samples

Particle size in μ	Percentage					
	Gullahalli	Tirthahalli	Bageshpur	Gollahalli	Hebbur	Chechoslo-vakian
10·0–7·0	3·0	12·5	10·0	15·5	14·0	..
7·0–5·0	5·0	13·0	10·0	8·0	10·0	..
5·0–4·5	4·5	4·0	2·5	4·5	7·0	2·5
4·5–4·0	2·5	7·0	2·5	6·5	3·0	2·0
4·0–3·5	3·5	8·0	9·0	6·0	3·0	6·0
3·5–3·0	7·5	1·5	4·0	8·5	5·0	3·0
3·0–2·5	15·5	8·5	5·5	3·5	14·0	16·0
2·5–2·0	6·5	10·0	19·0	5·5	3·0	13·0
<2·0	52·0	35·5	37·5	42·0	41·0	57·5

and also the percentage of unsettled matter. Particle size has been computed down to a radius of 2μ. Particles of size lower than 2μ have been treated as unsettled matter and their percentages have also been given. According to the international classification in soils, those fractions whose particles are less than 2μ in diameter are considered as clay fraction. Thus the percentage of unsettled fraction in the various samples gives us the value of 'clay fractions' of the samples studied. The Czechoslovakian sample has 58% unsettled matter and the Tirthahalli sample has 36%, these being the upper and lower limits respectively.

PLASTICITY

Plasticity is that property which enables a material to be deformed continuously and permanently without rupture during the application of a force which exceeds the yield value of the material.[12] A number of methods, some direct and others indirect, have been proposed for measuring the plasticity of the clays. Of the direct methods, the one mostly used is the 'Atterberg plasticity method'.[6] Although this method involves some personal factor, yet it can be relied upon for purposes of comparison. The Green's plastometer[7] does not, however, suffer from these disadvantages and it is possible to get reproducible values. Hence this method is used to determine the plasticity of the clay in the present work. In this method the rate of flow of the suspension through a capillary tube at various pressures is determined. The volume discharged per second is then plotted against the pressure producing the flow. For plastic substances, the relation is linear only at higher pressures and its intercept on the pressure axis gives the yield value.

In the methods of measurement of plasticity of clay pastes, the clay-water ratio is a very important factor. The plasticity increases to a maximum with the addition of water and then begins to decrease gradually with further dilution. To get comparable results, one should always work with the same clay-water ratio for the various samples and use the same capillary for the plastomer. Hall,[6] however, claims that with the same capillary, if the clay: water ratio for the various samples is adjusted to give the same yield value, then the steepest slope is given by the most plastic clay. Thus, it will be possible to compare the plasticity of the various samples.

APPARATUS

The plastometer consisted of a capillary of 2 mm. diameter and 2" in length fused on to a flask of 100 c.c. capacity. This would fit into a receiver which had been connected to a calibrated gas flow meter. A compressed

air cylinder was used as the source of pressure and a constant head blow off was used to regulate the pressure. To measure the pressure, a manometer was placed between the air cylinder and the sample container.

150 g. of the air-dry clay was mixed with 100 c.c. of water containing sodium carbonate (0·01%) and sodium silicate (0·01%) to function as peptising agents and the mixture was subjected to vigorous stirring. The slurry so prepared was kept in a tall stoppered cylinder at 30° C. for 24 hours. The sample was shaken thoroughly before introducing into the plastometer. 50 c.c. of the slurry was placed in the flask at constant pressure and the amount of the slurry flowing through the capillary per unit time was noted. The experiment was repeated at different pressures in the flask and the rate of discharge of the slurry at various pressures was noted. In the case of the Hebbur and Bageshpur samples, however, the plasticity was too high when the ratio of clay to water was 150: 100. In these cases, therefore, a clay water ratio of 80: 100 and 88: 100 respectively were maintained for the preparation of the slurry.

Figure 2 gives the mobility plotted against pressure expressed in terms of millimetres of mercury. For purposes of comparison of the plasticity of the different samples, mobility is expressed as flow in grams per second, following the method of Randolph and Donnenwirth.[8] The slopes of these curves indicate that the clay samples can be arranged in the following order of decreasing plasticity: Hebbur, Czechoslovakian, Bageshpur, Gollahalli, Thirthahalli and Gullahalli.

Dye Absorption

It has long been observed that clay minerals adsorb different amounts of dyes like methylene blue and malachite green. Galletti[9] has reported that the colloidal clay content can be determined by measuring the dye adsorption of the clays. Dye adsorption method is also considered as one of the (indirect) methods of measuring the plasticity of the clay. The dye adsorption of the different samples was, therefore, studied.

1 g. of oven dry-clay was mixed with 25 c.c. of aqueous 0·05% methylene blue (or malachite green) solution and stirred well. The solution was kept in contact with the clay for 15 minutes. It has been shown by Bosazza[10] that this interval of time is sufficient for the attainment of equilibrium. The solution was then centrifuged and the dye left in the supernatant liquid was estimated in a Duboscq colorimeter.

In Table II, the values for the dye adsorption of the different samples are given in an increasing order. These results indicate that there is a close correlation between the adsorption of methylene blue and malachite green.

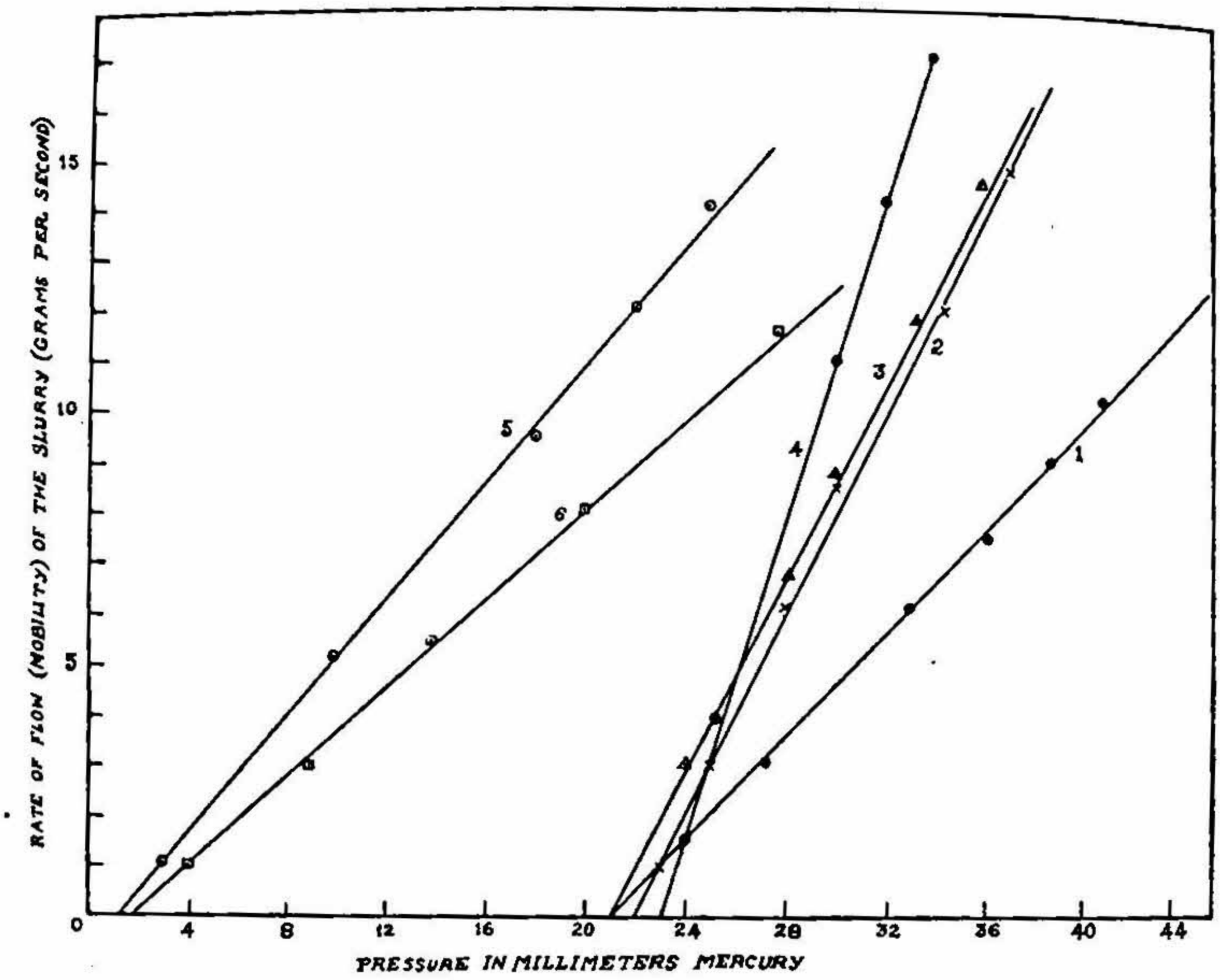

FIG. 2. 1. Gollahalli. 2. Czechoslovakian. 3. Bageshpur. 4. Hebbur, 5. Tirthahalli. 6. Gullahalli.

The ratio between the adsorption of malachite green to methylene blue is very nearly constant (Column 5, Table II). A similar correlation between

TABLE II

Sample	Adsorption of methylene blue (mgm. of dye/gm. of clay)	Adsorption of malachite green (mgm. of dye/gm. of clay)	B.E.C.	mal. green / me. blue	Methylene blue / B.E.C.	Increasing order of plasticity	Percentage particles less than 2·0 μ in size
1	2	3	4	5	6	7	8
1 Gullahalli	6·5	8·4	3·0	1·29	2·17	Gullahalli	52·0
2 Tirthahalli	19·7	26·0	4·3	1·32	4·58	Tirthahalli	35·5
3 Czechoslovakian	24·2	30·6	7·8	1·27	3·10	Gollahalli	57·5
4 Bageshpur	31·2	40·8	7·4	1·31	4·22	Bageshpur	37·5
5 Gollahalli	33·7	44·0	18·1	1·31	1·86	Czechoslovakian	42·0
6 Hebbur	79·3	101·2	29·8	1·28	2·66	Hebbur	41·0

the B.E.C. and the adsorption of the dye, gives a ratio varying between 1·9 and 4·6. Hendricks[11] has suggested that the organic bases react with the clay minerals in a manner similar to the base exchange phenomenon. The results noticed in this investigation are in qualitative agreement with the conclusions of Hendricks.

The data on plasticity of the clay samples (Column 7, Table II) has the same order as the dye adsorption in the case of four samples while in the other two there is a slight difference. This indicates that the statement that the dye adsorption can be employed to measure the plasticity is not entirely general.

The amount of clay less than 2μ in size is given in the last column of Table II. The results of the last column are not in the same order as in the first or second. It can, therefore, be concluded that the colloidal content of the clay sample cannot be correlated with the dye adsorption of the clays.

Conclusion

The results described in Part I and Part II indicate that although the clay samples 1–4 consist mainly of kaolinite minerals yet the physico-chemical properties (plasticity, dye adsorption) of the aqueous suspensions of the clay samples studied, vary to a large extent. This indicates that in addition to the clay mineral content, other physical properties like the state of division and degree of hydration, etc., also contribute considerably to the variation of the physical chemical properties.

Acknowledgment

The author is thankful to Dr. B. Sanjiva Rao and Dr. M. R. A. Rao for their interest and helpful suggestions during the course of the work.

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