PHYSICO-CHEMICAL INVESTIGATIONS OF SOME MYSORE CLAY SAMPLES

Part I. Determination of the Mineral Constituents of Clays

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The mineralogical composition of five Mysore clay samples and one Czechoslovakian sample has been calculated from the results of chemical analysis and compared with the data obtained by differential thermal analysis and determinations of base exchange capacity. Four of these samples are found to be kaolins, one a halloysite and the other a mixture of kaolin and montmorillonite. The relative merits of B.E.C. and the thermal curves for the determination of the clay minerals are discussed.

INTRODUCTION

The ceramic industries of Mysore State employ clay deposits which occur in various parts of the State. Although such clays have more or less the same composition as revealed by chemical analysis, their behaviour during processing are dissimilar. Since, such anomalies might be correlated with the presence of distinctly separate clay minerals in the different samples, and since very little information is available concerning this matter, it was considered worthwhile to study such clays by (*a*) differential thermal analysis and (*b*) measurements of base exchange capacity.

The clay minerals have generally been classified into kaolin, montmorillonite and illite groups. Kaolin group consists of kaolinite, dickite, nacrite, endellite, anauxite and halloysite. They have the general chemical composition $Al_2O_3.2SiO_2.2H_2O$, excepting in the case of halloysite which has one more molecule of adsorbed water. Their structure consists of one aluminium hydroxide sheet and one tetrahedral silica sheet held together by the valence bonds of four oxygen atoms that occur in each layer. Among the members of the kaolin group, the structures differ by a slight shift or rotation of the sheets as they are placed one above the other. This shift seems to be responsible for the minor differences in their physical and chemical properties. Most of the China clays contain kaolin minerals.

The members of the montmorillonite group are montmorillonite, pyrophyllite, montronite and saponite, having the general chemical composition

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$Al_2O_3 \cdot 2SiO_2 \cdot H_2O \cdot nH_2O$, where the nH_2O which is held between the silicate layers, can increase with the humidity of the atmosphere, thereby causing a corresponding expansion of the lattice. The members of this group, therefore, exhibit the property of swelling in water. The structure consists essentially of 2 silica sheets and one aluminium hydroxide sheet. The Al^{+++} can also be substituted by Fe^{+++} and/or Mg^{++} thereby upsetting the balance of the electrical charges and giving rise to high base exchange capacity.

The illite group consists of minerals which are similar to the white micas. The structure is essentially the same as of montmorillonite minerals in which the net negative charge developed by lattice substitution is balanced by K^+ which bridges the sheets of two successive units. Owing to this reason, the illite minerals do not possess the property of lattice expansion and do not exhibit swelling.

Experimental

Five representative samples of clays were collected from various districts of the State (Table I). These samples were washed with water and freed from coarse materials by settling. The clay suspension was then filtered, washed and air dried before use. The adsorbed water was determined by heating the sample to constant weight at 110° C., while the combined water along with volatile and organic matter was determined from the loss on ignitition at about 1000° C. A standard sample of Czechoslovakian clay was also employed in these studies for purposes of comparison.

Mineralogical Composition by Chemical Analysis

The clay samples dried to constant weight at 110° C., were analysed for SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, Na_2O and K_2O by standard methods. The results of the chemical analysis are given in Table I. These results have been employed to calculate the mineralogical composition by Wilson's method,[7] and the data obtained are given in Table II. According to Wilson, all clays are mixtures of clay-substance with quartz and feldspars and the latter can be calculated from the results of chemical analysis as follows:— Orthoclase ($K_2O \cdot Al_2O_3 \cdot 6SiO_2$) and albite ($Na_2O \cdot Al_2O_3 \cdot 6SiO_2$) are calculated from the corresponding values for K_2O and Na_2O respectively. Anorthite ($CaO \cdot Al_2O_3 \cdot 2 SiO_2$) is calculated from the CaO content of the clay. The balance of the Al_2O_3 is reckoned as the clay mineral, while the balance of SiO_2 or Al_2O_3 is expressed as quartz or alumina respectively. Hæmatite is calculated on the basis of Fe_2O_3 content.

Wilson's method is often criticised since the total alkali is taken to represent the feldspars although it is known that a good percentage of the alkali

could be present in the clays in the adsorbed condition. Added to this, the different clay minerals having the same chemical composition ($Al_2O_3 . 2SiO_2 . 2H_2O$) cannot be characterised by this method. Wilson's method can, therefore, give a quantitative idea of only the total clay minerals, in the clay sample and a semiquantitative idea regarding the sodium and potassium feldspars.

TABLE I

Chemical Analysis of the Clay Samples

Sample	SiO_2	Al_2O_3	Fe_2O_3	CaO	Na_2O	K_2O	Loss on ignition
1. Gullahalli .. .. (Kolar District)	42·85	42·71	1·14	..	0·13	0·40	12·16
2. Bageshpur .. .. (Hassan District)	45·52	39·97	1·00	0·50	0·40	1·00	11·60
3. Tirthahalli .. .. (Shimoga District)	47·03	38·84	0·59	0·25	0·29	0·30	13·07
4. Czechoslovakian .. (International standard)	48·20	37·40	0·80	0·21	0·10	0·32	12·99
5. Gollahalli .. .. (Bangalore District)	46·53	38·45	1·93	0·17	0·14	0·44	13·07
6. Hebbur .. .. (Tumkur District)	48·31	37·33	0·93	0·64	0·09	0·35	12·51

TABLE II

Clay-Mineral Content of the Samples

Sample	Ortho-clase	Albite	Anor-thite	Kaoli-nite	Hæma-tite	Quartz	Alumina
1. Gullahalli ..	1·17	0·55	..	93·99	0·57	..	3·80
2. Bageshpur ..	3·25	1·88	1·36	90·32	0·56	..	2·66
3. Tirthahalli ..	0·92	1·25	0·65	96·66	0·30	..	0·28
4. Czechoslova-kian ..	0·98	0·44	0·54	96·06	0·42	1·52	..
5. Gollahalli ..	1·35	0·62	0·43	96·30	1·00	0·21	..
6. Hebbur ..	1·07	0·41	1·65	93·79	0·48	2·54	..

It will be seen from Table II that the value for kaolinite varies from 90–96% in different samples, Tirthahalli sample containing the largest amount while Bageshpur the least. Feldspar content (orthoclase + albite) is highest in the Bageshpur sample while it is the least in Czechoslovakian. The iron content is the highest in the Gollahalli sample while it is the minimum in Tirthahalli. Alumina is present to the extent of 3% in both Gullahalli and Bageshpur while the Czechoslovakian and Hebbur samples have got an excess of quartz. Although the abovementioned minor differences in the mineral composition are found in the clay samples, these are not helpful in explaining the differences in physico-chemical properties of the samples.

DIFFERENTIAL THERMAL ANALYSIS

The method consists in the study of Time-Temperature records, in order to determine the endothermic or exothermic reactions produced in minerals, due to the formation of new solid phases during uniform heating. Different clay minerals undergo characteristic endothermic or exothermic reactions at specific temperature and this factor, therefore, serves for the identification of the clay mineral.

The method was first successfully applied to the study of clay minerals by Norton[4] and Grim.[2] These authors have found that kaolin group of clay minerals give an endothermic peak in the neighbourhood of 600° C., due to the dehydration of the mineral and an exothermic peak at 980° C., corresponding to the transformation of amorphous alumina to γ-alumina. The temperature of endothermic reaction happens to be 600°, 625° and 680° C., for anauxite, kaolinite and dickite respectively. Halloysite, on the other hand, has an additional endothermic reaction at 150° C., corresponding to the release of adsorbed water.

The montmorillonite group in general is characterised by three relatively small endothermic reactions followed by an exothermic reaction. The first peak (100–300° C.) corresponds to the loss of adsorbed water and often consists of a doublet rather than a single peak. The second peak occurs slightly above 700° C., but its position is not as definite as in the case of kaolin group. The temperature of the third peak varies between 840–930° C. The exothermic peak occurs in the neighbourhood of 1,000° C.

In the case of the illite group, the curves follow the general pattern of montmorillonite and are characterised by three endothermic peaks. It is distinguished from montmorillonite by the occurrence of the second peak at 600° C., and from kaolinite by its high exothermic peak at 980° C.

In general, it is found that the area under the peak is proportional to the percentage of the mineral present, under similar experimental conditions. The measurement of the area affords a method for the estimation of the mineral. There are two other factors which affect the temperature and magnitude of the endothermic or exothermic changes: (1) the rate of heating, and (2) the particle size of the mineral. In general, it is found that a high rate of heating increases the temperature of the thermal changes. The temperature of the occurrence of the peaks is also found to increase with an increase in the particle size. In order to get a quantitative knowledge of the endothermic and exothermic changes, it is therefore, essential to maintain a uniform rate of heating and also to maintain uniform particle size.

The apparatus used was similar to the one described by Norton[1] with minor modifications. The funace was michrone wound and was well lagged with asbestos. The rate of increase of the temperature was controlled by a variable transformer in conjunction with the furnace. The specimen holder consisted of a 18–8 stainless stell block with two lateral wells, one to contain the clay sample and the other for the ignited alumina, which served as the inert material. One chromel-alumel thermocouple was introduced into the alumina to measure the temperature of the inert sample. A second chromel-alumel thermocouple was introduced into the clay sample and was connected with the first to give the differential temperature between the inert sample and the clay. The outer terminals of the thermocouple (maintained at 0° C.) were connected to a K-type potentiometer to determine the temperature of the inert sample. The terminals of the differential thermocouple (also at 0° C.) were connected to a calibrated sensitive L & N galvanometer with lamp and scale arrangement to measure the current passing.

A heating rate of 12° C. per minute was maintained by a suitable manipulation of the variable transformer. The air-dry clay samples were passed through a 100-mesh sieve and kept over P_2O_3, in a desiccator for 48 hours. before use. The temperature of the inert sample was noted at the end of every two minutes. The differential thermal e.m.f. was recorded simultaneously. When the thermal changes occurred in the clay, the differential e.m.f. was recorded more frequently. The differential thermal curves are given in Fig. 1.

Curves I-IV (Fig. 1) have an endothermic peak at 620° C., and an exothermic peak at 980° C., which are characteristic of the kaolin minerals. Curve V has an additional endothermic peak at 150° C. This is characteristic of halloysite which has an endothermic peak at this temperature due to the loss of adsorbed water. In addition to the characteristic kaolin peak, sample
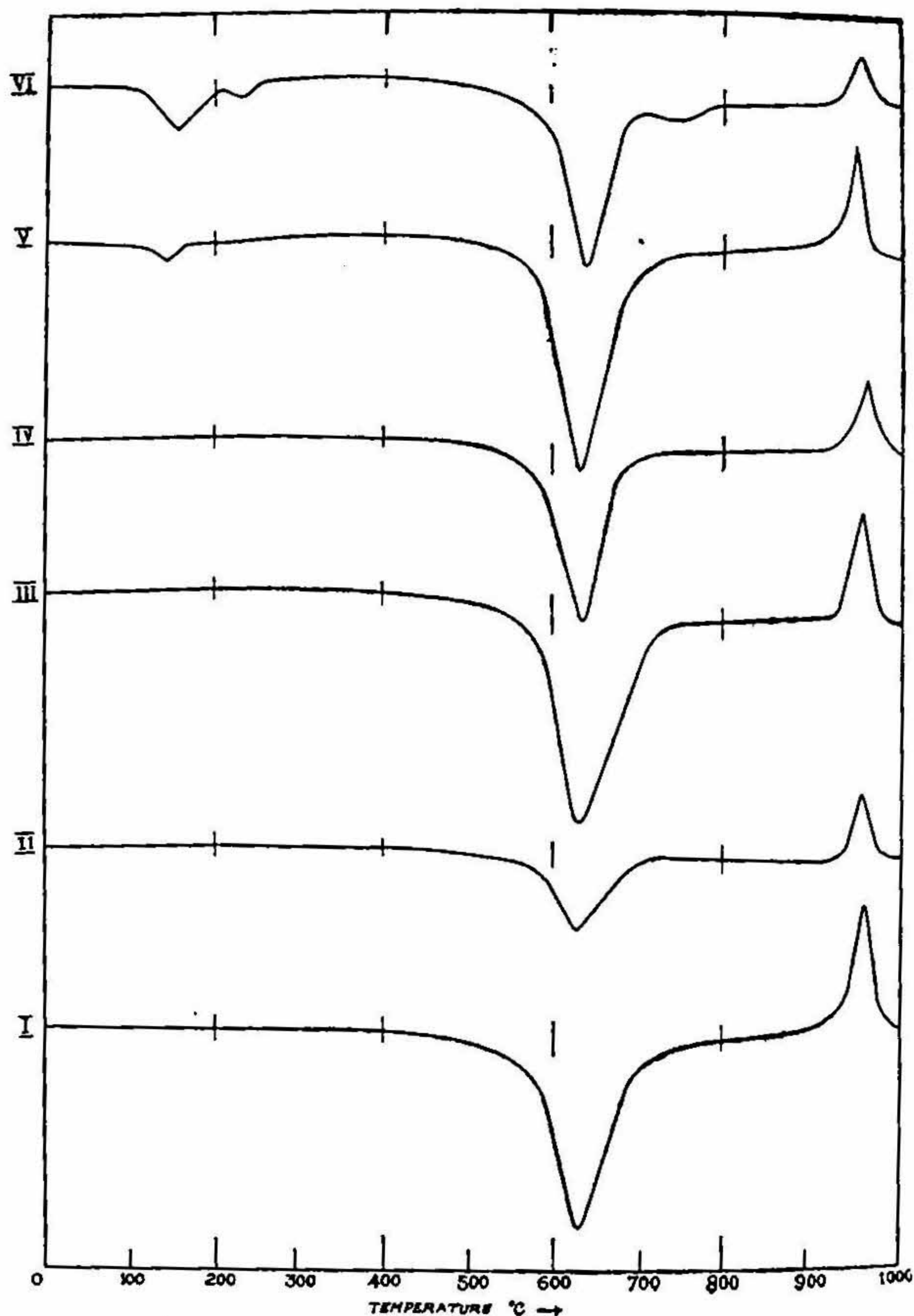
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FIG. 1. Differential Thermal Curves of the Clay Samples. I. Gullahalli. II. Bageshpur. III. Tirthahalli. IV. Czechoslovakian. V. Gollahalli. VI. Hebbur.

VI has a small endothermic doublet extending from 100°–250° C. and another peak at 700° C. These are characteristic of montmorillonite. Since the montmorillonite peaks are small compared to the kaolin peaks, sample VI must be predominantly kaolin admixed with a small quantity of montmorillonite. This has been further confirmed by the X-ray analysis of the sample by Dr. A. B. Biswas of the National Chemical Laboratory (unpublished). In the case of Curve II, the magnitude of the first (endothermic)

peak is much smaller than that for a normal kaolin sample (Curves I, III and IV). This is perhaps due to the relatively large quantity of feldspars, present in the sample (Table II) which interferes with the endothermic change.

BASE EXCHANGE CAPACITY (B.E.C.)

It has already been pointed out that montmorillonite minerals have a much higher B.E.C. than either kaolinites or illites. In general, it is found that the value of B.E.C. for kaolins will range from 3–15, while for illite and montmorillonite, the values range from 20–40 and 60–100 respectively. The B.E.C. is usually expressed as the number of milliequivalents of the base that can be exchanged for NH_4^+ when 100 g. of the clay are treated with ammonium acetate solution.

Parker's[5] and Schollenberger's[6] methods are generally employed for the determination of B.E.C. In these methods, the bases present in a weighed quantity of the clay are replaced by either Ca^{++} (Ba^{++}) or NH_4^+. The exchanged Ca^{++} (Ba^{++}) or NH_4^+ is then estimated quantitatively. These methods require large quantities of the clay sample (20 g.) for each determination and the exchange reactions and the washings of the excess reagent are time consuming.

Cantino[1] has developed a semi-micro method for the determination of B.E.C. employing ammonium acetate for the exchange of the base. The method has the advantage of using small quantities of material (about 1 g.) and is less time consuming. The following is the outline of the method employed for the determination of B.E.C.

One g. of the air-dried clay was digested for 25 minutes with 25 c.c. of 1N ammonium acetate solution (pH 7) at 60–70° C., and then centrifuged for 5 minutes after which the supernatant liquid was decanted. The process was repeated 4–5 times till the supernatant liquid gave a negative test for Ca^{++} since the Gullahalli sample did not have any Ca^{++}, the sample was subjected to ammonium acetate treatment 8 times for the base exchange purposes.

The residue was finally centrifuged and digested for 5 minutes at 45° C., with 10 c.c. of (ammonia-free) methyl alcohol. The contents were centrifuged to remove the supernatant alcohol. The process was repeated till the alcohol did not contain any ammonia as tested with Nessler's reagent. The ammonia present in the washed residue was estimated by the method described by Ma and Zuazaga[3] employing 2% boric acid solution for the absorption of ammonia. From the value of ammonia, the B.E.C. was calculated and expressed as milliequivalents of ammonia per 100 g. of clay.

Values for the B.E.C. of the clay samples studied along with the accepted values for the pure clay minerals are given in Table III.

Table III

Base Exchange Capacity of the Clay Samples

Sample	B.E.C.	Standard values for B.E.C. Sample	B.E.C.
1. Gullahalli	3·0	Kaolinite	3–15
2. Bageshpur	7·4	Halloysite	6–20
3. Tirthahalli	4·3	Illite	20–40
4. Czechoslovakian	7·8	Montmorillonite	60–100
5. Gollahalli	18·1		
6. Hebbur	29·8		

The values of B.E.C. for samples 1–4 are those for the kaolin minerals. This is in agreement with the conclusion from the differential thermal analysis. The B.E.C. of the Hebbur sample (6) indicates that it may belong to the illite group, but the differential thermal curve (Fig. 1) and the X-ray studies indicate that it is a mixture of kaolinite and montmorillonite. The montmorillonite detected in the sample may, therefore, be responsible for the high B.E.C. of sample 6. It can, therefore, be concluded that studies of B.E.C. alone may not give reliable idea about the nature of the clay mineral present.

Acknowledgment

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