EXPERIMENTAL

The experimental part of the present investigation consists of following:

Purification of vermiculite:

Raw vermiculite contains impurities like non-clayey matters, soluble and insoluble organic and inorganic compounds. For purification, 500 g. of the sample was handled at a time. The mineral was first shreded by means of hand into 1 to 3 mm size and milled in a pot mill under wet condition for a time period of 8 hours. After that it was sieved through 150 mesh screen and residue was subjected to milling under the same condition. The screened suspension was then blunged under large volume of water in a glass jar of 10 litre capacity. After proper slaking the suspension was thoroughly stirred. On allowing the suspension to stand for a few minutes, the nonclayey matters were found to be separated in large quantities from the platy mineral at the bottom of the jar, the top layer was carefully siphoned to another jar and this operation was repeated until no visible separation occurred. After waiting for 24 hours the suspension settled with separation of clear supernatant liquid at the top, which was again siphoned and H\textsubscript{2}O\textsubscript{2} (50 ml 20 v per two litres of suspension) was added and stirred to decompose the organic matter. Four such operations were separated until effervescence ceased. For removal of free iron and other soluble salt
the suspension was treated repeatedly with N/75 HCl. The excess acid and soluble salts were removed by repeated settling under large volume of water and siphonning the top-layer liquid. Finally the residual iron oxides were removed by following Na-dithionite-Na-citrate with NaHCO₃ buffer method. It is to be noted here that extremely fine fractions which were found to be contaminated with impurities were also rejected. Finally the clay was converted into Na-form by repeated leaching with 0.25 molar NaCl solution for complete conversion. After proper equilibration the excess electrolyte was washed by repeated leaching with distilled water, filtered through Buchner funnel, washed with distilled water until free from chloride and dried at 105°C, ground to powder and kept in a constant temperature incubator (36±1°C).

**Conversion of vermiculites into different cationic forms:**

Batchwise exchange technique was adopted for the conversion of Na-vermiculite into different cationic forms. For this purpose electrolyte solutions containing monovalent cations were prepared at 1(M) concentration, bivalent 0.5(M), trivalent 0.33(M) respectively. The exchange reaction was carried out at room temperature and under normal equilibrium condition. 100 g. of the original material in Na-form was equilibrated with 200 ml of the electrolyte solution containing the proper exchanging cation for a period of 48 hours. Then the mixture was filtered under suction and the residue was washed thoroughly until free from excess electrolytes and finally dried at a temperature of 60°C and stored in the incubator. The electrolyte solutions were taken in the form of chloride and aluminium as nitrate.
Chemical analysis of the vermiculite:

This was carried out by following standard method of silicate analysis. The constituents SiO₂ and Al₂O₃ were determined gravimetrically and Fe₂O₃, MgO, CaO as volumetrically.

Differential thermal analysis:

It was carried out in an automatic apparatus, Paulik Paulik Derivatograph (Hungarian Optical Works, Budapest). 0.7 g. of the powdered sample was taken in each case and the heating rate was maintained at 8°C/minute. The experiments were conducted up to 900°C with α-Al₂O₃ as the inert material.

X-ray analysis:

This was carried out to characterize the purified vermiculite. Powder pattern was taken, x-ray photograph was taken in Philips Debye Scherrer Camera of radius 57.3 cm Mn-filtered Fe-radiation.

The run was conducted at 30 KV and 10 ma and the exposure time was 8 hours.

Dehydration and rehydration under equilibrium condition:

The samples were equilibrated at a specified temperature and the loss in weight was recorded. The different cationic forms of vermiculite (2 g. sample of each) were placed in a porcelain crucible and heated in an electrically heated muffle furnace at the selected
temperature up to the point of equilibrium weight loss. The temperatures of heat treatment were 200°, 300°, 400°, 500°, 600°, 700° and 800°C.

After determining the weight losses the heat treated samples were successfully equilibrated at relative humidity of 17 per cent and 100 per cent, weighed after each stage, and finally placed in a thermostat (30°C).

The materials thus obtained, hereafter, referred to as the final thermostatted material, were subjected to the following determinations.

**Bulk-density** :

This was determined by taking the weight of a definite volume of the material in a graduated glass tube.

**Cation exchange capacity** :

The original as well as the final thermostatted materials were subjected to CEC determination. This was carried out by equilibrating 0.5 g. sample with exchanging electrolytes which was 0.1(M) CaCl₂ for all the monovalent cation substituted vermiculites and was 0.5(M) KCl for the rest. In all the cases the sample was taken in perfectly dry pyrex conical flask, 50 ml. of the exchanging electrolyte was added from pipette and allowed to equilibrate for 24 hours and then the liquid was decanted and analysed complexometrically with EDTA. For the monovalent
cation substituted vermiculites the CaCl₂ solution was titrated before and after exchange and from the change in concentration of Ca²⁺ the amount of exchange was determined. For the bivalent cations the liberated ions were titrated complexometrically from which the amount of exchange was calculated. Mg²⁺ and Ca²⁺ were determined by direct titration at pH 10.2 (AAC buffer) in the presence of solochrome black T indicator, Ba²⁺ was determined by displacement titration using Mg-EDTA solution at pH 10.2 in the presence of solochrome black T indicator.

**Method of leaching:**

In each case 0.5 g. of clay (on the basis of the completely dehydrated weight and in each case corresponding correction was made) was taken in a 100 ml clean dry pyrex conical flask. 50 ml of 0.1(N) H₂SO₄ solution was carefully added by means of a pipette. The mouth of the flask was covered with tin foil in order to avoid evaporation. After gentle swirling the flasks were arranged in a water bath by means of suitable clamps. The leaching operations were carried out at 98°C. For homogeneous temperature distribution a stirrer at the centre and the level of water in the bath was kept constant throughout the experiment. After equilibration for a definite period of time the flasks were carefully taken out, cooled to room temperature and filtered through a Whatman 40 filter paper using suction. The residue was repeatedly washed with distilled water and was finally made up to 250 ml. The silica and alumina in the leached phase were analytically determined.
Chemical analysis of extracted liquid :

i) Estimation of silica :

The amount of silica in the leached solution was determined colorimetrically in Hilger Pattern Biochem Absorptiometer.

Exactly 1 ml of solution was taken in a platinum crucible of 25 ml. capacity. 1.5 ml of distilled water and 1.5 ml 1(N) NaOH solution were added successively. The crucible was then covered with the lid and heated in a water bath for 2 minutes followed by addition of 5 ml distilled water, 2.25 ml of 10 per cent acetic acid and 2.5 ml of 10 per cent ammonium molybdate solution. It was again heated for 10 minutes and 1 ml saturated Na₂SO₃ solution was added. After heating the final mixture for 5 minutes the crucible was cooled under running tap water and the solution was carefully transferred to a stoppered pyrex test tube and the volume was made up to 15 ml with distilled water. After 8 minutes the transmittance was measured in a Hilger Pattern Colorimeter using 610 mμ filter.

ii) Estimation of alumina :

It was determined complexometrically using EDTA. Back titration method was adopted for the determination of aluminium in the leaching phase. 25 ml of the leached solution was taken in a 250 ml conical flask. To this solution a known excess of standard EDTA was added and boiled. After cooling this solution to room temperature, the PH was adjusted to 4.5 to 5 by the addition of ammonium acetate buffer.
This solution was then titrated with standard zinc-acetate (0.01M) in presence of xylenol orange indicator, until the colour changed sharply from yellow to violet. The iron content in the extracted liquid was determined in each case. For estimation of alumina compl- exometrically the corresponding value for iron was always deducted.

iii) Estimation of ferric oxide:

The iron content in the extracted liquid was determined by titration with standard Hg2(NO3)2 solution using 5 per cent NH4SCN solution as indicator.

Kinetics of dehydration:

The present kinetic study was divided into two heads:

i) expulsion of loosely bound interlayer water in the case of vermiculite.

ii) dehydration or expulsion of chemically combined water.

Both the rate studies were performed by carrying out isothermal experiments in a thermogravimetric apparatus. This consists of a thermobalance, and a platinum crucible (cylindrical in shape diameter = 1.5 cm, total capacity = 5 ml) which was suspended from one arm of the balance into the firing zone of a tubular furnace. The tip of the thermocouple of the temperature indicator was placed very close to the crucible and was maintained at the constant position. The temperature
of the furnace was raised and controlled by means of an adjustable variac. The control of temperature was within ± 0.5°C. For each experiment exact 0.5 g. sample was used and was spread to the same height in the crucible. The crucible with the sample (0.5 g.) was equilibrated in the incubator (36 ± 1°C) and then placed carefully into the firing zone of the furnace which was previously raised to the desired temperature. Dehydroxylation rate study was carried out in the same manner as stated above but the sample was preheated to 300°C in order to remove the loosely held water and then quickly inserted to the experimental reaction temperature. In each case weight loss was recorded as a function of time up to a point where three successive readings at 10 minutes interval were identical.

From the results log \( (L_\infty - L_t) / L_\infty \) was plotted against time, where \( L_\infty \) was the equilibrium loss or the loss in weight on completion of dehydration, \( L_t \) was the loss in weight at time \( t \). The reaction rate constant (K) was calculated from the slope of the straight line portion of the curves. Then the activation energy was calculated from the Arrhenius plots i.e. \( \log_{10} K \) against \( 1/T \) (\( T = \) absolute temperature).