

4. EXPERIMENTAL

4.1. Materials

4.1.1. Montmorillonite Clays:

Three montmorillonite clay samples were studied. These can be divided into two categories.

1. Montmorillonites from India
 - NK (Nilkanth Mine Chem, Rajasthan, India)
 - AP (Gujarat, India)
2. Commercially Purified Montmorillonite
 - PGV (Nanocor Inc., USA)

4.1.2. The Intercalants:

Alkylammonium cations were used as intercalants. The details of used intercalants are described in respective sections.

4.2. Preparation of Experimental Montmorillonite Clays

4.2.1. Purification of As-received Montmorillonitic Clays

Separation of pure montmorillonite phase present in the as-received clay is necessary for this study which can be done by fractionation of clay mineral. Before fractionation perturbing substances have to be removed from the bulk sample. In the bulk sample carbonates, organic matter may present. Coating of these substances can create aggregation and cementation of clay minerals. This creates inadequate dispersion of clay minerals during fractionation. As-received montmorillonitic clays from India were sieved (150 μ) to remove grit. Submicron fraction of clay specimens NK and AP was collected by sedimentation after decomposition of carbonates and organics. Purification of NK and AP was done following methods¹ as described below. Sample of PGV was taken as-received.

Removal of Carbonates

Removal of carbonates was done by addition of very dilute hydrochloric acid (0.01 M) and maintaining the pH of the suspension at around 4.5.

Removal of Organic Matter

After removal of carbonates small amount of 10% H₂O₂ was added to the sediment until no foaming was observed.

Fractionation

After the above treatments the clay dispersion obtained was fractionated by sedimentation to collect less than 1 μ particles. Thus sedimentation helped to facilitate the separation of impurities of larger size that are trapped between the non-exfoliated aggregations. Very dilute suspension of the raw clay (0.5%) was taken in a column (height 90 cm, diameter 30 cm). After 72 hours clay suspension containing clay particles less than 1 μ diameter was collected from the calculated height (50 cm).

4.2.2. Preparation of Sodium-montmorillonite Clays by Ion Exchange

All the clays (Including PGV) were converted to Na⁺-exchanged form by exchanging the dilute clay suspension (0.5%) with Amberlite 120 H (S.D. Fine Chem. Ltd, India) which was previously converted to Na⁺ -exchanged form by exchanging with 0.5 M NaCl solution.

Drying

The Na⁺-Mt clays were then dried at 105 \pm 10 °C and sieved (150 μ). The prepared clays were kept in desiccator for further experiments.

4.3. Instruments Used for Preparation of Intercalated Clays

The following processing equipment were used for synthesis of intercalated clays.

- Ultrasonication bath
- Stirring hot plate
- Buchner Funnel for vacuum filtration
- Vacuum oven

Preparation of intercalated clays is described in the respective sections with details.

4.4. Instruments Used for Characterization of Montmorillonite Clays and Intercalated Montmorillonite Clays

- Inductively Coupled Plasma Atomic Emission Spectrophotometer (ICP-AES), Spectro Analytical Instrument, Spectro Ciros Vision model, Germany.
- Particle Size Analyzer from Microtrac (USA), model S 3500.
- U.V. Visible Spectrophotometer for determination of Cation Exchange Capacity: PerkinElmer, Lambda 20 Spectrometer.
- Differential Thermal Analyzer: NETZCH Thermal Analyzer STA 409 instrument, Germany.
- X-Ray Diffractometer: X'Pert –Pro Diffractometer (PANalytical).
- Thermogravimetric Analyzer: Okay TGA fitted with Libratherm Instruments PID 330 Controller, Baisakh and Co., Kolkata, India.
- Fourier Transform Infrared Spectrophotometer: PerkinElmer, Model - Spectrum 100, FTIR Spectrophotometer.
- FESEM: Carl Zeiss, Supra 35 VP, Germany.
- TEM: TECNAI G² 30 ST, FEI Company, The Netherlands.

4.5. Techniques and Methods Employed for the Characterization

4.5.1. Chemical Analysis

SiO₂ was estimated gravimetrically and Na₂O and K₂O flame photometrically. ICP-AES (Inductively Coupled Plasma Atomic Emission Spectrophotometer) was used for estimation of other oxide constituents. Loss on ignition (LOI) was determined by heating the sample at 1000 °C for 60 minutes and recording weight loss.

4.5.2. Particle Size Analysis

Particle size analysis done by the Particle Size Analyzer from Microrac reports the particle size information using trilaser technology, which is an

extension of particle size analysis through light scattering technology. The ultrasonic power was 20 Watts and ultrasonication time was 20 seconds. Very dilute clay suspension 0.1 % was prepared by dispersing the dried clay (90 °C) in distilled water followed by 30 minutes ultrasonication in ultrasonication bath.

4.5.3. Determination of Cation Exchange Capacity (CEC)

The method used here² for the determination of CEC comprises an adsorption of copper complex ion by clay using the UV-VIS spectrophotometer as described below.

At first a 0.01 molar solution of copper triethylene tetramine complex $[\text{Cu}(\text{trien})]^{2+}$ was prepared to determine the CEC. For that purpose 500 ml 0.1 (M) CuSO_4 solution was first prepared. Then 1000 ml 0.01 (M) complex solution was prepared by mixing 100 ml 0.1 (M) CuSO_4 solution with 0.01 mole triethylene tetramine dissolved in distilled water. 100 mg of dry clay was accurately weighed in 25 ml centrifugal tubes. 8 ml of 0.01 molar complex solution was added and the sample was shaken for 30 minutes. The samples were centrifuged and 3 ml of the supernatant were filled into cuvetts. 1 ml 1 molar tris buffer was mixed with the supernatant to adjust the pH of the solution. The adsorption was measured near 574 nm by the U.V. Visible Spectrophotometer. From the concentration of adsorbed Cu (II) complex by the clay CEC was calculated.

4.5.4. Determination of Layer Charge

Layer charge is a significant characteristic of 2:1 layer phyllosilicates. The magnitude of the layer charge is used in the classification of 2:1 silicate clays. The CEC is a measure for the total layer charge including permanent charge and variable charge. The layer charge density gives the amount of permanent charges referred to the planar mineral surface. The permanent charge can be located in the octahedral and the tetrahedral sheet. The layer charge can be calculated from the structural formula of homoionic pure clay mineral specimens. From the occupancy of elements in the tetrahedral and octahedral sheets, the charge distribution between these sheets is estimated. Memut and Lagaly³ described a method to

determine the layer charge based on the measurement of basal spacing after exchange with alkylammonium cations of varying chain lengths. Layer charge heterogeneity within a clay mineral can also be determined by this method.

The intercalants used in this study were primary n alkyl ammonium cations with increasing carbon number two at a time to take an attempt to determine the layer charge of three Na^+ -Mt clays from the monolayer to bilayer transition following the method described by Mermut and Lagaly. When short alkyl chains are arranged in a monolayer arrangement within the interlayer space, the area of an alkylammonium ion, A_c , is determined by the following equation

$$A_c = 1.27 * 4.5 n_c + 14 (\text{Å}^\circ)^2$$

Where n_c is the number of the carbon atoms in the alkyl chain. The area of a half unit-cell of a given 2:1 phyllosilicate (A_e) is equal to $ab/2$, a and b are unit-cell parameters. When the monolayer of alkylammonium ions is close-packed, then A_c will be equal to A_e and the charge can be calculated from the following equation.

$$\text{Layer charge} = A_e / A_c = ab/2 / (5.67 n_c (\text{I}) + 14)$$

Where $n_c (\text{I})$ is the number of carbon atoms in a chain which are close packed in the monolayer, (ab) is the unit-cell surface area of the clay mineral. When the chain length increases above $n_c (\text{I})$ at the monolayer coverage, the alkylammonium ions will generate an incomplete bilayer and a shift in d value from 13.6 to 17.6 Å° will take place. In the case of charge heterogeneity, the cation density will vary from one interlayer to another, between the two limiting values calculated from the transition region. The value of n_c at $d(001)$ of 1.36 nm gives the upper value of layer charge, whereas the lowest value of n_c at the spacing of 1.76 nm provides the lower limit of the charge distribution. The average of both values is often close to the mean layer charge. Mean layer charge and the charge distribution thus can be calculated from the basal spacing in the transition range, *i.e.* between 13.6 and 17.6 Å° .

4.5.5. Differential Thermal Analysis (DTA)

Experimental montmorillonite clay samples were studied under nitrogen gas flow up to 800 °C at a heating rate of 10 °C/min in alumina crucible and using α -Al₂O₃ as a reference material.

4.5.6. X-ray Diffraction Analysis (XRD)

X-ray powder diffraction patterns were obtained using X'Pert –Pro diffractometer (PANalytical) with Cu-K α radiation. To enhance intensity of *00l* planes of experimental montmorillonite clays, oriented aggregates were prepared. Oriented aggregate mounts were placed on the shelf of desiccator containing ethylene glycol for saturating the sample with glycol. Desiccator was placed at 60 °C for 24 hours. Mounts were not removed until they were to be run on the X-ray diffractometer. The oriented and randomly oriented powder samples of montmorillonite clay were scanned between 2-70 ° (2 θ). The operating condition was at 40 kV/30 mA in a step scan mode. The step size was 0.05 °. The organoclays were examined between 2-10 ° (2 θ).

4.5.7. Thermogravimetric Analysis (TGA)

Thermogravimetric analysis was carried out using Okay TGA, Bysakh and Co. Kolkata fitted with Librathern Instruments PID 330 controller. The TGA curves were obtained in the range 60 °C to 850 °C. The heating rate was 10 °C.min⁻¹ in air atmosphere.

4.5.8. Fourier Transform Infrared (FTIR) Spectroscopic Analysis

Small amount of sample (approx. 200 mg) was thoroughly mixed with ground KBr in an agate mortar and the disc was prepared under vacuum at a pressure of 3.3 Kg/cm². FTIR spectrograms were recorded at a wave number range of 400-4000 cm⁻¹ to provide adequate characterization of the samples. Such coverage ensures that the most of the useful vibrations active in the infrared is included.

4.5.9. Swelling Study

Swelling is an important property of montmorillonite clay minerals. The hydration characteristics of the montmorillonite are influenced by the types of exchangeable cations and the background electrolyte concentration. There are two kinds of swelling processes: (1) crystalline or microscopic swelling due to hydration of exchangeable cations. It is a short-range particle interaction. Water penetrates the interlayer and forces them apart causing the clay to swell and this adsorption of water is an exothermic process. (2) Osmotic or macroscopic swelling due to the large difference in the ionic concentration close to the clay surface and the pore water, i.e., electrical double layer is set in, which is a long range particle interaction. It depends on ionic concentration, type of exchangeable ion, pH of the pore water and type of clay mineral itself.

For experimental montmorillonite clays swelling study was done by adding 1gm dried clay (90 °C) in 100 ml deionized water taking in a stoppard measuring cylinder. Swelling volume of the clay was recorded after 24 hours.

The swelling volume of intercalated clay was studied by slow and gradual addition of 0.25 g of dried clay (90 °C) in 10 ml nitrobenzene in a stoppard 25 ml measuring cylinder. The swollen volume of the organoclay was measured after 24 hours.

4.5.10. Field Emission Scanning Electron Microscopy (FESEM)

Field Emission SEM of the montmorillonite clay was performed using Supra 35 VP from Carl Zeiss, Germany with the operation voltage 10 kV.

4.5.11. Transmission Electron Microscopy (TEM)

Specimens were prepared for TEM study by carefully placing micro drops of clay suspension (in ethanol) on carbon coated copper grids. The specimens were examined using the TEM instrument with an operation voltage 300 kV. Special care was taken to avoid beam damages to the samples during investigation.

References

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3. Mermut, A. R.; Lagaly, G., Baseline studies of the clay minerals society source clays: Layer-charge determination and characteristics of those minerals containing 2 : 1 layers. *Clays Clay Miner.* **2001**, 49, (5), 393-397.