

# Influence of Exchangeable Cations on DTA Characteristics of Kaolinite and Montmorillonite Clays

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The influence of exchangeable cations in the structure of kaolinite and montmorillonite minerals on the phase transformation on progressive heat treatment, has been studied through DTA curves. Hydration energy of the cations influences the expulsion of water from the clay lattice. The high temperature phase conversions were also influenced catalytically by exchangeable cations.

THE pyrochemical changes that occur in clay minerals on progressive heat treatment are of great importance which mostly include dehydration, phase transformation, solid reaction, sintering and vitrification.

Kaolinites do not usually possess adsorbed or inter-layer water. But some poorly crystallised kaolinites indicate the presence of inter-layer water. Expulsion of crystalline water of kaolinite takes place in the temperature range of 400 to 600° as demonstrated first by Le Chatelier and later by others<sup>2-5</sup>. Sirazhiddinov and Arifov<sup>6</sup> observed that X-ray analysis of isothermally heated samples of kaolin at 600-1500° revealed the transformation of kaolin-metakaolin, amorphous Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-quartz. Pravakaram<sup>7</sup> reported the influence of exchangeable cations on the thermal reactions of kaolinite between 950 and 1000° and above 1000°. An attempt was made by Mitra and Bhattacharjee<sup>8</sup> to explain the mechanism of phase transformation of kaolinite to metakaolin.

Montmorillonites are quite different in dehydration characteristics from kaolinite. Unlike kaolinites, these contain appreciable amount of water which can be driven at relatively lower temperature (100 to 300°). Yoshio and Chuzo<sup>9</sup> studied the dehydration of exchangeable cations between 100 and 250°. Ross and Hendricks<sup>10</sup> also obtained similar results. Ferrandes and Rodrig<sup>11</sup> reported that for montmorillonite, the exchange cation has a great influence on the shape of the isotherm and on the activation energy. According to Mackenzie<sup>12</sup>, the amount of inter-layer water in montmorillonite is a function of hydration energy of the adsorbed cation.

Present investigation was undertaken to study systematically the influence of exchangeable cations on the differential thermal analysis curves of two different types of clays containing kaolinite and montmorillonite as the major constituents. In the kaolinite which has very low exchange value compared to that of montmorillonite, the exchan-

geable cations are held at the edges of the broken bonds whereas in the latter, the positions are in between the sheets.

## Experimental

Rajmahal china clay and Tinpahari bentonite (both of Indian origin) were selected for the present investigation. Both the clays were purified from the associated impurities, fractionated and ultimately converted into the mono-ionic forms by the method as communicated earlier<sup>13</sup>.

*Chemical analysis:* The clay samples were analysed chemically. The conventional Na<sub>2</sub>CO<sub>3</sub> fusion method was followed for analysis and the constituents were determined by standard methods<sup>14</sup>.

*Differential thermal analysis:* It was carried out in an automatic apparatus, Paulik Eradey Derivatograph (Hungarian Optical Works). Powder sample (0.7 g) was taken in each case and the heating rate was maintained at 8° per min. The experiments were conducted up to 1100° for kaolinites and 1500° for bentonites with  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> as the inert material.

*X-Ray analysis:* It was carried out to characterise the purified kaolinite and bentonite as well as some heat treated bentonite samples. Powder pattern was taken. X-Ray photographs were taken in a Guinier camera with CuK $\alpha$ -radiation of 1.5405 Å and Ni-filter. All the runs were conducted at 30 kV and 10 mA and the exposure time was 8 h.

*Determination of cation exchange capacity:* The CEC was determined after the dehydration-rehydration study. The sample dried at 100° prior to the determination was taken in 250 ml dry pyrex conical flask. The exchanging electrolyte solution (40 ml) which was 0.1 M CaCl<sub>2</sub> in the case of Na, K, and ammonium, and 0.2 M KCl in the case of Ca<sup>II</sup>, Mg<sup>II</sup> and Ba<sup>II</sup> forms of the clay, was added from a pipette and allowed to equilibrate for 24 h. The

liquid was then separated by filtration and analysed complexometrically with EDTA. For the mono-valent cation substituted clay, the  $\text{CaCl}_2$  solution was titrated before and after exchange and from the change in concentration of  $\text{Ca}^{II}$  ion, the amount of exchange was determined. For the divalent cations, the liberated  $\text{Ca}^{II}$ ,  $\text{Mg}^{II}$  and  $\text{Ba}^{II}$  were titrated by the same titrant from which the amount of exchange was calculated. All the titrations were carried out at pH 10.2 (ammonia-ammonium chloride buffer) with Solochrome Black T indicator.

## Results and Discussion

Water is an integral part of clay structure and complicated relationship between clay and water can be explained by the interaction of four such factors, *i.e.* the charge on the clay particles, their lamellar form, adsorption of water on the particles and the high surface tension of water.

Rajmahal china clay and Tinpahari bentonite as taken for the present investigation, were purified from the non-clayey matter and other associated organic and inorganic impurities<sup>18</sup> and subsequently fractionated to a definite size range,  $2\mu$  and below. They were always equilibrated in a constant temperature incubator ( $36 \pm 1^\circ$ ). The relevant physico-chemical characteristics of the clays are given in Table 1, and the values of kaolinite and bentonite

TABLE 1—CHARACTERISTICS OF RAJMAHAL CHINA CLAY AND TINPAHARI BENTONITE IN Na-FORM

Property	Rajmahal china clay	Tinpahari bentonite
$\text{SiO}_2$ %	46.92	51.30
$\text{Al}_2\text{O}_3$ %	39.21	27.31
$\text{Fe}_2\text{O}_3$ %	0.68	1.41
MgO %	—	1.86
Loss on ignition %	12.68	14.89
CEC meg/100 g	8.21	97.20

samples reveal that they essentially contain kaolinite and montmorillonite mineral, respectively. Again from an examination of the constituents, it appears that montmorillonite was of dioctahedral type with  $\text{Al}^{III}$  in the octahedral position and substituted by  $\text{Fe}^{III}$ ,  $\text{Mg}^{II}$  in the octahedral layer and  $\text{Al}^{III}$  in the tetrahedral layer for  $\text{Si}^{IV}$ . The predominant existence of kaolinite and montmorillonite phase in the experimental samples was also confirmed by X-ray analysis (results not shown).

The influence of exchangeable cations on the nature of bonding of water molecules in the clay structure has been studied through DTA which relates to the dislodging of both physically combined water and structural hydroxyl group by thermal energy. Some of the DTA curves have been presented in Figs. 1 and 2. The results are given in the Tables 2 and 3.

In the case of kaolinites, the low temperature endothermic peak due to the expulsion of surface water, was not observed because the clays were dried at  $100^\circ$  before analysis. The nature of the main endothermic peak which was associated with the expulsion of water from the mineral lattice, remained same for all cationic forms but the peak temperatures differed. Al-kaolinite showed the highest ( $610^\circ$ ) and Li-kaolinite the lowest ( $560^\circ$ ) peak temperature.  $\text{NH}_4$ , Be and Mg forms exhibited the same peak temperature ( $580^\circ$ ). The peak temperature of alkaline earth cations showed inverse relationship with the hydration energy of the cations (Fig. 3a).

The influence of exchangeable cations on the expulsion of inter-layer water was very much prominent with bentonite clay because the large internal surface of this 2 : 1 expanding lattice mineral being highly hydrated and gave differential thermal curve with a large endothermic peak. Only Ca forms of

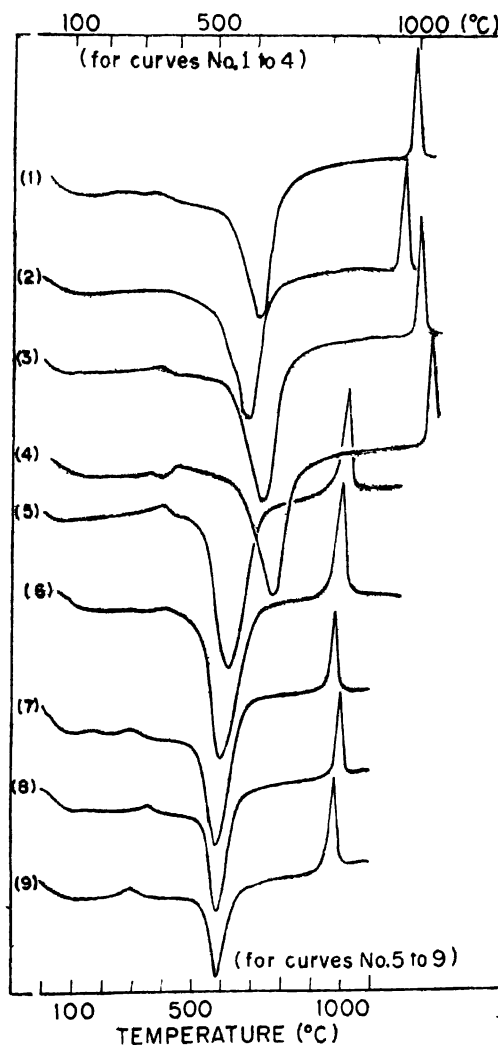


Fig. 1. DTA curves of kaolinite in different cationic forms : (1) Mg, (2) Ca, (3) Li, (4) Na, (5) Al, (6) Ba, (7)  $\text{NH}_4$ , (8) K and (9) Be.

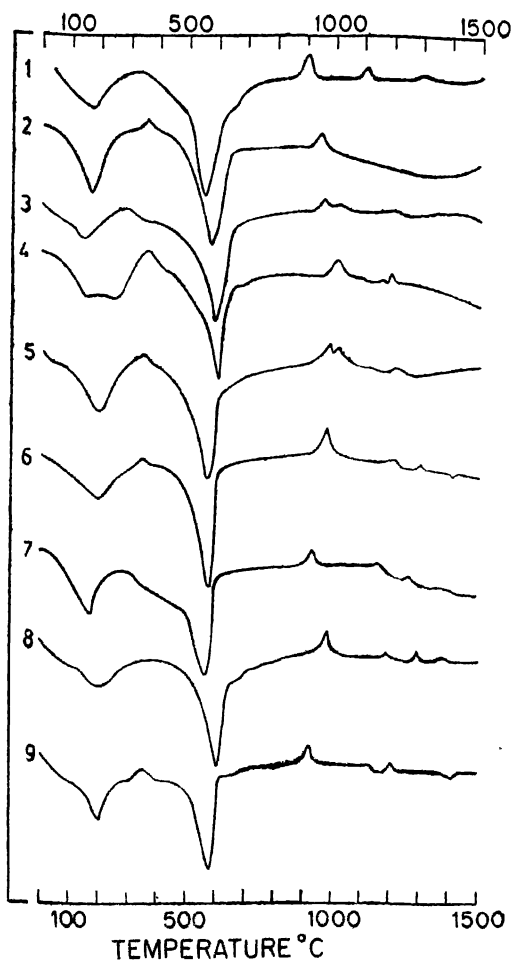


Fig. 2. DTA curves of bentonite in different cationic forms : (1) Li, (2) Na, (3) K, (4) Ca, (5) Ba, (6) Al, (7) NH<sub>4</sub>, (8) Be and (9) Mg.

Cationic forms of kaolinite	Peak temp., °C	
	Endo	Exo
Li	560	950
Na	600	990
K	595	995
NH <sub>4</sub>	580	975
Be	580	965
Mg	580	965
Ca	585	975
Ba	600	985
Al	610	1015

Cationic forms of bentonite	Peak temp., °C	
	Endo	Exo
Li	175, 540	890, 1095
Na	155, 565	940
K	135, 560	985, 965
NH <sub>4</sub>	140, 540	910, 1230
Be	205, 590	955, 1150, 1255
Mg	175, 555	915, 1175
Ca	190, 240, 590	980, 1165, 1205
Ba	195, 570	955, 985, 1220
Al	180, 575	960, 1200, 1300

bentonite showed double peak in the dehydration zone (190 and 240°, respectively). It is speculated that the above may be due to heterogeneity in the binding of water molecules around the cation and in the inter-layer position. Di- and tri-valent cation saturated montmorillonite possessed higher peak temperature compared to the monovalent ones which appeared to be due to the higher hydration energy of the former. The order of cations with respect to the peak temperature is as, Be-B > Ba-B > Ca-B > Al-B > Mg-B = Li-B > Na-B > NH<sub>4</sub>-B > K-B (B = bentonite).

Direct relationship between hydration energy and peak temperature, was observed in case of alkali metals (Fig. 3b). Exchangeable cations were also found to influence the dehydroxylation peak temperature of bentonite clay (Table 3). Like kaolinite, here also di- and tri-valent cations exhibited comparatively high peak temperature. The sequence of the cations differed to that in kaolinite which might be due to difference in the disposition of the exchangeable cations as well as hydroxyl groups in two places. In this connection it is also to be noted that the hydroxyl content of kaolinite was higher than that of bentonite. The sequence of peak temperature in relation to the exchangeable cations may be as, Ca-B = Be-B > Al-B > Ba-B > Na-B > K-B > Mg-B > NH<sub>4</sub>-B = Li-B.

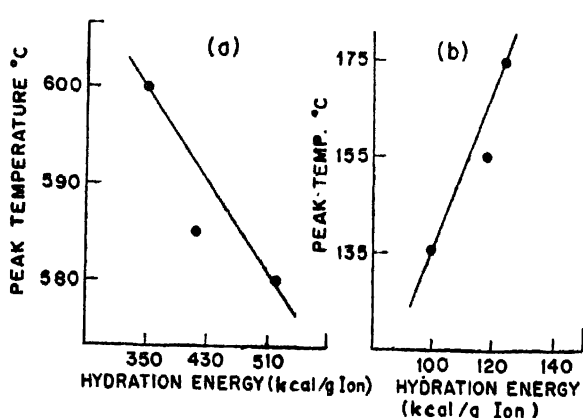


Fig. 3. (a). Hydration energy-dehydroxylation peak temperature relationship of alkaline earth metal substituted kaolinite clay. (b). Hydration energy-inter-layer water expulsion peak temperature relationship of alkali metal substituted bentonite clay.

After dehydroxylation, the clay structure decomposed into amorphous silica and alumina, which further transforms into several solid phases. This was indicated through the exothermic peaks in the DTA curves. There has been much dispute concerning the first exothermic reaction. This was thought to be due to crystallisation of  $\gamma$ -alumina

from amorphous ones by some workers. But others are of the opinion that this was due to nucleation of mullite. After going into the details of the nature of the reaction, it can be said that this transformation was influenced by the exchangeable cations and as such peak temperatures differed (Tables 2 and 3). The sequences of the cations with respect to the peak temperature may be written for kaolinite and bentonite as, Al-K > K-K > Na-K > Ba-K > NH<sub>4</sub>-K = Ca-K > Be-K > Mg-K > Li-K (K = kaolinite), Ca-B > Al-B > Be-B = Ba-B > Na-B > K-B > Mg-B > NH<sub>4</sub>-B > Li-B.

In both the cases Al form of the clays showed higher peak temperature indicative of maximum retarding effect. The action was thought to be purely catalytic. After dehydroxylation the cations quickly move into the lattice sites of high energy leaving their original sites. The accelerated catalytic action of Li and Mg might be due to the fact that these cations have a tendency to migrate into the octahedral sites which made the structure more unstable and the transformations took place rapidly. Still there was difference in the catalytic action. The peaks were more diffused in case of bentonite and the heights were comparatively well.

In kaolinite, size of the cations appeared to be important factor, whereas in bentonite, due to the presence of other cations (Mg and Fe in the octahedral position) the nature was more complicated and di- and tri-valent cations exhibited higher peak temperature and peak height.

As bentonite possessed higher C.E.C. than kaolinite, the influence of exchangeable cations on the high temperature peak (above 980°) was studied only with the former. The high temperature phases developed, are not the same for all the montmorillonites which is expected because of the variation in chemical composition.

Under the present conditions of the DTA experiment, Na-B did not show the second and third exothermic peaks. Three exothermic peaks were obtained with most divalent and trivalent cationic forms and two peaks with Li, K and Mg forms. This clearly indicates that the exchangeable cations

have got marked influence on the rate of formation of high temperature phases. The non-appearance of the peak does not infer that the development of the phases are totally inhibited but the reaction rate was too slow to be detected by the DTA method. The catalytic action in the region of second exothermic peak was different from that of the first one (indication of formation of different phases or different mechanisms). K-substituted bentonite showed lowest peak temperature. The peak with Ba and K bentonite was diffused in nature. In the third exothermic peak, Al forms exhibited the highest and Ca form the lowest peak temperature.

Montmorillonite generally belongs to the class of pyrophyllite minerals which after dehydroxylation gives a metastable phase. This on heating above 1100° forms a felted mass of cristobalite and mullite needles<sup>15</sup>.

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