

## A DIFFERENTIAL THERMAL ANALYSIS STUDY OF HOMOIONISED BENTONITES

V. THANIKACHALAM\* and B. VISWANATHAN\*\*

\*Department of Hydraulics and Water Resources, College of Engineering, Madras;

\*\*Department of Chemistry, Indian Institute of Technology, Madras, India

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Homoionised bentonites were prepared from commercial bentonites with hydrochloric acid. The Atterberg limits and the DTA curves were determined for the homoionised and commercial bentonites. This study shows that DTA can be used as a method for differentiation between clays containing mono- and divalent cations.

Differential thermal analysis has been widely used as a diagnostic technique for the investigation of clay minerals [1]. As far as thermal processes are concerned, the presence and the nature of exchangeable ions are of great importance since, for minerals of montmorillonite type with high charge density, they determine the characteristics of the DTA curves [2]. It is reported in the literature that the nature of the exchangeable cation influences the low-temperature endothermic effects, which are usually attributed to the difference in the hydration energies of different cations [3]. However, the exchangeable cations at times unexpectedly affect the high-temperature thermal effects (both endothermic and exothermic) from dehydroxylation and structural changes. It has been observed that the change in the temperature of the dehydroxylation peak depends on the size of the cation [4], thereby appearing to have a steric origin. The present report concerns the study of the DTA behaviour of commercial sodium and calcium bentonites and other homoionised bentonites of barium, ammonium, potassium and calcium ions, to confirm the mineral present and the completion of the homoionisation process and to study the effect of the exchangeable cations on the endothermic dehydration and dehydroxylation processes.

### Experimental

Homoionised bentonites having exchangeable ions such as  $Ba^{++}$ ,  $NH_4^+$ ,  $K^+$  and  $Ca^{++}$  were prepared from the commercial sodium bentonites. The chemical composition of the sodium bentonite used is  $(Si_{7.33}Al_{0.67}(Al_4O_{20})OH)_4$ . The ben-



tonite thus predominantly contained montmorillonite with trace amount of non-clay minerals such as quartz and organic impurities. The homoionised bentonites

were obtained with hydrochloric acid and the resulting hydrogen bentonites were exchanged with the desired cations from the added salt solutions. The homoionised bentonites were dried and powdered and the portions passing through a No. 200 sieve were used for DTA experiments. This study was undertaken to determine the effect of the homoionisation process in the bentonite clay. The Atterberg limits of the commercial and homoionised bentonites are presented in Table 1.

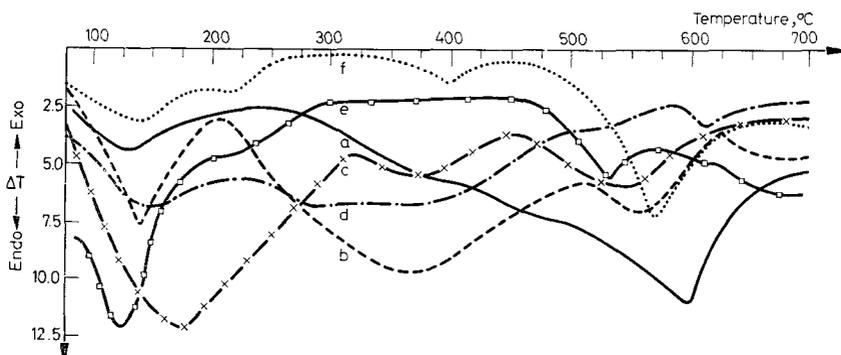


Fig. 1. DTA curves of bentonites: a) sodium (commercial); b) calcium (commercial); c) barium (homoionised); d) ammonium (homoionised); e) potassium (homoionised); f) calcium (homoionised)

The DTA curves were obtained by using a manual DTA apparatus employing chromel–alumel thermocouples. A heating rate of  $6.5^{\circ}/\text{min}$  was used. Both the differential and the furnace temperatures were recorded with a sensitive micro-voltmeter (Hewlett Packard 425A). Calcined alumina was used as reference material.

The DTA curves obtained for the different bentonites used in the present study are given in Fig. 1. The important peaks observed and the corresponding tempera-

Table 1  
Atterberg limits of bentonites

Ion present	Liquid limit	Plastic limit, %	Shrinkage limit, %
Sodium (commercial)	480	36	10
Calcium (commercial)	253	37	10
Ammonium (Homoionised)	154	38	15
Potassium (Homoionised)	142	36	17
Barium (Homoionised)	128	30	14
Sodium (Homoionised)	149	33	10
Calcium (Homoionised)	103	28	9

Table 2  
DTA results

Ion present	Peak temperatures, °C		
	I	II	III
Sodium (commercial)	130	...	595
Calcium (commercial)	168	368	560
Potassium (homoionised)	125	...	535
Barium (homoionised)	178	373	548
Ammonium (homoionised)	150	...	613
Calcium (homoionised)	168	398	570

tures are summarised in Table 2. Curves d, and e, in Fig. 1 clearly show that homoionised monovalent soils give rise to only two endothermic peaks, but the homoionised divalent soils (curves c and f) to three endothermic peaks.

For the clay minerals other than montmorillonite, the DTA curves are shown in Fig. 2a and for the montmorillonite clays one observes an inclined portion "mn" instead of a sharp drop in the curve. This inclined portion of the DTA curve has been attributed in the literature to the presence of organic matter in the clay minerals. The fact that such inclined portions are observable in the bentonite samples employed in the present study (Fig. 1 a to f) shows that the homoio-

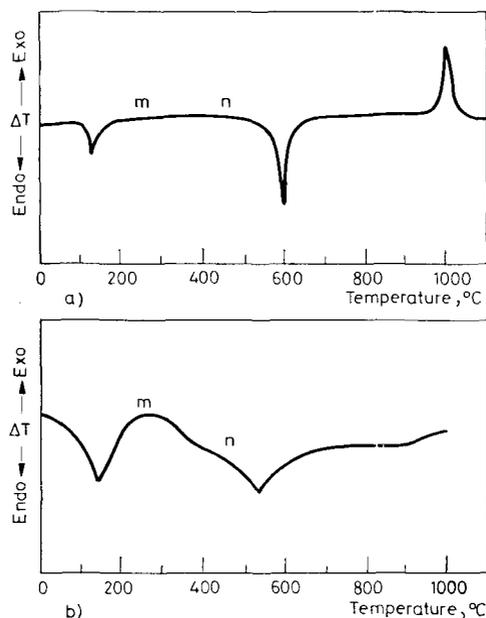


Fig. 2. Typical DTA curves for a) kaolinite, b) montmorillonite

nisation process still retains the montmorillonite characteristics. This interpretation is applicable only from the DTA point of view. The removal of some of the aluminium ions from the clay structure during the acid treatment is not fully revealed by the DTA curves. Structural changes as a result of acid treatment have been reported by Brown [5] from X-ray diffraction studies.

Generally, the DTA curves for montmorillonites may be considered in two parts, viz. a) removal of the adsorbed water in the temperature range 100–300°, and b) dehydroxylation in the temperature range 500–1000°. During the latter process the structure breaks down and recrystallisation takes place. In the case of bentonite samples, strong endothermic peaks are observed in the temperature range 100–300° as a result of the high degree of hydration. In this temperature range, the bulk of the water present in the interlayer spaces is lost. The second endothermic peak occurs in the temperature range 500–700° and the effect is usually weak for montmorillonite clays. This second endothermic peak is due to the loss of lattice water. If the bentonite clay contains divalent ions, a third peak occurs at a lower temperature (in the range 300–400°). The reason for the appearance of this third endothermic peak in divalent ion bentonite clays is not known. In conclusion, it may be stated that in homoionised soils two endothermic peaks are obtained for monovalent ions, while divalent bentonites give rise to three endothermic peaks, which can be used as a diagnostic method for the classification of clays.

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