

CHARACTERIZATION OF MONTMORILLONITE SATURATED WITH VARIOUS CATIONS

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Abstract

Emanation thermal analysis (ETA) supplemented by thermogravimetry (TG and DTG) and evolved gas analysis (water) were used for the characterization of the thermal behavior of montmorillonite samples saturated with lithium, sodium, magnesium and aluminum cations. The ETA revealed microstructure changes that occur during the gradual heating of the clay. These changes are associated with the dehydration, dehydroxylation and formation of an amorphous meta-montmorillonite phase, and its subsequent annealing and recrystallization. On the basis of the ETA results it was demonstrated that exchangeable metallic cations have a great effect on the thermal behavior of montmorillonite.

Keywords: emanation thermal analysis, evolved gas analysis, Na-montmorillonite saturated with lithium-, magnesium- and aluminum cations, thermogravimetry

Introduction

The exchange of cations in the clay mineral montmorillonite (mont) is accompanied by changes in size and shape of tactoids and flocs [1] and in the interlayer water structure [2]. These changes give rise to products differing in basal spacing (d_{001}) [3, 4], in the dehydration and dehydroxylation behavior [5], as well as in sorption properties of organic compounds [6]. The dehydration and dehydroxylation taking place upon heating montmorillonite are accompanied by changes in the solid phase microstructure [7, 8]. A collapse of the montmorillonite structure and a decrease of its basal spacing take place as the result of the dehydration (observed in the temperature range up to 200°C). The dehydroxylation process results in the formation of an amorphous phase rich in lattice vacancies, known as meta-montmorillonite. The annealing of the amorphous particles and their recrystallization, takes place on further heating of the sample [9].

The emanation thermal analysis (ETA) is a powerful tool for the 'in situ' characterization of microstructure changes taking place during heating solids [10]. In this technique radon atoms ^{220}Rn , emanating from samples impregnated by ^{228}Th and ^{228}Ra , are used as a probe for microstructural changes that occur in solids during thermal treatment. It was recently used in the study of microstructure changes during

dehydration and dehydroxylation of several smectites [9, 11]. In the present study the effect of different exchangeable cations on the thermal changes in the microstructure of montmorillonite is demonstrated by ETA curves. This is supplemented by TG/DTG and EGA (MS) curves, which supply information on the thermal reactions which are associated with mass-loss.

Experimental

Materials

Na-montmorillonite (Wyoming bentonite from Upton, Wyoming, USA, A.P.I. 25) was supplied by Wards Natural Science Est. and was used as received. Homoionic montmorillonites saturated with Li^+ , Mg^{2+} and Al^{3+} ions, were prepared as follows. A portion of 10 g of Wyoming bentonite, was dispersed in 800 ml water and stirred during two days. The stable clay suspension was separated from the sedimented quartz and 200 ml of 0.2 M aqueous solution of the respective chloride salt were added and the suspension was stirred. After two days the clay was washed several times by distilled water until it was free of chloride (examined by AgNO_3 solution). The solid products were air dried at 40°C .

Methods

For the ETA the homoionic montmorillonites were labeled by impregnation with acetone solutions of ^{228}Th and ^{228}Ra . Atoms of ^{220}Rn penetrated into the surface layers of the solid grains by recoil energy to a maximum depth of ~ 85 nm. The specific activity of the sample was 10^4 Bq g^{-1} . ETA curves were recorded on the upgraded Netzsch Type 404 Device. The samples were heated and cooled in air at a rate of 2.5 K min^{-1} , being overflowed by a constant flow of argon (40 ml min^{-1}) which carried the released radon atoms into the radioactivity detection chamber.

TG/DTG and EGA (MS) curves were recorded on STA 429 device (NETZSCH) coupled with a Mass Spectrometer (Balzers). X-ray diffractograms of oriented samples were recorded on a PHILIPS PW 1050/25 diffractometer, using CuK_α Ni-filtered radiation.

Results and discussion

Basal spacing (d_{001}) of montmorillonite samples saturated with varying cations were determined by XRD (Table I). These data give information on the hydration number and on the number of water layers in the clay samples, which were used in the present thermal analysis study. A monolayer of water separates between two TOT clay layers in the monovalent montmorillonites whereas a bilayer of water separates between them in the di- or trivalent clay. Glasser *et al.* [12] showed that the polyvalent ions tend to detach themselves from the silicate surface and incorporate in the water layers. They stated that the complete loss of the interlayer water is accompanied by a reduction in the basal spacing to 0.94 – 1.00 nm, the exact spacing depending on the size of the interlamellar cation.

Table 1 Basal spacing of air-dried homoionic montmorillonite samples determined by X-ray diffraction, the hydration number of the exchangeable cation and the number of water layers in the interlayer space of the homoionic montmorillonite

Exchangeable cation	d_{001}/nm	Hydration number of cation	Number of water layers
Na	1.24	3 or 4	1
Li	1.26	3 or 4	1
Mg	1.50	6	2
Al	1.50	6	2

TG/DTG and EGA (MS) curves of the different homoionic clay samples are presented in Figs 1–4. Two stages are identified in the mass-loss curves. Two peaks in the DTG and the evolved water analysis (MS) curves accompany these stages. The first stage is due to the dehydration of the clay. The DTG peak appears at the temperature of the highest dehydration rate and is located at 79, 83, 92 and 99°C in the curves of Li-, Na-, Mg- and Al-mont, respectively. At this stage free water is evolved

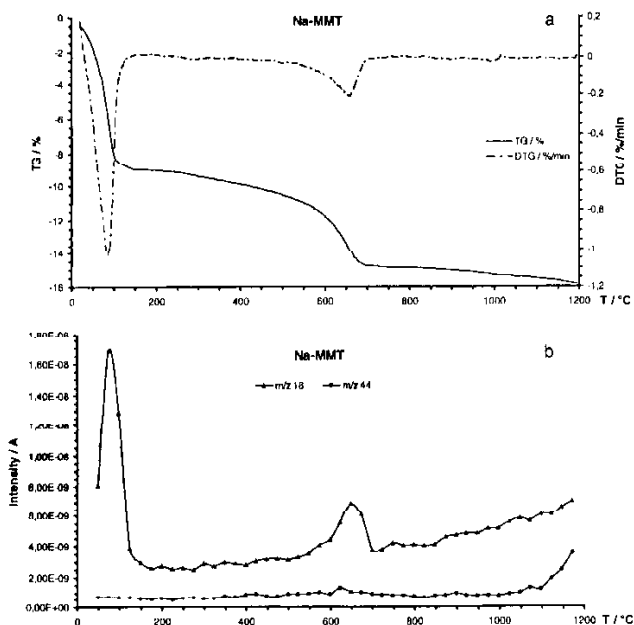


Fig. 1 Characterisation of water release taking place during heating in nitrogen of Na-montmorillonite (Upton, Wyoming, USA)
a) TG and DTG curve, b) EGA curve (mass spectrometric detection M 18 corresponding to water release, 44 to carbon dioxide)

from interlayer space of tactoids and intertactoid space of flocs. The higher temperatures of Mg- and Al-mont are in agreement with the higher number of water layers in the interlayer space of these clays, compared with Li- and Na-mont, and their larger tactoids and flocs, those of Al larger than those of Mg.

The DTG and EGA curves of Li-, Mg- and Al-mont show additional shoulders at higher temperatures representing dehydration that requires higher energies. That is the evolution of water molecules coordinated to the metallic cation by ion-dipole interaction. This kind of dehydration is not detected in the curves of Na-mont, but is well seen in those of the other montmorillonites. In agreement with the polarizing power of the cation, the ion-dipole interaction force increases in the order $\text{Li} < \text{Mg} < \text{Al}$. The thermal curves show that the dehydration stage is completed at 140, 200, 225 and $\sim 250^\circ\text{C}$ in Na-, Li-, Mg- and Al-mont, respectively. Concerning Al-mont, there is evidence that this cation forms poly-hydroxy species in the interlayer space [1] and that these species undergo thermal dehydroxylation in the temperature range $200\text{--}350^\circ\text{C}$ [13]. Fluctuations in the TG curve and the weak peaks in the DTG and EGA curves which are observed in this temperature range, may be due to this kind of dehydroxylation. This makes it difficult to estimate the exact temperature at which the first mass-loss stage of this clay terminates.

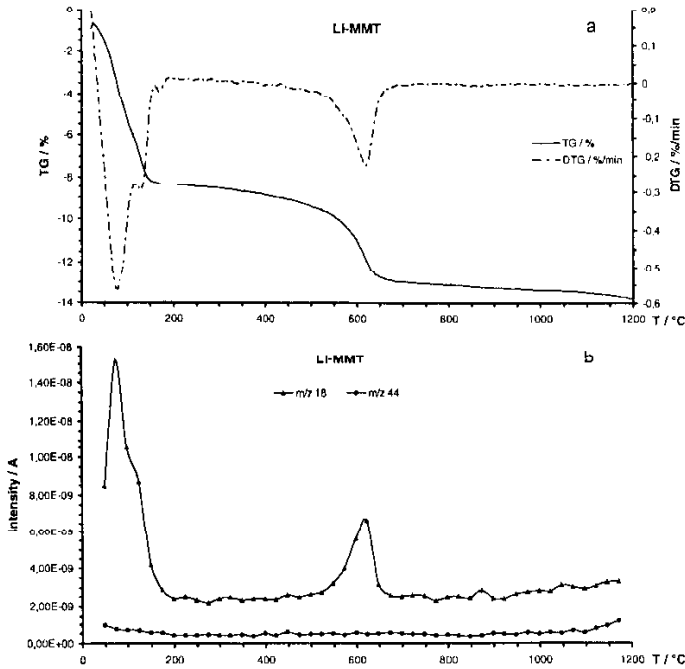


Fig. 2 Characterisation of water release taking place during heating in nitrogen of montmorillonite saturated with lithium ions; a – TG and DTG curve, b – EGA curve (mass spectrometric detection M 18 corresponding to water release, 44 to carbon dioxide)

Mackenzie [14] suggested that the amount of interlayer water depends on the hydration energy of the exchangeable cations and of the silicate surface, and that TG curves can give relative values for these amounts of water. For most di- and polyvalent cations (e.g. Mg and Al) the ion is more important than the layer surface, but for large divalent cations (e.g. Ba) and for monovalent cations the influence of the silicate surface on the hydration is dominant. Yariv [15] showed that the influence of the silicate surface on the hydration energy increases with tetrahedral substitution of Al for Si. The greater the substitution is, the stronger will be the bonds between water molecules and the oxygen plane of the TOT layer.

The second mass-loss stage is due to the dehydroxylation of the TOT layer. According to Bradley and Grim [16] the removal of hydroxyls leads to an increase of 0.01–0.03 nm in the *c*-axis and involves the expulsion of about one sixth of the oxygens of the octahedral sheet resulting in the creation of lattice vacancies. Heller and Kálmán [17] supposed that Li and Mg enter into the vacant octahedral sites of dioctahedral smectites during dehydroxylation.

According to the present TG curves dehydroxylation begins at 440 and 380°C in Na- and Li-mont, respectively and at much lower temperatures in Mg- and Al-mont. In these montmorillonites dehydroxylation probably starts before the complete evolution of water. For simplicity, we shall consider this stage to begin with the comple-

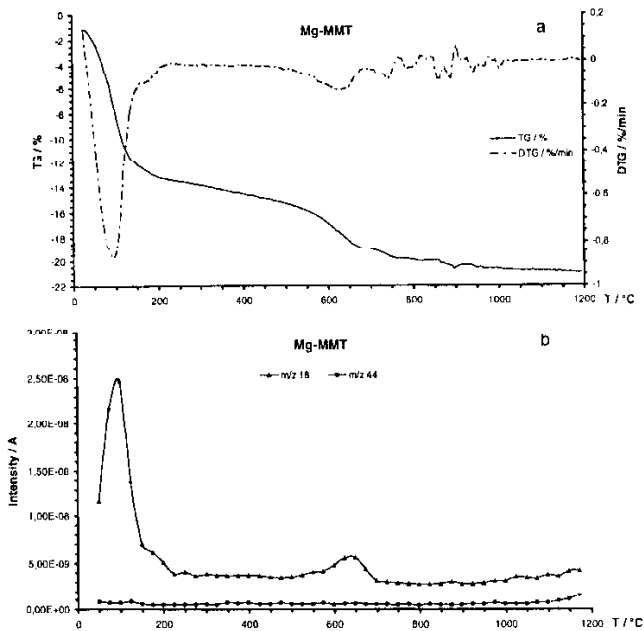


Fig. 3 Characterisation of water release taking place during heating in nitrogen of montmorillonite saturated with magnesium ions; a – TG and DTG curve, b – EGA curve (mass spectrometric detection M 18 corresponding to water release, 44 to carbon dioxide)

tion of the water evolution. From the TG, DTG and EGA curves it appears that the dehydroxylation is completed at about 700°C. At this stage the solid phase becomes amorphous and is named meta-montmorillonite. The dehydroxylation process is catalysed by protons originating from water coordinated to the exchangeable cation. These protons diffuse through the ditrigonal holes of the TOT layers towards the inner hydroxyls [18]. Peaks at 656, 618, 628 and 600°C in the DTG curves of Na-, Li-, Mg- and Al-mont, respectively, represent the highest dehydroxylation rate. Except for Li-, this temperature sequence is in agreement with the acid strength of the cations. It may be concluded that the catalytic effect increases with the polarizing power of the cation. It is therefore expected that the fine structure of the amorphous dehydroxylation product (meta-mont), will be dependent on the acidity of the exchangeable cation. The temperature ranges of the dehydration and dehydroxylation stages and the corresponding mass-losses are summarized in Table 2.

Small mass-loss is recorded in temperatures above the dehydroxylation reaction. According to the EGA (MS) curves this mass-loss is associated with the evolution of water. Shuali *et al.* [19] studied the thermal dehydroxylation and recrystallization of D₂O treated sepiolite. They showed that during the dehydroxylation process an amorphous meta-phase is formed with trapped D₂O. At the stage when this amor-

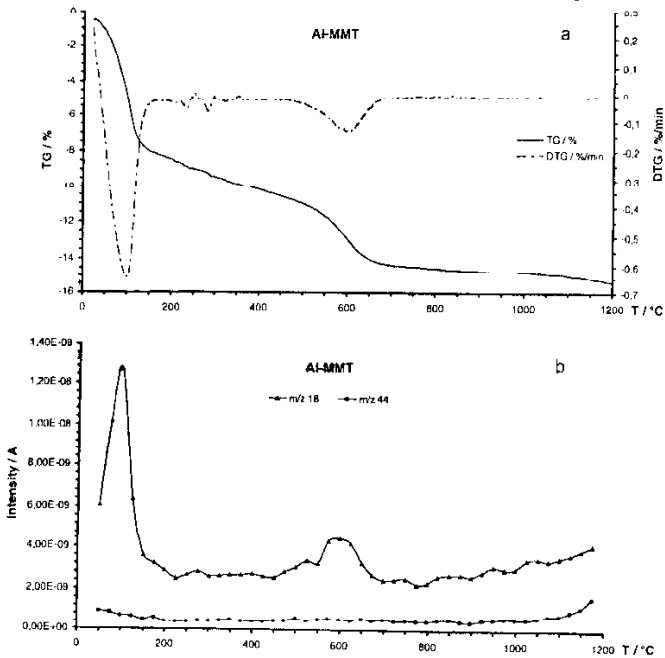


Fig. 4 Characterisation of water release taking place during heating in nitrogen of montmorillonite saturated with aluminium ions; a – TG and DTG curve, b – EGA curve (mass spectrometric detection M 18 corresponding to water release, 44 to carbon dioxide)

Table 2 Three stages of mass-loss in the thermogravimetry analysis of homoionic montmorillonites saturated with varying cations (% mass-loss calculated on the basis of calcined aluminosilicate at 1200°C)

Cation	First stage (dehydration)		Second stage (dehydroxylation)		Third stage (700–1200°C) (recrystallization)
	$T_{\text{range}}/$ °C	mass loss/ %	$T_{\text{range}}/$ °C	mass loss/ %	mass loss/ %
Na	20–140	8.2	440–700	4.7	0.7
Li	50–200	6.9	380–700	4.0	0.5
Mg	50–225	12.5	225–700	4.7	1.8
Al	50–250	7.9	250–700	4.3	0.9

phous phase is thermally recrystallized, the trapped D₂O is released. A similar phenomenon may occur in the present systems. The meta phase formed during the dehydroxylation of the clay contains trapped H₂O and these are released during the recrystallization stage. From the mass-loss at 700–1200°C it appears that there are differences in the water content of the different amorphous phases.

ETA curves of montmorillonite saturated with different cations, as well as that of untreated Wyoming bentonite (Na-mont) are presented in Fig. 5. A break in an ETA curve corresponds to the onset of a new solid-state reaction and a new microstructure of the solid phase. In the temperature range of the first mass-loss stage (the dehydration stage) all four monoionic montmorillonites behave very similar. All four ETA curves show first a rise in radon emanation rate, followed by a decrease in this rate. Evolution of water from the interlayer and intertactoid space shows in the ETA curve enhanced radon release from the liberated surfaces. Evolution of the last interlayer free water and coordinated water is accompanied by collapse of the interlayer space. This and the shrinkage of the flocs show in the ETA curve a decrease of radon release rate. The temperatures at which the emanation release rate reaches a maximum and a minimum differ from sample to sample. The maximum of each sample is reached near the temperature of the DTG peak and the minimum near the final temperature of the dehydration stage (Table 2).

In the temperature range of the second mass-loss stage (dehydroxylation stage, Table 2) ETA curves of Na-, Li- and Mg-mont show increase in radon emanation rate. This is due to amorphization and framework vacancies obtained during this process [20].

The dehydroxylation of Al-mont shows a complete different ETA picture; the rate of radon release E does not increase. The difference in behavior between Al- and the other montmorillonites may be attributed to the presence of Al-polyhydroxy cations in the interlayer space, which is common in Al-mont [1]. Aceman *et al.* [21, 22] studied by X-ray and IR spectroscopy the dehydroxylation of monovalent- and Al pillared-smectites. They showed that in the former there is a thermal diffusion of Si and Al atoms from one TOT layer to the neighboring layers whereas the thermal diffusion in the latter occurs only inside the layer or between the TOT layer and the interlayer pillar. Consequently, during the dehydroxylation the former builds a three-

dimensional amorphous framework and the latter preserves its two-dimensional layer structure.

Above 650°C, Na- and Li-mont show a decrease in the rate of emanation. This correlates with the annealing of the amorphous particles of meta-mont which was mentioned previously. According to the ETA curves of Mg- and Al-mont (Fig. 5) the annealing begins only at about 800°C, Mg before Al. The different behavior between the mono- and polyvalent montmorillonites at this stage may be due to differences in the fine structures of the amorphous phases. As we showed by TG, the formers were formed at higher temperatures with a small catalytic activity of protons whereas the latter started to be formed at lower temperatures with a high catalytic activity. It is also possible that the initial shape of the large tactoids and flocs of Mg- and Al-mont are preserved at these temperatures and are responsible for the different behavior of these montmorillonites. However, this requires further study.

Effects of the exchangeable cation on the intensity of the radon release rate were observed above 950°C. At this stage the formation of high temperature minerals is expected. As it follows from Fig. 5 enhanced radon release was measured above 1000°C with Li-, Mg- and Al-mont, whereas the original Wyoming bentonite showed relatively modest values of radon release rate. We assume that the original clay was highly compacted whereas the dispersion of this bentonite in water for the preparation of the homoionic samples resulted in a non-compacted material. The increase in the mobility of radon, which is an inert gas with atomic diameter of 0.38 nm, indicates a loosening of the interparticle contact between the assemblages.

Breaks in the ETA curves observed in Fig. 5 coincide well with the expansion-contraction behavior of Na-montmorillonite (Wyoming bentonite), described by Steger [23]. He observed an expansion of the sample during the formation of the de-

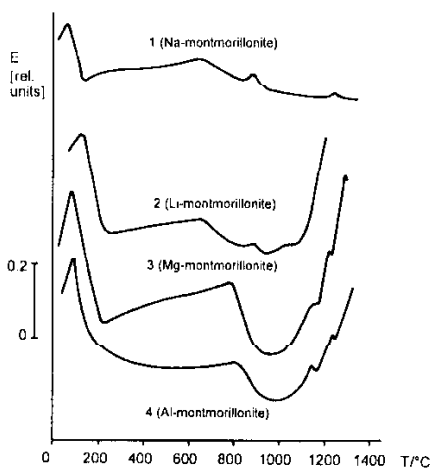


Fig. 5 Results of ETA of montmorillonite samples during heating in argon; 1 – Na-montmorillonite (Upton, Wyoming, USA), 2 – montmorillonite saturated with lithium, 3 – montmorillonite saturated with magnesium, 4 – montmorillonite saturated with aluminium

hydroxylated meta-phase, followed by a large contraction, which can be attributed to the annealing of the amorphous particles. After 950°C, with the recrystallization of the amorphous phase, the sample again expanded.

The break in the ETA curve of the original Wyoming bentonite (Na-mont) observed at 900°C (Fig. 5), can be ascribed to the formation of beta-quartz from pseudocrystalline quartz, which was found in this bentonite and in many types of montmorillonite [24]. As confirmed by X-ray study, the recrystallisation of β -quartz to β -cristoballite and the formation of mullite take place by heating Na-mont to high temperatures. Cristoballite and mullite (or cordierite) were found in Na- or Mg-mont. The ETA effects observed in the temperature interval above 1100°C correspond to the formation of high temperature phases, which depend on the exchanged cation.

Conclusions

The ETA made it possible to identify microstructure changes during heating homoionic montmorillonite samples saturated with different cations (lithium, sodium, magnesium and aluminium). Microstructure changes revealed by ETA, occur together with dehydration and dehydroxylation, which were confirmed by TG/DTG and EGA studies. They also occur with annealing of the amorphous particles of meta-montmorillonite and with its recrystallization to high temperature minerals, processes, which were previously confirmed by DTA, X-ray and expansion-contraction behavior studies.

Information on the thermal stability of the amorphous meta-montmorillonite phase and its annealing temperature were obtained by ETA under 'in situ' heating conditions. It appears that the fine-structure of the amorphous phase is determined by the acid strength of the exchangeable cation.

ETA, supplemented by TG/DTG and EGA (MS) showed that the exchangeable cations (Na^+ , Li^+ , Mg^{2+} , Al^{3+}) have a great influence on the thermal behavior of montmorillonite samples. The present study confirmed the hypothesis made earlier by Grim and Kulbicki [20] that exchangeable cations and admixtures have great influence on high temperature behavior, and consequently on the formation of high temperature phases of montmorillonite. Different high temperature behavior due to different cations may be due to differences in the fine structure of the meta-montmorillonite phase and also due to differences size and shape of initial tactoids and flocs.

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