

EFFECT OF THERMAL TREATMENT ON LANTHANIDE MONTMORILLONITES: DEHYDRATION

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(Received 6 February 1980)

ABSTRACT: Hydration/dehydration behaviour and the effect of various thermal treatments on montmorillonites saturated with lanthanide ions have been investigated by X-ray diffraction, thermal analysis (DTA, TG, DTG), IR spectroscopy and sorption-desorption of water vapour techniques. Heating at 150°C under 10^{-5} torr did not eliminate all the interlayer water of the montmorillonite, neither did it affect the CEC. Heating above 160°C caused a reduction in CEC. At 25°C La-montmorillonite takes up a maximum of three water layers in the interlayer space, the water molecules adopting a nonacoordinated distribution around the La^{3+} cation.

The dehydration behaviour of montmorillonite depends on various factors, principally the nature of the exchange cations and the composition of the silicate framework. Although the effects of thermal treatment on montmorillonite containing mono- and divalent exchangeable cations is adequately covered in the literature, corresponding data for montmorillonite saturated with trivalent exchangeable cations is lacking. In the present paper we describe the dehydration/hydration behaviour of montmorillonite saturated with lanthanide ions and also examine the effects of thermal treatment on the cation exchange capacity of the clay.

MATERIALS AND METHODS

All experiments were carried out on montmorillonite from the La Serrata bed, Almeria, Spain. Ln-montmorillonites were prepared from the original material following the procedure described by Bruque *et al.* (1980) (preceding paper, this issue).

DTA curves were obtained on a Mettler Thermoanalyzer-2, using calcined alumina as reference material and a heating rate of 10°C/min.

IR absorption spectra were obtained on a Perkin Elmer-325 apparatus with CsI prisms and windows. Samples were prepared in Nujol and Fluorolube suspensions and, in some cases, KBr disks.

X-ray diffraction data were obtained from a 114·83 mm Phillips camera using $\text{Cu K}\alpha$ radiation at 40 kV and 32 mA.

Evacuation and adsorption of water vapour were carried out in a vacuum apparatus similar to that described by Gutierrez Rios & Rodriguez (1961).

EXPERIMENTAL RESULTS AND DISCUSSION

Dehydration

The $d(001)$ spacings, interlamellar spacings (Δ) and the number of layers of water held

TABLE 1. Basal spacings, interlamellar spacings (Δ) and number of water layers of air-dried samples.

Sample	Basal spacing Å	Δ^*	Water layers
La-mont.	15.2	5.7	2
Ce-mont.	15.2	5.7	2
Sm-mont.	15.4	5.9	2
Gd-mont.	15.1	5.6	2
Er-mont.	14.6	5.1	2
Y-mont.	15.0	5.5	2

* Obtained by subtracting 9.5 Å (the assumed thickness of a montmorillonite layer) from the observed basal spacing.

by the air-dried samples are listed in Table 1. A marked capacity for water retention is shown by the Ln-montmorillonites.

The air-dried samples were progressively dried in a desiccator with phosphoric anhydride under vacuum and subjected to different thermal treatments, which contracted the basal spacings to the values listed in Table 2. From this data it may be inferred that the La-montmorillonite still contains a monolayer of water even after being heated to 120°C, since the 12.4 Å spacing corresponds to an interlayer distance equal to the size of a water molecule. The $d(001)$ spacings of the samples evacuated at 150°C and 10^{-4} torr correspond to interlayer distances of 0.6–0.8 Å. The water molecules must therefore be occluded in the hexagonal interstices of the tetrahedral sheet. These have a diameter of 2.5 Å and only partially admit the water molecule, leaving 0.7–0.8 Å outside the interstice. The lanthanide ions, with diameters between 2.2 and 1.9 Å, may be lodged in the hexagonal interstices. Evacuation of the La-montmorillonite at a higher temperature (180°C/ 10^{-5} torr) reduces the basal spacing by only 0.2 Å, and it could be that this treatment causes adjacent layers to shift in such a way that their hexagonal interstices coincide, thus allowing the residual water molecule to be fixed there.

TABLE 2. Basal spacings and interlamellar spacings (Δ) of heated and evacuated samples of Ln-montmorillonites.

Sample	Treatment	$d(001)$, Å	Δ
La-mont.	120°C	12.4	2.9
La-mont.	150°/ 10^{-4} torr	10.2	0.7
La-mont.	180°/ 10^{-5} torr	10.0	0.5
Ce-mont.	150°/ 10^{-4} torr	10.2	0.7
Sm-mont.	150°/ 10^{-4} torr	10.2	0.7
Gd-mont.	150°/ 10^{-4} torr	10.1	0.6
Er-mont.	150°/ 10^{-4} torr	10.3	0.8
Y-mont.	140°/ 10^{-4} torr	10.5	1.0

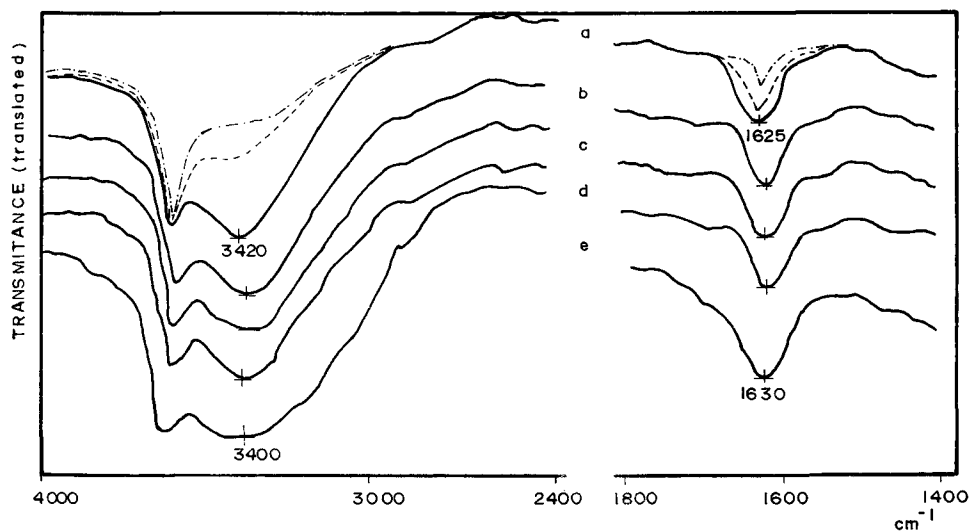


FIG. 1. IR spectra of Ln-montmorillonites: (a) La-; (b) Ce-; (c) Sm-; (d) Er- and (e) Y-montmorillonite (— air-dried; --- 150°C/10⁻⁴ torr; -·-·- heated at 280°C).

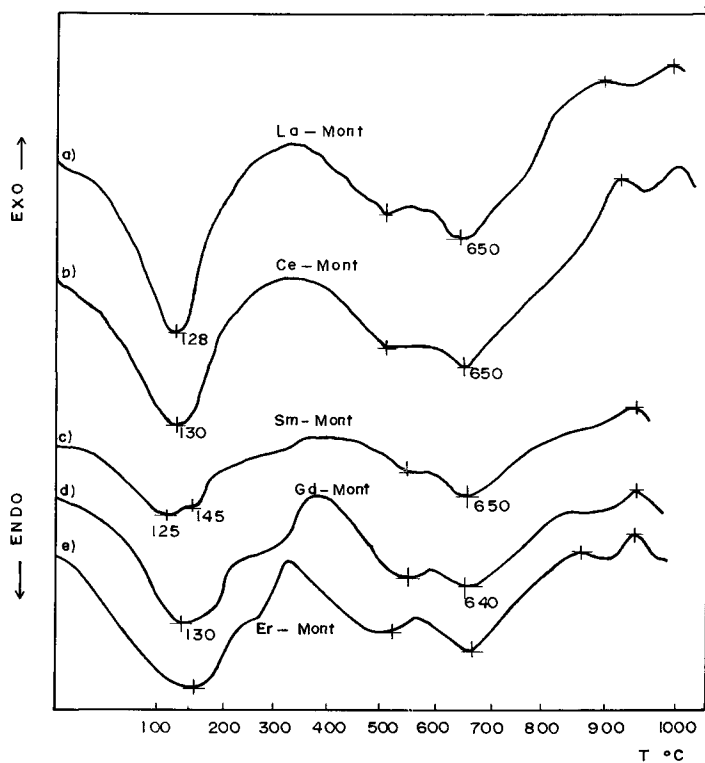


FIG. 2. DTA curves of Ln-montmorillonites.

IR spectra of the air-dried samples (Fig. 1) show two vibration bands due to water at 3400 cm^{-1} (ν_{OH}) and $\sim 1630\text{ cm}^{-1}$ (δ_{OH}). In the 3400 cm^{-1} band (ν_{OH} of the water molecules joined by hydrogen bonding) a slight shift towards lower frequencies occurs from the La- to the Gd-montmorillonite. This is ascribed to an increase in polarizing power of the cation, which acts more strongly on the water molecules situated in the first coordination sphere, transmitting this effect to the water molecules of the second sphere which is joined to the first by hydrogen bonding.

In Fig. 1, spectra of treated La-montmorillonite are represented by dashed lines. It can be seen that the intensity of the band at 3400 cm^{-1} decreases appreciably following both treatments. The intensity of the 1630 cm^{-1} band, however, decreases significantly only after heating the clay to 280°C .

These data, together with the X-ray measurements recorded in Table 2, confirm the presence of water in the samples subjected to evacuation and heating to 280°C .

Fig. 2 shows the DTA curves of La-, Ce-, Sm-, Gd- and Er-montmorillonite. A series of endothermic peaks between 100 and 300°C are present, these all corresponding to the loss of interlayer water. On passing from La- to Er-montmorillonite a shoulder appears; this increases in definition and shifts towards higher temperatures as the polarizing power of the cation increases.

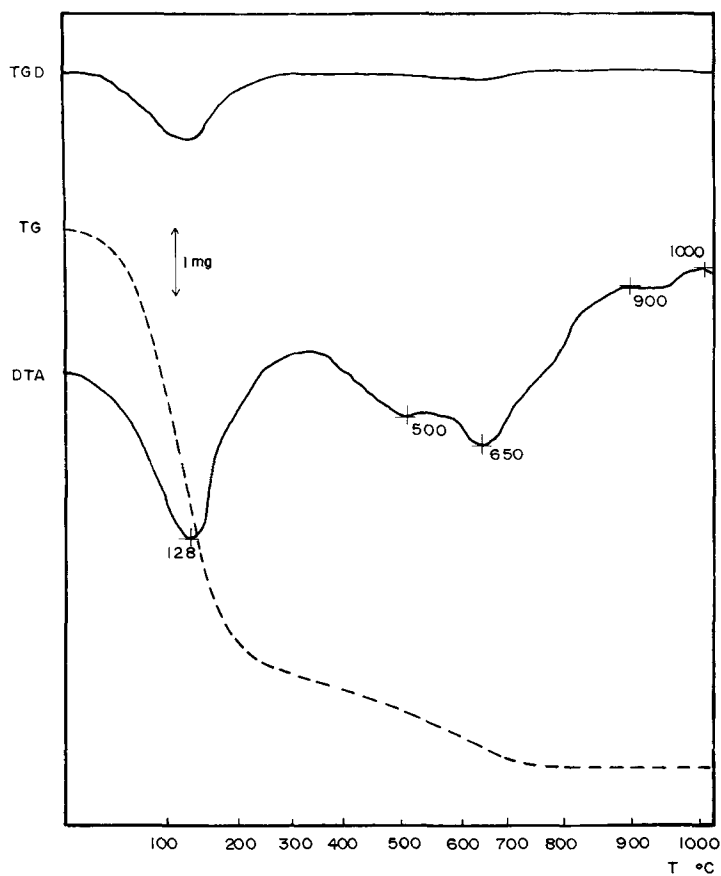


FIG. 3. DTA, TG and DTG curves of La-montmorillonite.

TABLE 3. Residual molecules of water per Ln^{3+} ion after treatment at $150^\circ/10^{-5}$ torr for 5 h.

Sample	CEC		
	mEq/100 g	Weight loss %	H_2O mol/ Ln^{3+}
La-mont.	97.6	5.8	0.9
Ce-mont.	96.7	6.0	1.1
Sm-mont.	95.1	6.0	1.2
Gd-mont.	93.7	6.1	1.4
Er-mont.	93.0	6.4	1.6
Y-mont.	93.0	6.3	1.5

Fig. 3 shows the DTA-TG-DTG curves of the La-montmorillonite. Two overlapping weight losses are seen on the TG curve, corresponding to loss of interlayer water and lattice (hydroxyl) water respectively. The DTA and DTG curves suggest that loss of interlayer water ends at $\sim 320^\circ\text{C}$. Assuming that this was, in fact, the case, the amount of lattice water was found to be 5.4% (expressed on a calcined (900°C) clay basis). This figure was used to calculate the amounts of residual water of the samples evacuated at $150^\circ\text{C}/10^{-5}$ torr (Table 3).

Effects of the thermal treatments on the CEC

In order to investigate the effect of thermal treatments on the permanence of the lanthanide ions in exchangeable form, amounts of Ln^{3+} ions associated with the montmorillonites were extracted with 2 M KCl, while controlling the pH of the exchange process to avoid solubilization of possible oxides and hydroxides formed due to dehydration. The pH of the exchange extraction solution was 6.3–6.8, 0.5–1.0 units below the value required for precipitation of the hydroxides (Moeller & Kremers, 1944). In Table 4 amounts of exchangeable Ln^{3+} in the samples submitted to different thermal

TABLE 4. Effect of heating on CEC of Ln-montmorillonite.

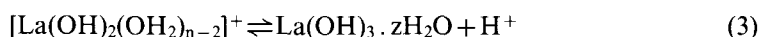
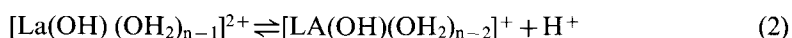
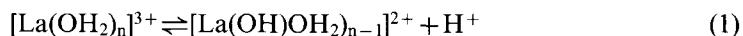
Sample	Treatment	Time	CEC (initial)	mEq $\text{Ln}^{3+}/100$ g (after treatment)
La-mont.	$140^\circ/10^{-4}$ torr	5 h/12 h	97.5	97.5
La-mont.	160°	8 h	97.5	88.0
La-mont.	240°	12 h	97.5	66.4
La-mont.	380°	12 h	97.5	19.6
Ce-mont.	$150^\circ/10^{-5}$ torr	5 h/12 h	96.7	96.5
Sm-mont.	$150^\circ/10^{-5}$ torr	5 h	94.8	95.1
Gd-mont.	$150^\circ/10^{-5}$ torr	5 h	93.5	93.8
Er-mont.	$140^\circ/10^{-4}$ torr	5 h	93.1	93.0
Y-mont.	$140^\circ/10^{-4}$ torr	5 h	93.2	93.0

Retention and CEC data based on weight of sample after heating to 900°C .

treatments are listed, all the data being referred to a constant sample weight. For comparison, the amount of exchangeable Ln^{3+} in the air-dried sample is also given.

The results in Table 4 indicate that heating lanthanide montmorillonite up to 150°C does not affect the CEC. Above 160°C the CEC begins to diminish, reaching very low values ($19.6 \text{ mEq}/100 \text{ g}$) for La-montmorillonite heated at 380°C . This drop in CEC on heating may be ascribed to three interdependent factors.

1. An increase in dissociation of the water directly coordinated with the cations, due to the polarizing power of these and the action of the surface electric fields. This dissociation is favoured by rise in temperature. Fripiat *et al.* (1965) and Fripiat (1970) indicate that such a dissociation would produce H^+ ions. Liberation of these ions may be explained by the following hydrolysis equations:



The existence of hydrolysis was confirmed in the present investigation by measuring the pH of a suspension of La-montmorillonite previously heated at 380°C . A decrease of 2.5 pH units was observed compared to the air-dried sample.

2. Dehydration. As water is lost, the polarizing effects of the cation are concentrated on fewer water molecules, thus increasing hydrolysis.

3. Partial destruction of the montmorillonite structure. The montmorillonite heated at 240 and 380°C changed colour. This may be ascribed to the formation of Fe^{3+} , either due to oxidation of Fe^{2+} within the structure or displaced from octahedral sites by partial destruction of the structure and subsequently transformed into the oxide or hydroxide. The presence of Fe^{3+} was detected by extraction with KCl in acid media ($\text{pH} = 3$), thus confirming that some destruction of the framework occurred.

Isotherm of water vapour sorption over La-montmorillonite at 25°C

Fig. 4 shows the water vapour sorption–desorption isotherm at 25°C on La-montmorillonite previously evacuated at $140^\circ\text{C}/10^{-4}$ torr. The distance between branches increases towards low pressures ($P/P_o < 0.1$) where there is a change in slope of the curve. This may be ascribed to the formation of stable hydrates.

X-ray measurements of the basal spacings corresponding to the initial point (evacuated sample), adsorption maximum ($P/P_o = 0.71$), and the end of desorption ($P/P_o = 0.02$) are listed in Table 5. The swelling of the interlayer space implies penetration by the water molecules, which form three molecular layers when the basal spacing is 16.6 \AA . At this adsorption maximum the La^{3+} ions presumably adopt nonacoordinated surroundings, similar to the stable hydrates of the La(III) salts, with tricapped trigonal prism geometry. Assuming that six water molecules situated at the triangular bases of the prism are partially lodged (0.5 \AA above and below) in the interstices of the tetrahedral layer of oxygen atoms of the silicate layers then the resulting interlamellar distance agrees well with the lattice measurements ($\sim 8.1 \text{ \AA}$) of the tricapped trigonal prism given by Sinha (1976) for the $\text{La}(\text{OH}_2)_9^{3+}$ ion. The change in slope of the desorption branch seems to indicate the formation of stable hydrates in the interlayer space, where two layers of water remain partially lodged in the interstices between tetrahedral oxygen atoms. The persist-

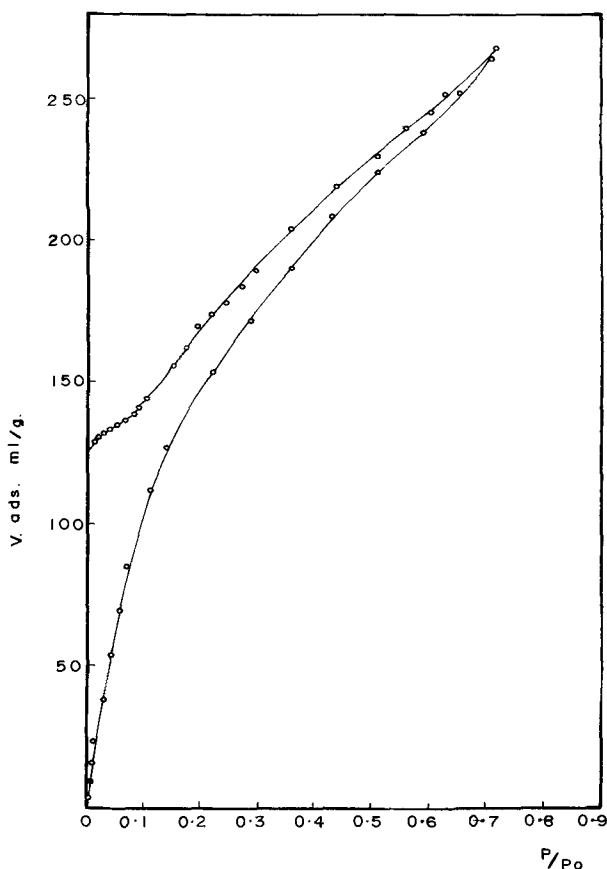


FIG. 4. Sorption-desorption isotherm of water vapour on La-montmorillonite at 25°C.

TABLE 5. Basal spacings (001), interlamellar spacings (Δ) and number of water molecular layers retained at various pressures by La-montmorillonite at 25°C (see Fig. 4).

Basal spacing Å	Δ Å	Water layers	P/P_o
16.6	7.1	3	0.710
14.0	4.5	2	0.019
10.2	0.7	0	10^{-5} (140°C)

ence of water at the end of the desorption reflects the strong ion-dipole interaction exercised by a cation of high charge. The existence of only one endothermic peak in the DTA curve at 125°C and the substantial loss of water observed when the samples are heated indicate that only one type of interaction is exercised on the water molecules and that it is very much weakened by rise in temperature, as happens with ion-dipole forces.

ACKNOWLEDGMENT

The authors thank Dr Girela Vilchez (Estación Experimental del Zaidín, Granada) for his help with the thermal analyses and also for his useful suggestions.

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RÉSUMÉ: Le comportement lors de l'hydratation et de la déshydratation, ainsi que l'effet de traitements thermiques variés sur des montmorillonites saturées avec des ions lanthanidiques, ont été suivis par diffraction des rayons X, analyse thermique (ATD, TG, TGD), spectroscopie infra-rouge ainsi que par des techniques de sorbtion et désorbition de vapeur d'eau. Un chauffage à 150°C sous 10^{-5} torr n'élimine pas toute l'eau inter-feuillets de la montmorillonite et n'affecte pas la CEC. Un chauffage au-dessus de 160°C provoque la diminution de la CEC. A 25°C la montmorillonite-La fixe au maximum 3 couches d'eau dans l'espace inter-feuillets, les molécules d'eau adoptant une coordinance neuf par rapport aux cations La^{3+} .

KURZREFERAT: Es wurde das Hydratation/Dehydratation-Verhalten und der Einfluß verschiedener thermischer Behandlungen auf mit Lanthanidionen gesättigten Montmorillonit untersucht. Als Methoden wurden die Röntgendiffraktometrie, Thermoanalysen (DTA, TG, DTG), IR-Spektroskopie und die Sorbtion-Desorbition von Wasserdampf angewendet. Durch Aufheizen bis 150°C unter 10^{-5} torr wurde das in der Zwischenschicht des Montmorillonits gebundene Wasser nicht vollständig ausgetrieben. Ebenso blieb die KAK davon unberührt. Durch Aufheizen über 160°C wurde eine Reduktion der KAK erreicht. Bei 25°C nimmt der Montmorillonit maximal 3 Wassermolekülschichten in der Zwischenschicht auf. Die Wassermoleküle nehmen eine nicht koordinierte Verteilung um das La^{3+} -Ion ein.

RESUMEN: Se estudia la hidratación, deshidratación y efectos de diversos tratamientos térmicos sobre Montmorillonitas saturadas con iones Lantánidos, aplicando técnicas de difracción de rayos X, análisis térmico (ATD, TG, TGD), espectroscopia infrarroja e isoterma de sorción-desorción de vapor de agua sobre La-Mont.

Se concluye que no es posible eliminar el agua interlamina en su totalidad por tratamiento a 150°C/ 10^{-5} torr, y que los tratamientos térmicos hasta 150°C no influyen en la CCC; a partir de 160°C se produce una disminución de la misma. Por último se concluye que la adsorción de vapor de agua a 25°C por La-Mont, da lugar a un máximo de tres capas moleculares, con una posible distribución nonacoordinada en torno al catión La^{3+} .