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Retention of La(III) and Nd(III) by Montmorillonite*

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An understanding of the chemical behaviour of the actinides in nature is of major importance in order to design safe repositories for high-level radioactive nuclear wastes. Geochemical data indicate that montmorillonite will be the major component responsible for ion sorption.

La and Nd simulate Am and Cm in studies on the interaction of the latter with clay minerals. It has already been observed that lanthanide–montmorillonite shows a decrease in cation-exchange capacity, *CEC*, upon heating at temperatures above 160 °C [1]. Miller *et al.* have examined the sorption of Eu(III), Ho(III) and Yb(III) on an Upton, Wyoming, montmorillonite, with temperature [2] and pressure [3] as variables. They claim that hydrolysis and migration into octahedral sites are likely mechanisms for 4f ions fixation. The aim of this paper is to determine the mechanisms of the interaction upon heating in air of La(III) and Nd(III) with montmorillonite. A montmorillonite was used having the structural formula: $(Si_{7.64}{}^{4+}Al_{0.36}{}^{3+})^{IV}(Al_{3.09}{}^{3+}Fe_{0.28}{}^{3+}Mg_{0.69}{}^{2+})^{VI}$-$O_{20}(OH)_4$.

Experimental

The montmorillonite which has been used comes from Los Trancos, Almeria, Spain, and consists of the <2 μm fraction. After removal of carbonates and organic matter, the sample was saturated with sodium. This Na–montmorillonite, Na–Mt, was used as a starting material for the preparation of the montmorillonite saturated with La(III), La–Mt, and Nd(III), Nd–Mt, respectively.

Infrared, FT-IR, spectra were recorded in a Fourier Transform Nicolet 5 DXE spectrometer. X-ray powder diffraction diagrams were obtained with a Siemens Kristalloflex D-500 instrument; basal spacings were examined using oriented aggregate preparations and quartz was used as an internal standard for *b*-dimension measurements.

Results and Discussion

The unheated lanthanide–montmorillonite after wetting and drying 24 h at 60% relative humidty shows an interlamellar spacing which corresponds to a double-sheet complex. Upon air-heat treatment of the samples, at 300 °C for 24 h, for the La–Mt and Nd–Mt samples it takes a long time of re-expansion with water before showing noticeable bands in the X-ray diffractograms. Once that induced period is over, the 001 spacings show that the lanthanide–montmorillonite are still capable of swelling.

However, it has already been mentioned that montmorillonite saturated with lanthanides shows upon heating a decrease in *CEC* [1], which has been partially attributed to a migration of the 4f ions from their interlamellar sites to octahedral ones [2]. In order to investigate the possibility of a migration mechanism in La–Mt and Nd–Mt, the OH infrared stretching and bending modes of initial and air-heated (300 °C, 24 h) samples have been studied. Figure 1 shows the spectra in the region 3800–3450 cm^{-1} for the samples indicated, previously evacuated at 150 °C for 30 minutes to eliminate the broad band at 3400 cm^{-1} corresponding to molecular water. The spectra of the La–Mt samples coincide with those of Nd–Mt. The dominant absorption at 3620 cm^{-1} is due to AlAlOH groups. Neither a shift in the maximum nor the new bands is observed upon heating. In ref. 2 the appearance upon heating of a shoulder at 3700 cm^{-1} has been reported in Ln–montmorillonite (Ln = Eu, Ho, Yb) spectra, which the authors interpret as due

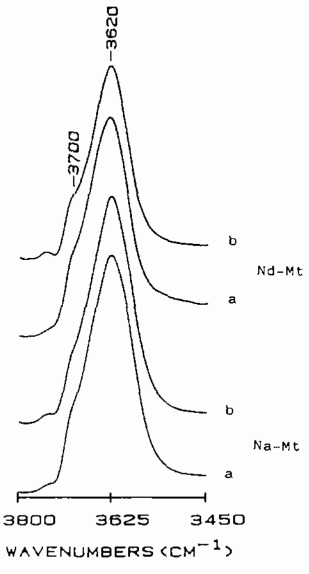

Fig. 1. FT-IR spectra of sodium and neodymium montmorillonites evacuated 30 minutes at 150 °C; (a) initial samples, (b) air-heated samples (300 °C, 24 h).

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to octahedral migration of the exchangeable cations. Nevertheless, Fig. 1 shows the shoulder at 3700 cm^{-1} in the FT-IR spectra of the initial samples, even in the case of the reference sample, Na–Mt, without any appreciable change in relative intensity upon heating.

OH groups are oriented at approximately 16° to the clay layers, but on octahedral migration of the exchange ions they will shift to 90° orientation. When the angle of incidence of the infrared beam was increased with the oriented films of the initial and heated La–Mt and Nd–Mt samples, no appreciable change was observed in the FT-IR spectra.

The FT-IR spectra obtained of OH bending modes, in the region 950–750 cm^{-1}, show again no shift of the bands upon heating.

The possibility of octahedral migration has been finally examined through measurements of the *b*-dimension of the montmorillonite unit cell. This magnitude is known to be a function of the montmorillonite water content and of isomorphous substitution. No increase upon heating has been observed in the *b*-dimension of the lanthanide–montmorillonite, which is not consistent with the 4f ions migration to vacant octahedral sites.

The above FT-IR and X-ray results do not support an octahedral migration as a likely mechanism for lanthanide fixation by montmorillonite on heating in air at 300 °C. Therefore, the hydrolysis of the hydrated interlamellar 4f cations appears as the only likely mechanism.

Upon heating a shoulder at 1700 cm^{-1} appears in the La– and Nd–montmorillonite spectra; spectra of the air-dried films of H-montmorillonite show broad absorption bands at 2900 cm^{-1} and 1700 cm^{-1}, which are thought to be due to hydronium ions. In addition, the protonation of taken up NH_3 has been studied as a more sensitive proof. The samples were evacuated at 150 °C, treated at the same temperature with gaseous NH_3 ($P = 100$ torr) and then the FT-IR spectra were obtained, Fig. 2. The shoulder at 1460 cm^{-1}, due to NH_4^+, shows that hydrolysis occurs even during the preparation of the lanthanide samples, the extent of the reaction increasing with heating. The intensity of the carbonate band, which impurifies the air-handled samples, serves as a reference. Therefore, the hydrolysis of the exchangeable hydrated 4f ions to poly-hydroxy cations generates observable hydronium ions, thus confirming the proposed mechanism for La(III) and Nd(III) fixation by montmorillonite.

The molecular water content has been examined through the HOH bending absorption band at 1630 cm^{-1}. The intensity of this band decreases dramatically upon heating, which means a parallel decrease in the molecular water content. In montmorillonite two types of interlayer water can be differentiated; one labile attributed to molecules in outer coordination spheres of the exchangeable cations, giving a very broad band; another consists of the more firmly held water, directly coordinated to the cations in a first sphere, which shows unusually strong absorption at 1630 cm^{-1}. The above mentioned decrease in the intensity of that band for La–Mt and Nd–Mt should be attributed to a decrease in the second type of interlamellar molecular water.

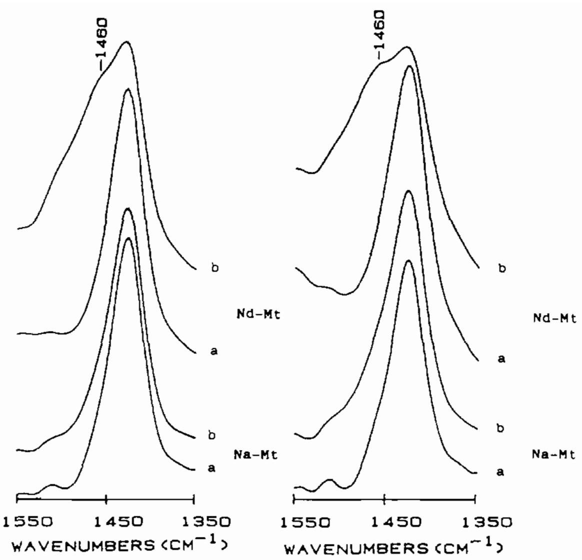

Fig. 2. FT-IR spectra of sodium and neodymium montmorillonites evacuated at 150 °C (left), and after treatment at the same temperature with gaseous NH_3 ($P = 100$ torr) (right). (a) corresponds to the initial samples and (b) to the air-heated (300 °C, 24 h) ones.

We are not going to discuss here the complex ecological consequences of the mechanism found for the previously known decrease in *CEC* when Ln–montmorillonites are air-heated, at the expected initial temperatures at canister surfaces. However, it must be emphasized that the present results do not support the octahedral migration mechanism suggested in other publications, through which the simulated actinide ions would become non-exchangeable.

Acknowledgement

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