

UPTAKE OF LANTHANIDES BY VERMICULITE

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Abstract—The uptake of Ce^{3+} , Nd^{3+} , Gd^{3+} , Er^{3+} , and Lu^{3+} on vermiculite was studied using cation-exchange measurements, infrared spectroscopy (IR), and X-ray powder diffraction (XRD). The reaction was followed by measuring the amount of lanthanide ions (Ln^{3+}) taken up by n-butylammonium-exchanged vermiculite in relation to amount of Ln^{3+} salt added and the pH of the equilibrium solution. The amount of Ln^{3+} taken up in excess of the CEC value increased with the hydration energy of the lanthanide ion and with the pH of the n-butylammonium-exchanged vermiculite suspension. At equilibrium solution pHs of 3–4.5, the uptake of Ln^{3+} ions was only slightly greater than the CEC, whereas at pHs >4.5 the amount taken up by the vermiculite increased sharply. The uptake of Ln^{3+} ions beyond the CEC of the vermiculite is probably related to the hydrolysis of Ln^{3+} ions on the vermiculite interlayer surface. The appearance of a band at $1715\text{--}1720\text{ cm}^{-1}$ in the IR spectra of the Ln^{3+} -exchanged vermiculite suggests a strongly acidic medium in the interlayer space. The Ln^{3+} -exchanged vermiculites gave XRD patterns having 002/001 intensity ratios greater than that of Mg-exchanged vermiculite.

Key Words—Hydration energy, Hydrolysis, Infrared spectroscopy, Ion exchange, Lanthanide ions, Vermiculite, X-ray powder diffraction.

INTRODUCTION

The study of the uptake of lanthanide ions (Ln^{3+}) by clay minerals may contribute useful information about the interactions of radioactive waste products and clay-bearing media (Miller *et al.*, 1982). The distribution of the rare earth elements in soil clays is also related to the composition of the parent rocks and thus may be used to determine the origin of these rocks (Bonnot-Courtois and Jaffrezic-Renault, 1982). Little is known, however, about the exchange of Ln^{3+} ions on clay minerals. Several recently published works reported that Ln^{3+} ions can be taken up by clay minerals in excess of their theoretical cation-exchange capacities (CEC); the authors of these works suggested that this uptake in excess of the CEC is due to a hydrolysis process of such ions on the clay mineral surfaces (Brucque *et al.*, 1980; Miller *et al.*, 1982; Laufer *et al.*, 1984).

If hydrolysis occurs, solution pH is obviously a critical factor in the uptake of Ln^{3+} ions by clays, but no detailed investigations on the relation between solution pH and exchange of Ln^{3+} ions on clays have been reported to date. The present work was therefore designed to evaluate the effects of pH on the uptake of five lanthanide ions (Ce^{3+} , Nd^{3+} , Gd^{3+} , Er^{3+} , and Lu^{3+}) by vermiculite from solutions ranging in concentration from 1.5×10^{-3} to 2.5×10^{-2} N.

EXPERIMENTAL

The vermiculite used came from Benahavis, Spain. The natural sample was pretreated with H_2O_2 to exfoliate the mineral and to separate it from external impurities. Hand-picked individual crystals from the pretreated sample were examined by XRD and found to be pure. A sample was saturated with Ca^{2+} by treat-

ing it twice with 1 M $CaCl_2$ and washing out the excess salt with deionized water. The Ca-exchanged sample was calcined at $900^\circ C$ and analyzed chemically (Olivera, 1986). The structural formula calculated from this analysis is: $Ca_{0.58}(Mg_{4.98}Fe^{3+}_{0.80}Ti_{0.22})(Si_{5.48}Al_{2.38}Fe^{3+}_{0.14})O_{20}(OH)_4$. The CEC was determined to be 150 meq/100 g, based on the weight of the sample heated at $900^\circ C$ (Olivera, 1986).

Selected flakes (5×2 mm) of vermiculite were converted to the n-butylammonium form using the method of Serratosa *et al.* (1970). The n-butylammonium-exchanged vermiculite was dispersed in water to form a suspension. CEC studies were carried out using the $<5\text{-}\mu m$ size fraction.

Ion-exchange isotherms

The exchange of Ln^{3+} ions on n-butylammonium-exchanged vermiculites was studied by means of two types of experiments:

- (1) Prior to the addition of the Ln^{3+} salts, a suspension of n-butylammonium-exchanged vermiculite was divided in two portions. The pH of each portion was adjusted to 7.10 and 5.10 by addition of HCl. Increasing volumes of $LnCl_3$ solutions (pH = 4–4.5) were then added to aliquots of each suspension of n-butylammonium-exchanged vermiculite. The final concentration of added $LnCl_3$ ranged from 1.5×10^{-3} to 2.5×10^{-2} N.
- (2) Fixed quantities of $LnCl_3$ equivalent to twice the CEC of the vermiculite were added to aliquots of the suspension of the n-butylammonium-exchanged vermiculite, followed by small amounts of HCl or pure n-butylamine to vary the pH of the equilibrium solutions from 2.5 to 7.

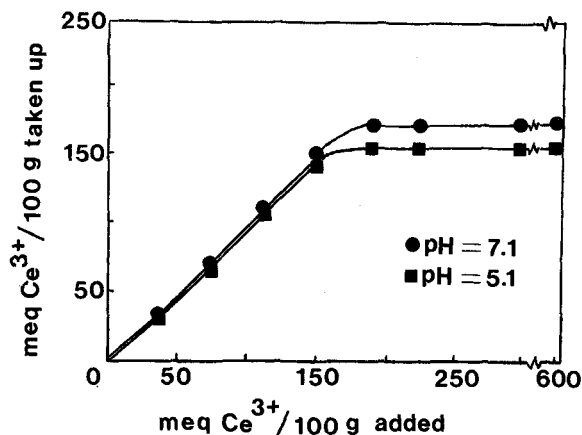


Figure 1. Ion-exchange isotherms (25°C) of Ce^{3+} on n-But NH_3 -exchanged vermiculite at two initial pHs of the clay suspensions (vermiculite weight referred to 900°C).

In all experiments, the final concentration of the vermiculite suspensions was 4 mg/ml (based on the weight of the sample heated at 900°C). The final volumes of the suspensions were 25 ml, the temperature was 25°C, and the shaking time of the clay-salt suspension was 24 hr.

Photometric analysis

After shaking the clay- Ln^{3+} salt suspension for 24 hr, the mixture was centrifuged and the supernatant was collected. The solid residue was washed twice with 25 ml of deionized water. The three supernatants were mixed together and subsequently analyzed. The lanthanides were determined spectrophotometrically with Arsenazo III following the analytical procedure of Goryushina *et al.* (1963). The experiments were carried out with a Kontron Uvikon 810 double-beam spectrophotometer.

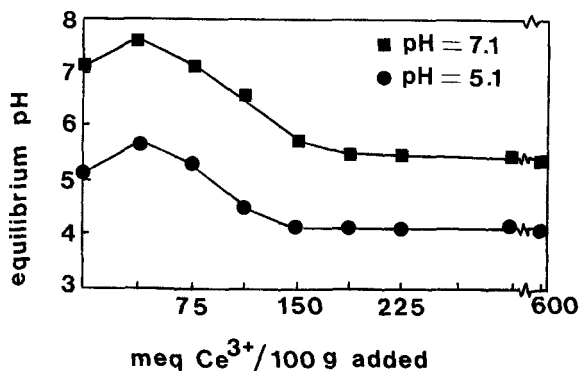


Figure 2. Variation of the equilibrium pH as a function of the amount of Ce^{3+} added (vermiculite weight referred to 900°C).

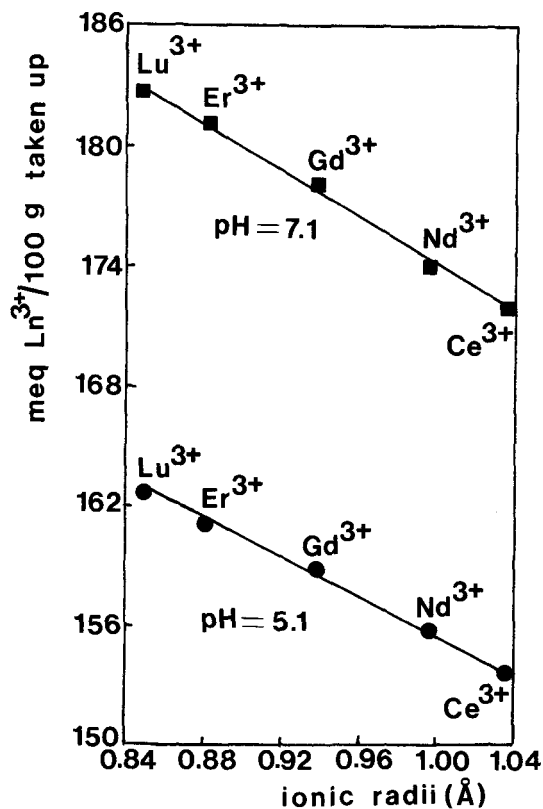


Figure 3. Uptake of Ln^{3+} by n-But NH_3 -exchanged vermiculite as a function of Ln^{3+} ionic radii, at two initial pHs of the clay suspension (vermiculite weight referred to 900°C).

Infrared spectroscopic and X-ray powder diffraction studies

For IR and XRD studies, films (4–5 mg/cm²) were prepared from n-butylammonium-vermiculite (< 2 μm) suspension by sedimentation on a flat glass surface covered with a thin film of polyethylene. Once dry, the films were separated from the support, and the vermiculites embedded therein were converted to the lanthanide form by immersion in 0.1 M Ln^{3+} chloride solutions.

IR spectra were obtained using a Beckman 4260 spectrophotometer. The XRD patterns were recorded on a Siemens D500 diffractometer using monochromatic $\text{CuK}\alpha$ radiation.

RESULTS AND DISCUSSION

Ion-exchange studies

Figure 1 illustrates the uptake of Ln^{3+} ions by vermiculite in relation to the amount of the Ln^{3+} salt added and to the initial pH (i.e., the pH before adding the Ln^{3+} salt). All Ln^{3+} ions used in this study showed similar, but not identical, behavior. Two distinct regions are apparent in these isotherms. In the low con-

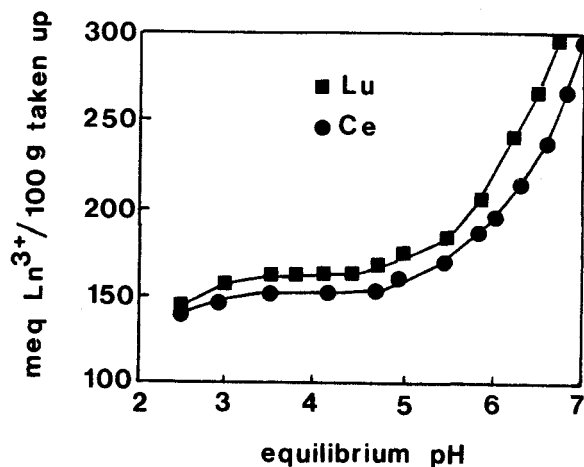


Figure 4. Ion-exchange isotherms of Ce^{3+} and Lu^{3+} on n-But NH_3 -exchanged vermiculite as a function of the equilibrium solution pH, at 25°C (vermiculite weight referred to 900°C).

centration region the slope of the isotherm approaches unity, which indicates that practically all the Ln^{3+} added was taken up by the vermiculite, suggesting a great affinity of the vermiculite for Ln^{3+} ions. In this region, Ln^{3+} uptake was independent of the initial pH. A second region of the isotherm is apparent at concentrations exceeding the CEC of the vermiculite. In this region of the isotherm, Ln^{3+} uptake depended on the initial pH of the suspension. For the Ce^{3+} experiment (Figure 1) at a pH of 5.10, the curve is sharply asymptotic indicating that the exchange reaction was quasi-stoichiometric; at 7.10, however, a Ce^{3+} uptake of about 20 meq/100 g (900°C) in excess of the CEC was noted.

Figure 2 plots the equilibrium pH against the quantity of Ln^{3+} salt added. In the experiment having an initial pH of 5.10, the equilibrium pH stabilized at 4.15 following the addition of 150 meq Ce^{3+} /100 g (900°C), which represents an addition of Ln^{3+} salt equal to the CEC of the vermiculite. At an initial pH of 7.10, however, the equilibrium pH stabilized at 5.50 following the addition of 185 meq Ce^{3+} /g (900°C). At this equilibrium pH, the amount of Ce^{3+} taken up was 172 meq/100 g (900°C), suggesting that the lanthanide ions were taken up in excess of the vermiculite CEC, even under acid conditions.

Figure 3 shows the amount of Ln^{3+} ions taken up by the vermiculite at saturation level as a function of the ionic radius, at two initial pHs of the suspension. At both pHs, the Ln^{3+} content increased inversely with the ionic radius and was always in excess of the CEC of the vermiculite. The excess uptake increased with the initial pH. Figure 4 shows the isotherms for Ce^{3+} and Lu^{3+} as a function of the equilibrium solution pH. From these isotherms, the excess uptake of Ln^{3+} ions started at pH 3; it was nearly constant, however, as

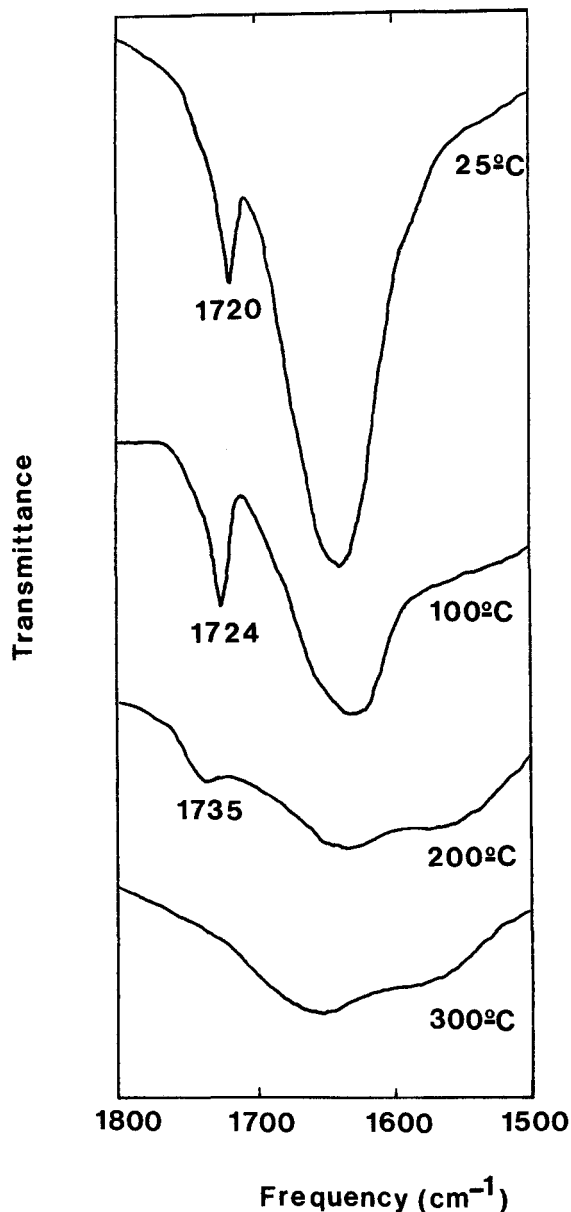


Figure 5. Infrared spectra of a film of Nd^{3+} -exchanged vermiculite heated at different temperatures.

high as pH 4.5 and increased appreciably at higher pH. The uptake of Ln^{3+} ions increased with the hydration energy of the ion.

Inasmuch as this clay mineral has no octahedral vacancies, the above results suggest that the uptake of Ln^{3+} ions in excess of the CEC of the mineral took place by hydrolysis in the vermiculite interlayer space, as expressed by the following equation: $[\text{Ln}(\text{OH}_2)_x]^{3+} \rightleftharpoons [\text{Ln}(\text{OH})_y(\text{OH}_2)_{x-2y}]^{(3-y)+} + y\text{H}_3\text{O}^+$, where $y < 3$. The hydrolysis process assumes the dissociation of water coordinated to the central metallic ion. The protons

Table 1. Properties of the supernatants in equilibrium with lanthanide-vermiculite gels.

Ion in supernatant	pH	pLanthanide	pLanthanide + 3pOH	pK _s
Ce ³⁺	2.93	2.72	35.90	20.16
	4.15	2.71	32.36	
	4.90	2.74	30.04	
	6.00	2.85	26.85	
	7.00	4.18	25.18	
Nd ³⁺	3.17	2.72	35.21	21.55
	4.08	2.72	32.48	
	4.92	2.74	29.04	
	5.96	2.85	26.97	
	6.95	4.27	25.42	
Gd ³⁺	3.02	2.72	35.63	22.75
	4.06	2.72	32.48	
	5.15	2.79	29.04	
	6.19	3.07	26.50	
	6.90	4.27	25.57	
Er ³⁺	3.00	2.73	35.73	23.20
	4.06	2.74	32.48	
	5.00	2.78	29.78	
	6.22	3.11	26.45	
	6.85	4.28	25.63	
Lu ³⁺	3.03	2.72	35.63	23.46
	4.09	2.74	32.47	
	4.98	2.79	29.85	
	6.18	3.12	26.58	
	6.71	4.27	26.14	

generated may subsequently be exchanged with other Ln³⁺ cationic species in the solution. This mechanism is supported by the observed decrease in pH caused by Ln³⁺ additions of 37.5 meq/100 g (900°C) (Figure 2).

The observed order of uptake of the lanthanide series (Figure 3), Ce < Nd < Gd < Er < Lu, agrees with Mortland and Raman (1968) who concluded that hydrolysis increases with cation hydration energy and occurs even in fully expanded clays if the hydration energy of the metal ion involved is large (i.e., >500 kcal/mole). Miller *et al.* (1982) reported hydroxy lanthanide cations in a montmorillonite interlayer on the basis of IR frequency shifts of deuterated hydroxyl groups.

From the data of the isotherms (e.g., Figure 4) the ionic products $[\text{Ln}^{3+}] \cdot [\text{OH}^-]^3$ for the species in the equilibrium supernatants were calculated (Table 1). From these data, the precipitation of Ln³⁺ ions in the interlayer space is unlikely, because the ionic product values are much less than the solubility products (K_s).

Aagaard (1974) observed that several clay minerals took up the heavy Ln³⁺ ions (i.e., those having smaller ionic radii) in relatively greater amounts than they took up light lanthanide ions. From this, he suggested that the Ln³⁺ ions were taken up in the anhydrous state. On the basis of XRD, IR, and thermal data, Olivera *et al.* (1987) suggested the presence of abundant water in Ln³⁺-exchanged vermiculites. Further confirmation

Table 2. 001 spacing and intensity ratio of basal reflections (air-dried) of vermiculite as related to interlayer ion.

Interlayer ion	d(001) (Å)	I ₀₀₂ /I ₀₀₁
Mg ²⁺	14.40	0.03
Ce ³⁺	15.05	0.10
Nd ³⁺	15.00	0.12
Gd ³⁺	14.82	0.15
Er ³⁺	14.75	0.15
Lu ³⁺	14.70	0.15

of the existence of hydroxy lanthanide cations in the vermiculite interlayer space is provided by the fact that after treating a Ln³⁺-exchanged vermiculite with 2 N NaCl at pH 5, Na did not completely replace interlayer Ln³⁺ ions (Olivera *et al.*, 1986.) Miller *et al.* (1982) concluded that hydroxy lanthanide cations migrated to the hexagonal holes on the oxygen surface. Consequently, the strong interactions of these hydroxycations with vermiculite were due not only to electrostatic attraction, but also to other types of forces, such as hydrogen bonds with or without Van der Waals interactions (Laufer *et al.*, 1984).

Trivalent lanthanide ions hydrolyze only slightly in solution before precipitation of the hydroxide at pH > 6 (Baes and Mesmer, 1976). The results obtained in the present work suggest that the presence of vermiculite increases the tendency of these ions to hydrolyze. In the interlayer space of clays, the polarization of water is influenced by both the central metal ion and the distribution of the layer charge (Mortland and Raman, 1968). In vermiculite, this charge is localized on the oxygens of Al–O–Si linkages, and thus a single tripositive ion cannot neutralize three charge sites. A lanthanide ion reduces its charge by means of hydrolysis to make the neutralization more effective (McBride *et al.*, 1975).

Infrared spectroscopy

The hydrolysis of Ln³⁺ ions in vermiculite is also supported by the fact that hydrated free protons were found in the homoionic Ln³⁺-exchanged samples. These hydrated free protons were detected by the appearance of a band at 1715–1720 cm⁻¹ in the IR spectra, which is attributed to the ν₄ vibration mode (Gillard and Wilkinson, 1964) (Figure 5). The disappearance of this band at high temperature is attributed to the migration of the protons to negative charge points in the interior of the layer. Although the equilibrium solution pH (4.5) at which the homoionic Ln³⁺ samples were obtained nearly precludes the hydrolysis of the Ln³⁺ ions, air drying of the films provided further hydrolysis. Consequently, the degree of hydrolysis of these ions was inversely related to the interlayer water content (Mortland and Raman, 1968; Miller *et al.*, 1982).

X-ray powder diffraction

In the Ln^{3+} -exchanged samples, the 002 reflections appeared to be intensified relative to the 001 reflections (Table 2). Bassett (1958) interpreted this phenomenon in a Cu^{2+} -vermiculite to be due to increased electron density in the interlayer space. The results of the Ln^{3+} -uptake experiment suggest that the increased interlayer electron density was due not only to the greater atomic numbers of the Ln^{3+} ions, but also to the increase in the interlayer cation content.

The basal spacings of the Ln^{3+} -vermiculites were slightly larger than those of Mg^{2+} -vermiculite (Table 2), suggesting the presence of a double layer of water molecules. The data in Table 2 also suggest that Ce and Nd ions have hydrated sizes greater than Gd, Er, and Lu ions in the vermiculite interlayer space. Solvated Ce and Nd ions should have nine water ligands in their primary hydration sphere, whereas Gd, Er, and Lu ions have eight (Habenschuss and Spedding, 1979).

CONCLUSIONS

The observed uptake of Ln^{3+} by vermiculite, in excess of its CEC, appears to be the result of hydrolysis of such ions on the interlayer surface of the vermiculite. Because of hydrolysis, the uptake varied throughout the lanthanide series in such a manner to suggest a direct relation between the magnitude of the uptake and the hydration energy of the Ln^{3+} ions.

This study also illustrates the importance of pH on the uptake process of Ln^{3+} ions by clays, chiefly because pH determines the charge of the sorbed cationic species. Strong localization of the vermiculite layer charge is believed to be responsible for the observed decrease of three units in pH, at which Ln^{3+} ions begin to hydrolyze in the presence of vermiculite.

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