

An Investigation of Increase of Sorption of Strontium with the Exchange of Lithium on Montmorillonite

Niranjan Chandra Dutta,* Takashi Iwasaki, Yoshio Onodera, Hiromichi Hayashi, and Takako Nagase
Inorganic Materials Section, Tohoku National Industrial Research Institute, 4-2-1 Nigatake, Miyagino-ku, Sendai 983-8551

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Sorption of Sr^{2+} ions on Na-montmorillonite was carried out in Sr^{2+} ions and in binary solutions of Sr^{2+} and Li^+ ions at 220 °C for 24 h under hydrothermal condition. Sorption of Sr^{2+} ions was found to be substantially increased by the assistance of Li^+ ions. FT-IR spectra revealed that migration of Li^+ ions in the hexagonal hole of montmorillonite and subsequent exchange with Sr^{2+} ions affected OH-stretching bands caused an increase of Sr-sorption.

The safe disposal of strontium radionuclide is always conceived as a problem because it is the common constituent of radioactive waste, having a long half-life period and hazardous actions. Migration of Li^+ ions in the montmorillonite under heat treatment has been observed either in the vacant octahedral sites^{1,2} or in the hexagonal hole of montmorillonite.^{3,4} Furthermore, Alvero et al.⁵ proved that migrated Li in the hexagonal hole could move back to the interlayer by the hydrothermal treatment. Also, exchangeability of migrated Li^+ ions was proved by Jaynes and Bigham.⁶ Suitability of using montmorillonite as a sorbent in the clay barrier system is determined by the amount of sorption of radionuclide. Thus, the present study is undertaken to observe a substantial increase of Sr-sorption in the binary solution of Sr^{2+} and Li^+ ions on the hydrothermal treatment of montmorillonite at 220 °C for 24 h.

Na-montmorillonite (STx-1, white, Gonzales county, Texas, U.S.A.) was prepared (2 μm) by treating with 1 M NaCl solution and by centrifuging and removing excess salts by dialysis. Then, it was dried at 50 °C for 8 h. The cation exchange capacity of Na-montmorillonite was determined by the treatment of 1 M NH_4Cl solution and found to be a value of 0.96 meq·g⁻¹. After that, 0.1 g of Na-montmorillonite was fully dispersed into 10 mL of the 0.3 M Sr^{2+} solution, and then Li^+ solution, ranged from 0.01 to 0.15 M, was added. Each of the reacting mixtures was taken in the closed vessel and heated at 220 °C under hydrothermal condition for 24 h. By centrifuging, solid and liquid phases were separated, and the concentration of Sr^{2+} ions in the liquid phase was determined with ICP. Sorption of Sr^{2+} ions in the clay was calculated from the difference in concentrations in the liquid phase before and after the reaction. Na^+ ions remained in the montmorillonite was extracted with NH_4Cl solution and measured with an AAS.

Table 1. Sorption of Sr^{2+} , Li^+ ions and remained Na^+ ions in the montmorillonite (\pm signifies a standard deviation for the replicates of estimation)

Conc. (M)	Sorption of cations (meq·g ⁻¹)		Na^+ remained (meq·g ⁻¹)	
Sr^{2+}	Li^+	Sr^{2+}	Li^+	Na^+
0.3	0.00	0.68±0.07	0.00±0.00	0.28±0.05
0.3	0.01	0.72±0.05	0.05±0.01	0.22±0.06
0.3	0.02	0.79±0.08	0.06±0.02	0.15±0.08
0.3	0.05	0.82±0.04	0.08±0.01	0.07±0.06
0.3	0.10	0.85±0.07	0.09±0.03	0.04±0.02
0.3	0.15	0.87±0.06	0.10±0.03	0.01±0.01

Then, Li^+ ions in the solution phase were also measured using AAS (Table 1).

Sr-sorption was determined to be 0.68 meq·g⁻¹, 0.28 meq·g⁻¹ of Na^+ ions remained in the clay (Table 1). Sr^{2+} ions could not replace all Na^+ ions in the clay due to its larger size and higher hydration energy.⁷ Similar sorption reaction of Sr^{2+} ions in presence of Li^+ ions caused a substantial increase of Sr-sorption (Table 1). It appears to be due to the exchange of migrated Li^+ ions with Sr^{2+} ions.^{5,6} A decrease of basal spacings (d_{001}) from 13.9 Å of Sr-Mt to 10.2 Å of Sr-Li-Mt indicates a tendency of collapsing the interlayer by the substantial increase of Sr-sorption. An endeavour has been also made to get the insight of montmorillonite structure using FT-IR. FT-IR spectra show similar structure of Na-montmorillonite and Sr-montmorillonite³ following heat treatment at 220 °C. An analysis of FT-IR spectra of Sr-montmorillonite (Sr-Mt) and Sr-Li-montmorillonite (Sr-Li-Mt) has been shown (Table 2). It reveals a little change of different band positions corresponding to Si-O and OH bending frequencies (400-1200 cm⁻¹) due to the migration of Li^+ ions in the hexagonal hole.^{3,4} This little change is due to the small amount of Li^+ ions contained in the montmorillonite after exchange with Sr^{2+} ions (Table 1).

Moreover, an analysis of resolved OH-stretching bands (3600-3700 cm⁻¹) (Figure 1) of Sr-Mt (similar to Na-Mt due to aforesaid cause) and Sr-Li-Mt with the help of high resolution of Fourier transformation⁴ reveals a distinct difference of

Table 2. Position of bands (cm⁻¹) of Sr-Mt, Sr-Li-Mt in the region^a of 400-1200 cm⁻¹

Sample	Si-O (apical)	Si-O (basal)	AlAlOH ^b	AlLiOH	AlMgOH ^b	M-O ^b	Si-O-Al ^b	Si-O-Si (bending)
Sr-Mt	1125	1035	915	Nil ^c	846	626	520	465
Sr-Li-Mt	1125	1038	915	812	846	629	520	467

^aAs only Li^+ ions change the bands of this region, Sr^{2+} ions³ cannot due to larger size. However, OH-stretching component bands (3600-3700 cm⁻¹) are not shown here, change of these bands is described with the effect of Sr^{2+} ions (higher quantity) in presence of Li^+ ions (Figure 1). ^bThe corresponding band intensity (%) of Sr-Li-Mt has also been found to be decreased in accordance with the migration of Li^+ ions in the hexagonal hole. ^cThis band was not appeared (Nil) due to absence of Li^+ ions in Sr-Mt sample.

hydration shell of montmorillonite. A shift of AlMgOH component band from 3601 to 3604 cm^{-1} indicates that trioctahedral AlMgLi grouping did not occur, as Li^+ ions could not migrate into the vacant octahedral site.^{3,4} The absorption band at 3619 cm^{-1} of Sr-Mt is assigned to be AlAlOH⁴ shifted to 3623 cm^{-1} for Sr-Li-Mt attributing to a stronger association of Sr^{2+} ions with the polarization of OH⁸ groups in presence of Li^+ ions. The band at 3629 cm^{-1} of OH-stretching vibrations⁴ coordinated by 2Al changed to 3636 cm^{-1} for Sr-Li-Mt sample. It shows a pronounced shift due to stronger hydration of Sr^{2+} ions suggesting an increased Sr-sorption in comparison to Li-Mt.⁴ The sharp band of AlMgOH at 3676 cm^{-1} of Sr-Mt is changed to a broad peak at 3681 cm^{-1} for Sr-Li-Mt indicating also an increased association of Sr^{2+} ions with OH groups in

comparison to Li-Mt.⁴ Moreover, the band position at 3656 cm^{-1} has been assigned for the vibrations of residual water molecules weakly hydrogen bonded to surface oxygens⁴ is changed to a broad band at 3658 cm^{-1} (with a shoulder near by) with a tendency of merging with a band at 3649 cm^{-1} (which might be for the highly resolved band of same type of vibrations) revealing a tendency of OH groups coordinated to Li^+ ions in localities of trioctahedral character.⁹ Other bands, such as, at 3670 cm^{-1} (which is changed to a hump at the same position) and at 3687 cm^{-1} (which is shifted to 3693 cm^{-1}) are found to be unassigned in the literature.^{10,11} Above all, the distinct change of different assigned OH-component band positions (Figure 1) corroborates a stronger interaction of Sr with OH groups due to substantially increased Sr-sorption in Sr-Li-Mt sample.

The results, taken together, imply that an increase of Sr-sorption could be achieved by the migration of Li^+ ions and subsequent exchange with Sr^{2+} ions at the hydrothermal treatment of montmorillonite at 220 °C.

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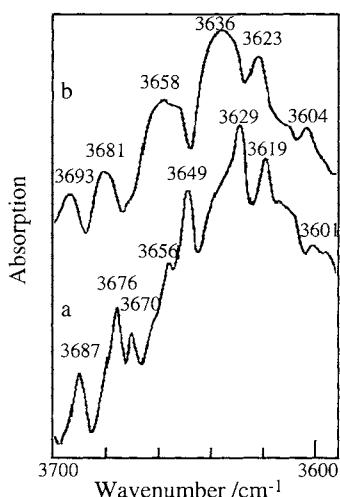


Figure 1. FT-IR Spectra of Stretching-OH Components of Sr-Mt (a) and Sr-Li-Mt (b).