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Hydration and hydrolysis of samarium (III) in montmorillonite clay: a neutron diffraction study

O Sobolev[1], **L Charlet**[1], **G J Cuello**[2], **A Gehin**[1], **J Brendle**[3] and **N Geoffroy**[1]

[1] LGIT-OSUG, University of Grenoble I and CNRS, BP 53, F-38041 Grenoble Cedex 9, France
[2] Institut Laue-Langevin, 6 rue Jules Horowitz, BP 156, F-38042 Grenoble Cedex 9, France
[3] LMPC, UMR CNRS 7016, ENSCMu, UHA, 3 rue A Werner, 68093 Mulhouse Cedex, France

Abstract
Neutron diffraction with isotopic substitution was carried out at room temperature on hydrated samples of Sm montmorillonite, prepared at pH = 4 and 8, in order to find out whether Sm is present as aqueous $Sm(OH)_3^o$, Sm^{3+}, or intermediate hydrolyzed species, and how it is linked to the clay surface. It was found that the number of hydrogen atoms (5.5 ± 2.0) nearest to Sm^{3+} at pH = 4 is equal to or even slightly smaller than that of oxygen atoms (7.5 ± 1.0). This means that Sm^{3+} is bound to the clay surface and it is probably partially hydrolyzed. This result is very close to those obtained earlier for Yb^{3+} and Nd^{3+}, despite the different methods of sample preparation and the different mineralogy of the samples.

1. Introduction

Montmorillonites are swelling clays consisting of negatively charged aluminosilicate layers held together by interlayer cations. Under humid conditions the interlayer cations and the internal clay surfaces are hydrated. Montmorillonite is the main component of bentonite, a natural clay widely used in industry. Bentonite was selected as the most suitable buffer material for a high level radioactive waste repository [1]. The main function of the clay buffer material is to retard the migration of the radio nuclides in the case of corrosion of the waste package material.

The lanthanides are of interest because they can be considered as chemical analogues of actinides such as Pu^{3+} and Am^{3+}. The results for Nd^{3+} and Yb^{3+} exchanged Wyoming montmorillonite obtained by means of neutron diffraction with isotopic substitution were reported in [2]. It was found that Nd^{3+} and Yb^{3+} are only partially hydrated and that they are bound to the clay surface probably as a result of heat treatment at $100\,°C$ during sample preparation. It was supposed that this treatment was sufficient to cause the lanthanide ions to dehydrate and to bind irreversibly to the oxygens of the clay surface.

The aim of the present experiment is to investigate by means of neutron diffraction with isotopic substitution the structural parameters of the hydration, hydrolysis and sorption of Sm^{3+}, in the interlayer space of the montmorillonite as a function of pH, which is an important variable for radioactive waste management. The experimental results are obtained for Sm montmorillonite hydrated samples, prepared at pH = 4 and 8, in order to find out whether Sm is present as sorbed aqueous $Sm(OH)_3^o$, Sm^{3+}, or intermediate hydrolyzed species, and how it is connected to the clay surface.

It is therefore interesting to compare our results with those of Pitteloud *et al* [2] because of the following differences in the sample preparation and clay composition:

- We did not heat the samples at $100\,°C$ as in [2].
- The synthetic montmorillonite used in our experiment did not contain any substitution of Si^{4+} by Al^{3+} in the tetrahedral sheet in contrast to the Wyoming montmorillonite reported in [2]. Negative charge caused by these tetrahedral substitutions leads to the possible formation of inner-sphere surface complexes with interlayer cations [3].

Due to the above differences in sample preparation we could expect our experimental results to be different as well.

For example, for the strongly hydrated Ni^{2+} cation it was found that it is fully hydrated and located in the middle of the interlayer space [4].

2. Method

A detailed description of the neutron diffraction with isotopic substitution method can be found elsewhere [2, 4]; here we will only introduce some basic concepts.

In a diffraction experiment the intensity, $I(Q)$, of scattered neutrons is measured as a function of the scattering vector $Q = 4\pi/\lambda \sin\theta$, where 2θ is the scattering angle, and λ is the neutron wavelength. This expression is valid assuming elastic scattering (Bragg law) as usual in diffraction experiments. When we measure diffraction patterns for two samples that are identical except for the isotopic composition of one of the elements, as for ^{152}Sm (Sm) and ^{154}Sm (Sm′), the difference in the two intensities $I(Q)$ is

$$\Delta_{Sm}(Q) = I_{Sm}(Q) - I_{Sm'}(Q)$$
$$= c_{Sm}(\overline{b_{Sm}^2} - \overline{b_{Sm'}^2}) + c_{Sm}^2(b_{Sm}^2 - b_{Sm'}^2)\,[S_{SmSm}(Q) - 1]$$
$$+ \sum_{\alpha \neq Sm} 2c_{Sm}c_\alpha(b_{Sm} - b_{Sm'})b_\alpha\,[S_{Sm\alpha}(Q) - 1], \quad (1)$$

where c_α is the atomic fraction and b_α is the mean coherent scattering length of element α. $S_{\alpha\beta}(Q)$ are the partial structure factors. In other words, all partial structure factors not involving the substituted element (Sm in our case) are eliminated in this first-order difference function. This difference is better defined when there is enough contrast between the two isotopes; in our case the scattering lengths for ^{152}Sm and ^{154}Sm are -5.0 fm and 9.3 fm, respectively [5]. By Fourier transforming, one gets $G_{Sm}(r)$, the weighted sum of the partial radial distribution functions $g_{Sm\beta}(r)$,

$$G_{Sm}(r) = \frac{1}{2\pi^2\rho_n r}\int_0^{Q_{max}}\left[\Delta_{Sm}(Q) - c_{Sm}(\overline{b_{Sm}^2} - \overline{b_{Sm'}^2})\right]$$
$$\times Q\sin(Qr)\,dQ = A_{SmSm}[g_{SmSm'}(r) - 1]$$
$$+ \sum_{\alpha \neq Sm} A_{Sm\alpha}\left[[g_{Sm\alpha}(r) - 1]\right] \quad (2)$$

with

$$A_{SmSm} = c_{Sm}^2(b_{Sm}^2 - b_{Sm'}^2)$$
$$A_{Sm\alpha} = 2c_{Sm}c_\alpha(b_{Sm} - b_{Sm'})b_\alpha \quad \text{for } \alpha \neq Sm. \quad (3)$$

3. Experiment

A synthetic montmorillonite used for sample preparation was made at LMPC, Mulhouse, France [6]. The isotopes ^{152}Sm and ^{154}Sm were obtained as oxides from CHEMGAS, France (www.chemgas.fr). The $^{152}Sm^{3+}$ and $^{154}Sm^{3+}$ 0.05 mol l^{-1} stock solutions were prepared by dissolution in H_2O–HCl and D_2O–DCl solutions at pH 3. Portions of Na montmorillonite, each of 2.5 g, were suspended in 20 ml of H_2O (D_2O). Before being suspended in D_2O, the Na montmorillonite was dried in an oven at 65 °C for 3 days. 15 ml aliquots of ^{152}Sm or ^{154}Sm stock solution were added to each of these suspensions. The acidity was adjusted first to pH = 3 and the system was

allowed to equilibrate for 3 days, and then the acidity was adjusted with NaOH (NaOD) to pH = 4 or to 8. After 6 months of equilibration, the samples were filtered and dried for 2 weeks at room temperature either in the laboratory for the H_2O samples or in a dry glove box for the D_2O samples. The solid samples were then crushed to a fine powder and placed for another 3 weeks in a 70% humid atmosphere regulated with saturated KI–H_2O (D_2O) solutions.

The water content, 205 mg g^{-1} for H_2O hydrated samples and 220 mg g^{-1} for D_2O hydrated samples, was determined gravimetrically. These numbers correspond to 8.6 and 9.2 water molecules per unit cell, respectively. The interlayer (001) spacing of the samples, determined using x-ray diffraction, is in all cases equal to 15.8 Å. This indicates a double layer of water molecules in the clay interlayer, which is consistent with the water content analysis. The Sm content in the samples was measured using ICP-OES after a total dissolution in HF/HNO$_3$. The composition of the samples is given by the following simplified unit cell formula:

$$Sm_{0.25}[(Al_{3.25}Mg_{0.75})Si_8O_{20}(OH)_4], \quad 8.6H_2O \text{ or } 9.2D_2O.$$
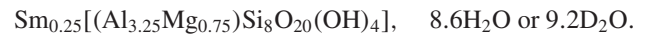
The ^{152}Sm and ^{154}Sm isotopes were chosen because of the good contrast in scattering length (see the previous section) and relatively high abundance of the natural Sm. Another reason is to avoid the high degree of resonant adsorption of the natural Sm.

The neutron diffraction measurements on the hydrated powder samples were performed on the D4C diffractometer at the reactor neutron source of the Institut Laue-Langevin, France [7]. The incident wavelength was 0.6958 Å, calibrated using a Ni powder reference. The samples were filled in a 6.8 mm i.d. 7.0 mm o.d. cylindrical vanadium container sealed with a metallic O-ring. The loaded sample container was weighed before and after each measurement to verify that no dehydration had occurred. Diffraction patterns were measured at ambient temperature (298 K) for each sample, as well as for the empty sample container, the instrument background and a 6.08 mm diameter vanadium rod. The data were corrected for background, empty container, attenuation, and multiple scattering, and normalized to the scattering from vanadium, taking into account the energy dependent neutron scattering cross sections of light and heavy water.

4. Results and discussion

The corrected, normalized intensities, $I(Q)$, for the H_2O and D_2O hydrated ^{152}Sm montmorillonite samples prepared at pH = 4 are shown in figure 1. The data for the ^{154}Sm montmorillonite samples and for pH = 8 look very similar. The first-order differences $\Delta_{Sm}(Q) = I_{152}(Q) - I_{154}(Q)$ for H_2O and D_2O hydrated samples are shown in figure 2. Their Fourier transforms, the composite radial distribution functions $G_{Sm}(r)$, describing the correlations between Sm atoms and other neighbor atoms, are shown in figure 3. The back Fourier transform of the function $G_{Sm}(r)$ is also shown in figure 2. For this back transformation the unphysical oscillations of $G_{Sm}(r)$ at distances below 2 Å (represented by dashed lines in figure 3)
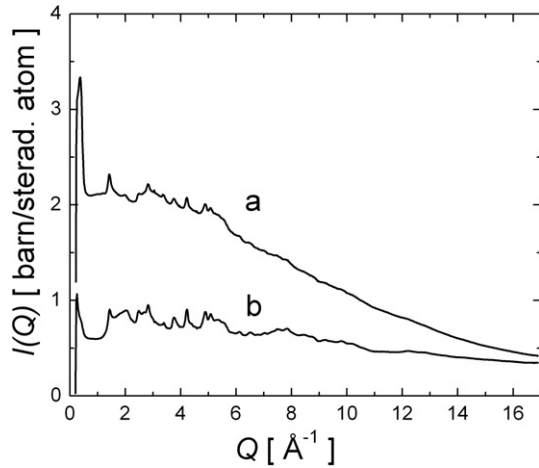
Figure 1. Normalized neutron diffraction intensities, $I(Q)$, for ^{152}Sm montmorillonite (a) in the H_2O hydrated form and (b) in the D_2O hydrated form.
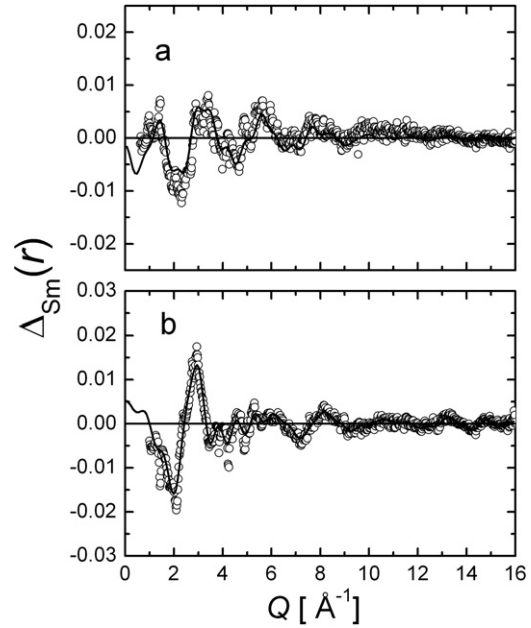
Figure 2. First-order difference functions for the samples prepared at pH $= 4$: (a) $\Delta_{Sm}^{H}(Q)$, for Sm montmorillonite H_2O hydrate and (b) $\Delta_{Sm}^{D}(Q)$, for Sm montmorillonite D_2O hydrate. Lines represent the back Fourier transform of $G_{Sm}(r)$ functions shown in figure 3.

Table 1. Coefficients $A_{Sm\alpha}$ (barns) (equation (3)).

| α	H_2O hydrated Sm montmorillonite	D_2O hydrated Sm montmorillonite
Si	5.45×10^{-4}	5.15×10^{-4}
Al	1.84×10^{-4}	1.74×10^{-4}
Mg	6.62×10^{-5}	6.25×10^{-5}
O_{clay}	0.00229	0.00216
H_{clay}	-2.45×10^{-4}	-2.32×10^{-4}
O_{water}	8.19×10^{-4}	8.28×10^{-4}
H_{water} (D_{water})	-0.00106	0.0019
Sm	8.83×10^{-6}	8.33×10^{-6}

were replaced by the theoretical value $G_{Sm}(0) = -\sum_{\alpha} A_{Sm\alpha}$ (equations (2) and (3)). The coefficients $A_{Sm\alpha}$ are given in table 1.

The peak at 2.5 Å can be identified as corresponding to the Sm–O distance. The peak around 3.1 Å corresponds to Sm–H correlations. In the case of the H_2O hydrated sample this peak has negative amplitude due to the negative scattering length of hydrogen. The $G_{Sm}(r)$ obtained for different pH values look

similar, although at pH $= 8$, the Sm–O distance is slightly shorter than that reported above for pH $= 4$ (figure 4). Three reasons could be supposed for this difference in Sm–O distance (though it is just slightly outside the error bars): hydrolysis, precipitation, adsorption at the edges of clay plates [8] possible at higher pH. We could not obtain the $\Delta_{Sm}(Q)$ and $G_{Sm}(r)$ curves for D_2O hydrated Sm montmorillonite for pH $= 8$ because of H_2O contamination in one of the samples.

Due to the large statistical errors we did not calculate second-order differences, which could provide more information on Sm–H and Sm–O correlations. The coordination numbers N_O and N_H were calculated by integration of the $G_{Sm}(r)$ peaks at 2.5 and 3.1 Å. Results of these calculations together with corresponding distances r_{SmO} and r_{SmH} are shown in
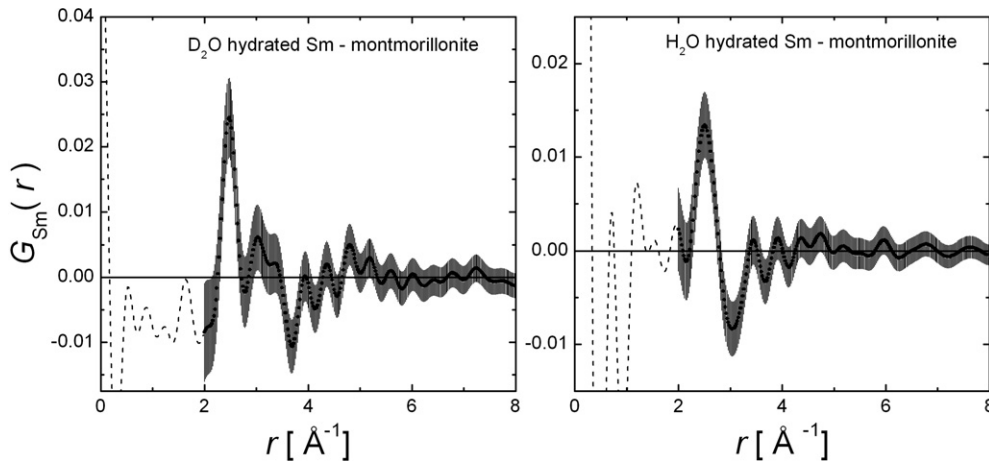
Figure 3. Composite pair distribution functions $G_{Sm}(r)$ obtained for pH $= 4$.

Table 2. Mean distances and coordination numbers found for the first coordination shells of Sm^{3+} (this work) and other lanthanide ions (other authors).

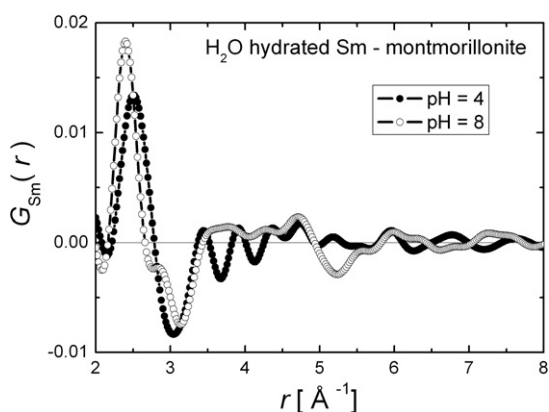|	r_{LnO} (Å)	r_{LnH} (Å)	N_O	N_H	Reference
Sm montmorillonite pH = 4	2.5 ± 0.04	3.06 ± 0.05	7.5 ± 1.0	5.5 ± 2.0	This work
Sm montmorillonite pH = 8	2.4 ± 0.03	3.1 ± 0.05	7 ± 1	3.6 ± 2.0	
1.0 m $Sm(ClO_4)_3$ aqueous solution	2.47 ± 0.02	3.12 ± 0.02	8.54 ± 0.2		[9]
Nd montmorillonite	2.47 ± 0.02	3.18 ± 0.02	7.1 ± 1.0	6.4 ± 2.0	[2]
Yb montmorillonite	2.33 ± 0.02	2.98 ± 0.02	7.2 ± 1.5	5.9 ± 3.0	[2]

Figure 4. Composite pair distribution functions $G_{Sm}(r)$ compared for different pH values.

table 2. The numbers given for pH = 4 are the averages of the values obtained for H_2O and D_2O samples. The N_H value found at pH = 8 is smaller than that at pH = 4; however due to large error bars it is hard to say whether the N_H value difference is a real effect.

Our results are very similar to those obtained for Nd and Yb montmorillonite [2]. Again, like in that case we observe a small reduction of N_O in comparison to the aqueous solution [9] and much stronger decrease of the number of hydrogens N_H. The observed N_H/N_O ratio cannot be explained without assuming the cation to be in contact with the clay siloxane surface and to be only partially hydrated. The authors of [2] assumed that this effect was the result of the mild heat treatment at $100\,°C$ performed during sample preparation in the case of Yb and Nd [2]; and in this way the lanthanide ions dehydrate and bind irreversibly to the clay layers. This interpretation, however, is not supported by the results of the present work. In our case we did not treat the samples in the same way, but we observe the same dehydration process. Then, the dehydration of Sm depends neither on the sample preparation nor on the clay mineralogy.

On the other hand, neutron results are in disagreement with those obtained by other methods, where the lanthanide cations were found to be localized at the middle of the clay interlayer, fully hydrated [10, 11]. This difference in the results can be explained assuming that hydration and sorption of the lanthanide cations depend on the concentration of the cations in the interlayer. For neutron diffraction experiments

the clay sample is fully saturated with lanthanide cations, and a low water content is needed. In this case the cations can be hydrolyzed and present in the clay interlayer as $Sm(OH)^{2+}$, $Sm(OH)_2^+$ and $Sm(OH)_3^o$ species. These species being more hydrophobic than trivalent cations can be dehydrated and can stick to the clay surface, as was demonstrated for large monovalent cations Cs^+ and K^+ by means of molecular dynamics simulations [12–14].

It is worth mentioning that our x-ray data and water content analysis of the samples indicate a double layer of water molecules in the clay interlayer, whereas one might expect a collapse to lower interlayer water content if Sm is bound to the clay surface and dehydrated. Like in [2], we could suppose that some smaller quantity of Sm^{3+} cations is still fully hydrated and this is sufficient to prevent the clay interlayer from undergoing collapse.

5. Summary

The coordination of Sm in the montmorillonite interlayer was studied by means of neutron diffraction with isotopic substitution. It was found that the number of hydrogen atoms (5.5 ± 2.0) nearest to Sm^{3+} at pH = 4 is equal to or even slightly smaller than that of oxygen atoms (7.5 ± 1.0). This means that the Sm^{3+} ion is binding to the clay surface via oxygen siloxane atoms, and it is probably partially hydrolyzed. This result is very close to those obtained earlier for Yb^{3+} and Nd^{3+}, though the sample preparation methods and sample mineralogy differ for the two studies.

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