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Structural identification of europium(III) adsorption complexes on montmorillonite

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A study of trivalent europium retention onto Na-montmorillonite is presented, combining both macroscopic and microscopic points of view. In order to investigate the metal sorption mechanisms at a molecular level and therefore experimentally identify both clay reactive sites and sorption equilibria, laser-induced fluorescence spectroscopy (LIF) and X-ray photoelectron spectroscopy (XPS) on europium ion loaded montmorillonite have been performed. Moreover, since this clay is an alumino-silicated mineral, we have interpreted our experimental results in terms of interactions between a metal ion and a cation exchange site, and distinct "aluminol" and "silanol" edge sites. Therefore, identical structural investigations have been carried out on both Eu/alumina and Eu/silica systems. These comparisons have allowed us to determine the nature of the europium surface complexes and thus led to an experimental definition of the sorption equilibria involved in the retention process. The obtained lifetime values and the Eu 3d XPS spectra of europium sorbed on the three solids have shown that this metal is sorbed, on the montmorillonite clay, on exchange sites as an outer-sphere complex and onto both "aluminol" and "silanol" edge sites as inner-sphere surface complexes, depending on the pH value and the ionic strength of the suspension.

Introduction

The study of the mineral–water interface is of fundamental interest since the associated interfacial reactions play an important role in the fate of the metals in the geosphere. Nevertheless, it is a rather complex process to quantify the physico-chemical parameters and to model these geochemical processes.[1,2] Waste repositories and metal migration through ground water are part of this effort, especially the long-term repository of nuclear fuels in deep geological sites, which is one of the major issues arising from the nuclear fuel cycle.[3,4] In order to assess the safety of this kind of storage in an underground disposal site, the migration of radiotoxic elements through the geosphere must be evaluated. This migration depends mainly on the radionuclide's capability to interact with the numerous natural materials (inorganic or organic matter) present in the ground. Sorption and precipitation constitute the bulk of these interactions[5–8] and can thus be an important retardation factor. However, these sorption phenomena depend on many different parameters such as the pH and the ionic strength of the solution, the metal concentration, the presence of a complexing agent, the specific surface area and the density of functional surface groups of the mineral as well as the acid-base behavior of the mineral surface. Consequently, the direct determination of the retention parameters, such as sorption equilibrium constants, is rather difficult. In order to quantify these retention processes, various thermodynamic models have been developed, such as ion exchange and surface complexation.[9–15] Nevertheless, most of these models, which usually involve direct modeling of macroscopic data, do not always lead to a unique and accurate representation of the retention processes. Therefore, such a thermodynamic approach needs to be completed with investigations at a molecular level in order to provide direct evidence of the involved mechanisms.[16–23] These structural characterizations will thus allow one to experimentally determine the different surface species and consequently the associated sorption equilibria, which will be used in the modeling procedure.[24–26]

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The structural investigations, presented in this paper, were carried out using two complementary spectroscopic techniques, laser spectrofluorimetry and X-ray photoelectron spectroscopy (XPS). Both methods, by analyzing the emission spectra, the corresponding lifetime values and the XPS binding energies, will provide the number of the surface species, information about the nature of the surface metal complexes, the identification of an inner- *vs.* outer-sphere complexes and the possible presence of a precipitate on the surface.

Among the radionuclides that could be potentially released from geological radwaste repositories and then migrate through the ground, the trivalent ions represent an important part. We propose here to investigate the interaction of trivalent europium ions with the Na-montmorillonite clay. This solid has been chosen because it could be a mineral representative of natural clay, which might be used as an engineered barrier thanks to its low permeability and its high sorption capacity. Up to now, many studies have been published on the retention properties of such a mineral,[27–36] but only a few have been devoted to a complete study combining both macroscopic and microscopic points of view.

Since the approach presented in this paper is mainly microscopic, montmorillonite, which is formed by two-dimensional sheets of tetrahedral SiO_4 and octahedral $Al(O,OH)_6$, will be considered as an assembly of cation exchange sites and distinct "aluminol" and "silanol" edge sites. The exchange process mainly depends on the ionic strength, while retention onto the edge sites is usually strongly dependent on the pH since the corresponding surface groups exhibit an amphoteric behavior. Therefore, we present, in this paper, the results obtained on the Eu/montmorillonite system together with the results obtained on the Eu/γ-alumina and Eu/silica systems as references. The choice of these two references implies that the XPS binding energies together with the decay time values depend mainly on the bounds Eu–O–(Al) and Eu–O–(Si), whatever the structure of the substrate.

Experimental

A Materials

In order to obtain the homoionic Na-montmorillonite clay from a Wyoming bentonite, marketed under the name Volclay, the following steps were performed: after dispersion in a 0.1 M HCl solution for 24 h, the suspension obtained was neutralized by adding concentrated NaOH solution and centrifuged. Then, clay purification to remove all soluble phases (such as calcite) and sodium saturation to convert the clay into the homoionic Na form were performed by adding a 0.5 M NaCl solution for 3 days. The rinsing operations were next realized by dialysis with a suspension volume over deionized water volume ratio equal to 0.5. The rinsing water, changed 2 times per day, was tested by conductivity. Moreover, since chlorine ions are well-known to be fluorescence quenchers, we have checked (using proton-induced X-ray emission) that all chlorine ions were removed during the above washing step. Although the experiments were conducted in aqueous solution, the specific surface area of the clay was determined on a dry sample using the N_2-BET method. This surface was found to be 35 $m^2\ g^{-1}$ (Coulter SA 3100) and the cation exchange capacity (CEC) was determined as 63 mequiv per 100 g by using the ammonium acetate method. Moreover, in order to verify that no alteration of the montmorillonite occurred during the purification process, infrared spectroscopy has been performed to verify the absence of an amorphous silica phase, which is a sign of clay alteration.

The reference oxide compounds, a silica gel (60H Merck) and a γ-alumina (90 Merck), were used without any further purification. The N_2-BET specific surface areas of the alumina and silica were 140 and 380 $m^2\ g^{-1}$, respectively.[37,38]

Europium(III) stock solutions (about 10^{-1} M) were prepared by dissolution of a weighted amount of $Eu(NO_3)_3{\cdot}6H_2O$ (Fluka) in an acidified $NaClO_4$ solution (pH = 1) to avoid cation hydrolysis and then kept under argon atmosphere. All exact europium concentrations were determined by ICP-AES.

B Sorption data collection

The uptake of europium ion onto the clay and the two reference solids was studied at room temperature (298 K), through a batch technique using crystal polystyrene ([Eu] = 10^{-3} or 10^{-4} M) or high density polyethylene tubes ([Eu] = 2.10^{-7} M). The choice of the containers was guided by preliminary measurements that have shown that in our different experimental conditions (ionic strength, pH and cation concentrations) the europium sorption onto the tube walls is negligible. For most experiments, a ratio of 200 mg of solid for 20 mL of europium solution ($m/V = 10$ g L^{-1}) was used, with europium concentrations ranged from 2×10^{-7} to 2×10^{-3} M. The initial pH value was varied between 3 and 9 by adding to the suspension negligible volumes of concentrated $HClO_4$ or NaOH solutions of analytical grade (0.1 M). The ionic strength was held constant at 0.5, 0.1 or 0.05 M with $NaClO_4$ solutions. The suspensions were stirred in sealed tubes for 8 days. Note that, in these conditions, the air volume above the liquid was around 15 mL, which corresponds to an estimated dissolved CO_2 concentration less than 1.2×10^{-5} M, whatever the experimental pH conditions. The presence of europium carbonate species was checked by the spectroscopic measurements described in the following section. The final pH value for each tube was directly measured in the suspension with a combined Ag/AgCl Bioblock glass electrode (using NaCl as electrolyte) and a Tacussel pH-meter. Then, the solid was removed from the solution by centrifugation (3 h at 3500 rpm) and the supernatant was used to quantify the europium uptake on the substrate by ICP-AES measurements. The errors bars associated to the calculated sorption rates are assumed to be ±5%. The solids were finally dried at room temperature and stored in a drier (room temperature) before being analyzed using laser-induced fluorescence spectroscopy (LIF) and XPS.

C Spectroscopic measurements

The room temperature (298 K) fluorescence measurements on the dried samples were performed using a Continuum Nd:YAG pulsed laser (7 ns pulse duration), a SPEX 270 M Jobin-Yvon monochromator coupled with a Hamamatsu Photonics photomultiplier and a Princeton Instruments Inc. Model PG 200 pulse generator controlled by a PC with Princeton Instruments Inc. WINSPEC program. The samples were excited at 355 or 532 nm. The time-dependent emission decays of the europium $^5D_0$ multiplet were recorded with the same setup and fitted to multi-exponential laws in order to determine the corresponding lifetimes. The error bars associated to the lifetimes are lower than 10% (variation of the decay time value for several samples prepared under the same experimental conditions).

All XPS spectra were collected on an electron spectroscopy for chemical analysis (ESCA) apparatus with a multi-detection electron analyzer (VSW HA150, fixed analyzer transmission mode: FAT). An unmonochromated Mg Kα source (1253.6 eV and halfwidth of 0.9 eV) was used for both survey (FAT = 90 eV) and narrow (FAT = 22 eV) scans. The powdered samples were fixed on a copper plate in the analytical chamber (10^{-9} mbar vacuum). The charge effect was corrected using the internal reference C 1s line from adventitious aliphatic carbon (284.6 eV). The recorded lines, Eu 3d and C 1s, were fitted using the XPSPEAK 3.0 program[39] after subtraction of the background (Shirley baseline). The europium 3d spin-orbit splitting was fixed at 29.9 eV. It is known that the XPS spectral resolution is problematic with conventional lab sources. Therefore, we have determined the Eu 3d width corresponding to our setup by analyzing reference europium samples [$Na_3(Eu(CO_3)_3{\cdot}6H_2O$, $K(Eu(CO_3)_2{\cdot}3H_2O$;, $Eu_2(CO_3)_3{\cdot}3H_2O$, $Eu(OH)_3$]. Then in the fitting procedure, the full width at half maximum (FWHM) was kept constant to 4.6 eV. In addition, within the accuracy of the method, two surface species can be discriminated when the difference between their respective binding energies is more than 0.2 eV.[40] Consequently, we consider in the present work that the environment of each surface species is quite well defined, and thus each spectral future (FWHM = 4.6 eV) corresponds to one single complex (no continuum of surface sites). Moreover, we have checked that exposure to ultra-high vacuum has no effect on the samples by comparing the Eu(III) fluorescence signals before and after the XPS experiments.

Results

A Eu(III)/Na-montmorillonite

A1 Sorption edges. The sorption edges of the europium ion ([Eu(III)] = 0.1 mM, $m/V = 2$ g L^{-1}) on Na-montmorillonite corresponding to three different ionic strengths ($NaClO_4$ 0.5, 0.1 and 0.05 M) are presented on Fig. 1(a). Below pH 6, the curve exhibits a plateau for all ionic strengths considered. The position of this plateau appears to strongly depend on the ionic strength value: the higher the ionic strength, the lower the extent of sorption. This is the classical behavior involved in the interaction between metal ions and permanently negatively charged sites, which corresponds to an ion exchange process. Between pH 6 and 7 the europium sorption increases to greater than 95% for pH near 7 and it keeps this value for higher pH, which is indicative of the existence of another sorption mechanism in this pH region. For comparison, Fig. 1(b) presents the europium sorption data obtained for the limiting experimental conditions regarding the total metal ion concentration ([Eu(III)] = 10^{-3} and 2×10^{-7} M, $m/V = 10$ g L^{-1}). We can stress that whatever the ionic strength and europium concentration, the shape of the retention curve is the same with an increase of the sorption *versus* pH in the same region. Only the position of the sorption plateau depends on the conditions, as mentioned before.

When surface complexation models are used, a reversibility of the sorption processes is required. Then, before modeling the sorption edges, we have checked this point. The protocol considered was to perform the sorption step and then to add a negligible volume of concentrated acidic solution to the supernatant in order to decrease the final pH value. After 8 days of shaking, the final europium concentration was measured and compared to the sorption edge. This protocol allows one to perform the reversibility experiments for a constant total cation concentration. For example, after sorption ($[Eu(III)]_{tot} = 10^{-4}$ M, $I = 0.5$ M, $m/V = 10$ g L^{-1}) two different volumes of concentrated $HClO_4$ solution were added to two experimental points corresponding to pH 7 (uptake around 90%). After 8 days of shaking, the final pH values were found to be 6 and 3.6. The determination of the aqueous europium concentration led to 25% for pH 6 (instead of 22%) and 19% for the lower pH value (instead of 20%). These results are in perfect agreement with those obtained from the sorption experiments, which clearly shows that the sorption processes under study are fully reversible and thus allow one to use a surface complexation model.

A2 Spectroscopic investigations. According to the above macroscopic observations, a structural study of the sorbed europium species on clay was performed in order to (i) identify the reactive metal sorption sites towards the Eu(III) ion involved in our experimental conditions and (ii) characterize the resulting surface complexes.

The europium fluorescence spectra and the corresponding lifetimes (gate width = 8 μs) were recorded at 298 K for samples prepared in $NaClO_4$ solutions presenting different ionic strengths and pH values. Nevertheless, the mass-to-volume ratio was kept at 10 g L^{-1} for all samples. Fig. 2 shows, as an example, the emission spectra obtained for an initial europium concentration equal to 2×10^{-3} M, an ionic strength equal to 0.05 M and for pH values corresponding to the bottom (pH = 3.1) and the top (pH = 7.1) of the retention curve. The emission wavelengths are located at 579, 592 and 616 nm for both pH values of the suspension, but the relative intensities clearly depend on the pH (Fig. 2), which indicates that the sorbed species are probably different at the bottom and the top of the retention curve. The same behavior (shape and wavelengths) has been found for all europium concentrations. This is corroborated by the lifetime measurements since for pH 3.1, the corresponding decay time is 75 μs, whereas for pH 7.1, three distinct values were measured (75, 135 and 250 μs).

Samples prepared at intermediate pH values have shown that the 75 μs decay is the only one observed when the pH is lower than 4. Then another value (250 μs) appears, which remains for pH values higher than 7. Moreover, when the pH exceeds 6.5, the third value (135 μs) appears. Finally, for the samples prepared at pH 7.6, these three values are still measured.

In order to check whether these second and third decay times correspond to reactive sites on the clay surface or to precipitated carbonate or hydroxide species, we have recorded the emission spectra and the associated lifetimes of different europium carbonates and europium hydroxides compounds. Two of these are shown as examples on Fig. 3. The shapes of these spectra are totally different from those obtained with the loaded montmorillonite and thus we can assume that no europium precipitation occurs during the sorption experiments. Consequently, these first results clearly indicate that the europium ions interact with only one site at pH 3.1, but for pH between 5.5 and 7.6, other surface sites of montmorillonite are involved in the retention process.

In order to corroborate these results, XPS experiments were then carried out on all the sorbed samples. The Eu $3d_{5/2}$ XPS spectra for samples prepared with [Eu(III)] = 10^{-3} M, $NaClO_4$ 0.1 M, $m/V = 10$ g L^{-1} and pH 5 or pH 7 are presented in Fig. 4. The spectrum corresponding to the lower pH value [Fig. 4(a)] is well-fitted with only one component located at 1137.0 eV, while for the one associated to pH 7 [Fig. 4(b)], two binding energies (1137.0 and 1134.4 eV) are needed to account for the total signal, according to a FWHM held at 4.6 eV. In this last case, it was impossible to achieve a good fit

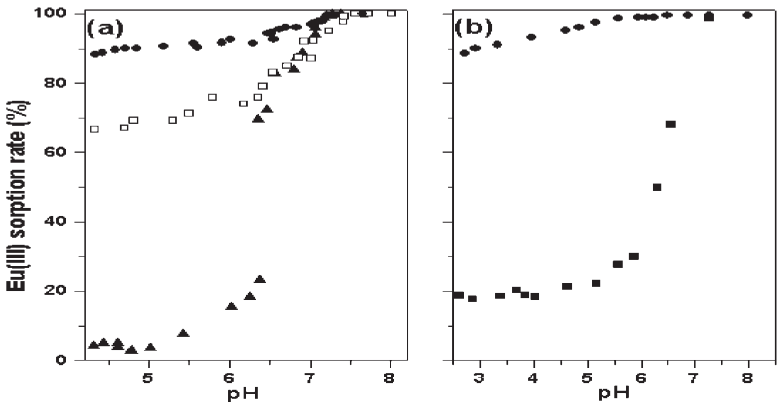

Fig. 1 Sorption edges of the Eu(III)/montmorillonite system: (a) $m/V = 2$ g L^{-1}, [Eu(III)] = 0.1 mM, with I (●) 0.05, (□) 0.1, (▲) 0.5 M; (b) $m/V = 10$ g L^{-1}, $I = 0.1$ M, with [Eu(III)] (●) 0.2 μM, (■) 1 mM.

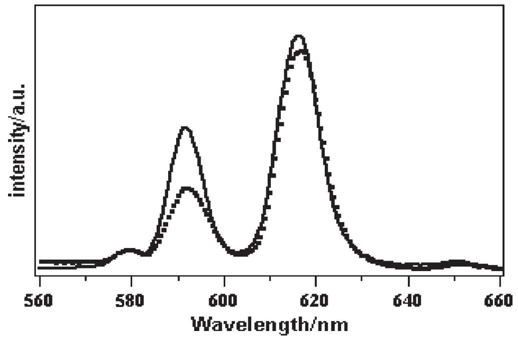

Fig. 2 Fluorescence spectra of Eu(III) sorbed onto Na-montmorillonite with $I = 0.05$ M, [Eu(III)] = 2 mM: (solid line) pH = 3.1, (dotted line) pH = 7.1.

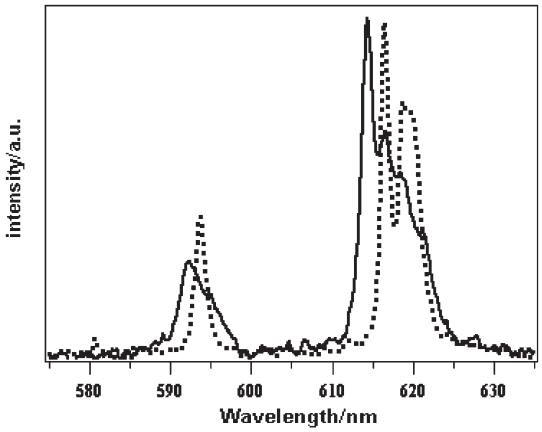

Fig. 3 Fluorescence spectra of two solid compounds: (dotted line) $Na_3Eu(CO_3)_3 \cdot 6H_2O$ and (solid line) $Eu_2(CO_3)_3 \cdot 3H_2O$.

considering only one component with the same FWHM = 4.6 eV. Therefore, we can assume that these two different binding energies correspond to two different chemical environments, which are associated to two different sites on the montmorillonite, already observed by the above optical investigations. Note that for the samples prepared at pH 7, the relative intensity of the component located at 1137.0 eV is much smaller than the one at 1134.4 eV.

From the structure of montmorillonite, several different sites could interact with metal ions: cation exchange sites, "aluminol" and "silanol" edge sites. In order to clearly identify the reactive sites towards Eu(III) ion, we have performed the same experiments with alumina and silica as reference substrates, which can be regarded as the "basic structural units" of the clay. This means that the "aluminol" and "silanol" surface groups on the montmorillonite exhibit the same behavior on the alumina and silica surfaces from a structural point of view and thus, lead to similar surface complexes.

B Eu(III)/alumina and Eu(III)/silica systems

B1 Sorption edges. Fig. 5 shows the europium sorption edges corresponding to both alumina and silica solids in $NaClO_4$ medium ([Eu(III)] = 10^{-4} M, $NaClO_4$ 0.1 M, $m/V = 10$ g L^{-1}). Each sorption edge spreads over roughly one pH unit for both systems. Nevertheless, the sorption edge is observed from pH 5 for the Eu/alumina system while it is only observed from pH 6 for the Eu/silica one. Since the specific surface area of silica (380 m^2 g^{-1}) is higher than the alumina one (140 m^2 g^{-1}), the experimental conditions correspond to a lower surface coverage for silica than alumina. Moreover, it is well-established that the lower the surface coverage, the higher the sorption edge for a known pH value.[41] Then, since the sorption edge is located at lower pH values for alumina, it is probably indicative of a stronger affinity of the "aluminol" sites (compared to "silanol" ones) towards europium species.

B2 Spectroscopic investigations. The sorbed europium emission spectra were recorded for several samples prepared at different pH values ranging from 5 to 7. An example corresponding to Eu(III) sorbed on γ-alumina is shown in Fig. 6 ([Eu(III)] = 10^{-3} M, $NaClO_4$ 0.1 M, $m/V = 10$ g L^{-1}, pH 6). All these spectra present the same shape and the same peak positions (579, 592, 615 and 619 nm). Moreover, for all analyzed samples, only one decay time was measured: 250 ± 20 μs. This value agrees perfectly with the one already reported in the literature for the same system under similar experimental conditions.[42]

For the loaded silica samples, the shape and the position of the fluorescence spectra is also unaffected by the pH values of the suspension (Fig. 6). Nevertheless, in that case (Eu/silica system), two different lifetime values were measured irrespective of the pH value: 130 and 350 μs.

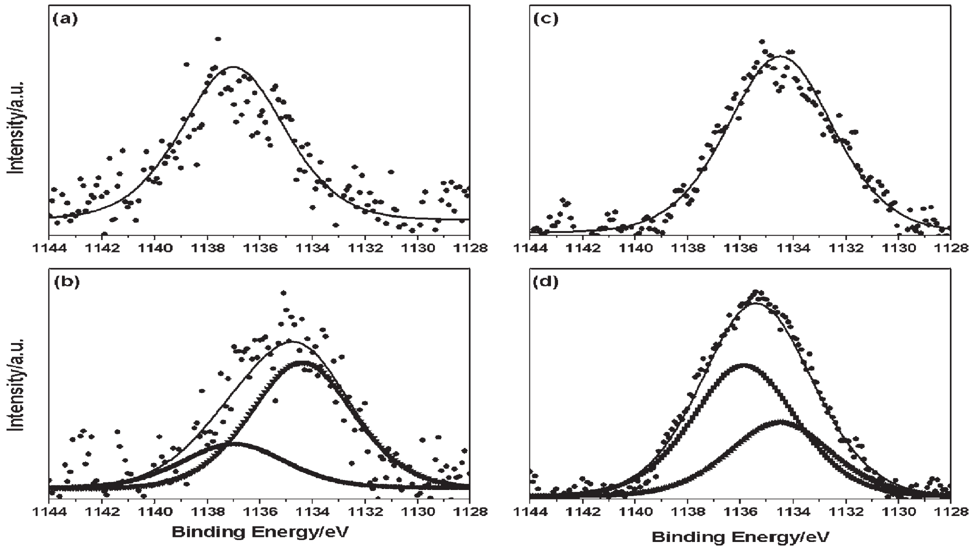

Fig. 4 Typical Eu $3d_{5/2}$ spectra obtained for Eu(III)/montmorillonite for (a) low and (b) high pH values and for the (c) Eu(III)/alumina and (d) Eu(III)/silica systems: experimental data (discrete points), calculated curves (solid lines) and components (symbols).

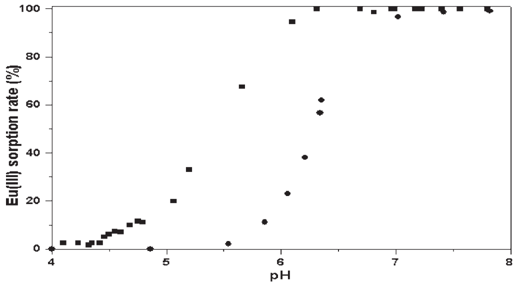

Fig. 5 Sorption edges of (■) Eu(III)/alumina and (●) Eu(III)/silica, $m/V = 10$ g L^{-1}, [Eu(III)] = 0.1 mM, $I = 0.1$ M.

Moreover, for alumina as well as silica system, it was shown that no precipitated carbonate or hydroxide species were formed, as was found for the montmorillonite system.

The Eu $3d_{5/2}$ XPS results for both reference systems are in agreement with the fluorescence study. Indeed, only one binding energy (1134.5 eV, FWHM = 4.6 eV) was necessary to fit the Eu(III)/γ-alumina system, whereas the Eu(III)/silica spectrum is fitted with two components located at 1134.3 and 1135.9 eV (FWHM = 4.6 eV) as shown in Fig. 4(c) and 4(d), respectively.

Discussion

In Table 1 are summarized the results obtained from the structural investigation. As it can be noticed, the europium ions interact with different sites of the montmorillonite, depending on the pH of the suspension. The values (75 µs and 1137.0 eV) found for the Eu(III)/montmorillonite system at pH 3 and 5 are not obtained on the reference substrates. The uptake rates of these samples correspond to the plateau of the sorption edge. Therefore, these values appear to be correlated with the europium ion sorbed on the cation exchange sites located in the interlayer spaces of the clay. Such an interpretation has already been reported for another montmorillonite clay in the literature.[34] Moreover, the lifetime value depends on the surrounding of the fluorescent ion and in particular on the number of quencher molecules such as water molecules. The value of 75 µs corresponds thus to a fully hydrated europium ion surrounded by nine water molecules[43] and it is indicative of outer-sphere europium adsorption complexes within the clay layer.

For pH values ranging from 6.5 to 7.5, these values (75 µs and 1137.0 eV) are still observed, together with new decay times of 250 and 135 µs and a new peak at 1134.4 eV. By comparison with the results obtained from the reference oxides, we can propose that the 250 µs species corresponds to europium sorption onto "aluminol" edge sites while the 135 µs peak corresponds to its retention by "silanol" edge sites of the montmorillonite. In the XPS results, the binding energy (BE) value of 1134.4 eV is roughly the same as the one obtained for alumina (1134.5 eV) but is also the same as one obtained for silica (1134.3 eV). Considering the accuracy of ESCA (0.2 eV), the lower binding energy observed for montmorillonite can be attributed to europium interaction with both "aluminol" and "silanol" edge sites. This interpretation fits quite well with the fluorescence results.

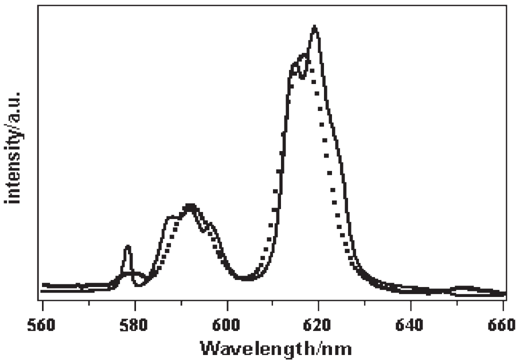

Fig. 6 Fluorescence spectra of Eu(III) sorbed onto (solid line) alumina with $I = 0.1$ M, [Eu(III)] = 0.15 mM, pH = 6.1 and onto (dotted line) silica with $I = 0.1$ M, [Eu(III)] = 1 mM, pH = 7.3.

Table 1 Spectroscopic characteristics of Eu(III) species sorbed on Na-montmontrillonite, alumina and silica

System	pH	Lifetime/µs	Eu $3d_{5/2}$ BE^a/eV
Eu(III)/montmorillonite	$3 < pH < 4.5$	75	1137.0
	$pH > 6$	75, 135, 250	1137.0, 1134.4
Eu(III)/alumina	$4 < pH < 7$	250	1134.5
Eu(III)/silica	$6 < pH < 7.5$	130, 350	1134.3, 1135.9

[a] Binding energies at ±0.2 eV.

The optical and XPS data thus permit the identification of three distinct reactive sorption sites for Eu(III) sorbed on montmorillonite.

Summary

Both macroscopic and microscopic investigations were performed in order to study the sorption mechanisms of trivalent europium retention onto Na-montmorillonite. Laser-induced fluorescence spectroscopy and X-ray photoelectron spectroscopy performed on europium ion loaded montmorillonite and europium sorbed onto alumina and silica has allowed us to characterize the structure of the europium surface complexes and has thus led to an experimental definition of the associated sorption equilibria. The europium ions interact with three different clay sites: exchange sites, "aluminol" and "silanol" edge sites. Below pH 4, only the interlayer site is active towards europium and the metal is sorbed as an outer-sphere complex, whereas, above pH 6, the three sites interact with the europium species. Thus, spectroscopic techniques are very powerful tools to investigate the retention processes since they allow an experimental definition of the sorbed species. Nevertheless, since weak signals are often obtained when surface processes are investigated, the coupling of several techniques is a fundamental point to reach an unambiguous characterization of these systems.

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