Effects of the presence of Fe(0) on the sorption of lanthanum and lutetium mixtures in smectites

Evgeny Galunin[a], María D. Alba[b,*], Maria J. Santos[c], Miquel Vidal[a]

[a] *Departament de Química Analítica, Universitat de Barcelona, Martí i Franqués 1-11, 08028 Barcelona, Spain.*

[b] *Instituto de Ciencia de Materiales de Sevilla, Consejo Superior de Investigaciones Científicas - Universidad de Sevilla, Av. Américo Vespucio 49, 41092 Sevilla, Spain.*

[c] *Departamento de Química, Universidade Estadual de Londrina, Londrina, PR, 86051-990, Brazil.*

Correspondence author: Tel.: (+34) 954489546; Fax: (+34) 954460665; email: alba@icmse.csic.es

ABSTRACT

The sorption of La and Lu mixtures was examined in two bentonites after incubation for three months at 20 and 80°C with Fe(0), as a laboratory approach to evaluate the effects of waste canister corrosion in a deep repository on the performance of clay engineered barriers. The sorption/desorption parameters were determined from batch tests in two ionic media: deionized water and, to consider the additional effect of cement leachates, 0.02 mol L^{-1} Ca.

Results from XRD analyses showed the formation of crystalline FeO(OH), goethite, in a few samples and the degradation of the bentonites due to Fe(0) oxidation during incubation. Moreover, the EDX spectra showed that the lanthanides were sorbed primarily at smectite sites, although sorption onto goethite was also observed, whereas Fe(0) particles did not contribute to lanthanide sorption. The formation of goethite could explain the high K_d values measured in a few scenarios (e.g., those with single solutions or mixtures with the lowest initial concentration of the competitive lanthanide in which high affinity sites governed sorption), with up to 3-fold increases over the values obtained without Fe incubation. However, at higher lanthanide concentration, K_d values decreased or remained constant compared to the samples without Fe incubation, which could be explained by bentonite degradation. In the Ca medium, as much as 5 times lower K_d values were obtained, because of the competitive effect of the Ca ions, especially for Lu in the MX80 bentonite. This indicated that the small number of high affinity sites had been diminished.

The sorption data were satisfactorily fitted to a two-solute Langmuir model. In addition, K_d values correlated well with desorption data, which showed that the larger the decrease in K_d, the larger the increase in sorption reversibility. It is suggested that corrosion products from the metal canister might compromise the long-term radionuclide retention of the clay-engineered barriers.

1. Introduction

A deep geological repository (DGR), designed for the long-term management of radioactive waste, is a multi-barrier system consisting of engineered and backfill barriers surrounded by an additional geosphere barrier (McCombie et al., 2000; Astudillo, 2001; Chapman, 2006). Engineered barriers are commonly constructed with bentonite due to its low hydraulic conductivity and diffusivity and its high cation sorption capacity and buffering properties (Meunier et al., 1998; Landais, 2006; Pusch, 2006). In addition, bentonite retards the diffusion of radionuclides through sorption processes, and it is able to react with the radioactive leachate (Coppin et al., 2002; Bradbury and Baeyens, 2005). However, the effectiveness of these clay-engineered barriers, which are located between the metal container storing the spent nuclear fuel and the external concrete barriers, may be compromised by the buildup of degradation products, such as iron resulting from the corrosion of the metal canister or alkaline calcium-enriched leachates from the concrete barriers (Metcalfe and Walker, 2004; Kumpulainen et al., 2010).

Smectites, the main constituents of bentonite, react chemically with iron, which alters their properties (Lantenois et al., 2005; Wilson et al., 2006a, 2006b; Perronet et al., 2007; Anastácio et al., 2008; Bennett and Gens, 2008). Under the conditions expected in the repository, alteration of smectite would most likely increase hydraulic conductivity and porosity/permeability and decrease its swelling pressures and cation exchange capacity (CEC) (Bildstein et al., 2006; Carlson et al., 2007; Gaudin et al., 2009; Savage et al., 2010). The mineralogical changes leading to the destabilization of the smectite structure as a result of the formation of corrosion products such as magnetite, hematite, goethite and serpentine-like minerals have also been investigated (Smart et al., 2002; Lantenois et al., 2005; Bildestein et al., 2006; Carlson et al., 2007; Gaudin et al., 2009). However, corrosion products from metal canister degradation may also contribute to the retardation of radionuclide transport upon release from the waste canister (Viani et al., 1997).

Because there is still a lack of data concerning the direct effects of the presence of Fe on radionuclide sorption in smectites, here we study the effect of Fe(0) on the sorption/desorption pattern of a lanthanide mixture in two smectites that have previously been used in investigations dealing with clay-engineered barriers, the MX80 and FEBEX bentonites. Lanthanum and lutetium, were used as trivalent actinide analogues due to their chemical similarity (Chapman and Smellie, 1986; Buil et al., 2007). Sorption experiments were carried out after incubation of the bentonites for 90 days at two temperatures, 20 and 80^{o}C (the latter simulating DGR conditions), in the presence of Fe(0) (Lantenois, 2003; Perronet et a., 2007). Sorption experiments were conducted in pure water and in a Ca-enriched aqueous solution, to simulate the role of cement leachates in lanthanide sorption. Sorption data were fitted with a two-solute Langmuir equation to facilitate the comparison of the scenarios examined. Last, sorption reversibility was estimated from desorption tests and was compared with the sorption pattern.

2. Materials and Methods

2.1. Smectite samples

The FEBEX and MX80 bentonites which were used in this study have been extensively investigated in the recent past in many countries (Triphaty et al., 2004). The main initial characteristics of the clays (Fernandez et al., 2004; Montes-H et al., 2007) are summarized in Table 1. MX80 bentonite contains more monovalent cations than bivalent cations, whereas the opposite is valid for FEBEX bentonite. The layer charge of the smectite present is 0.76 e/uc and 1.19e/uc respectively for the MX80 and FEBEX bentonite respectively, yielding a higher cation exchange capacity for the FEBEX bentonite.

In all the samples, the < 2 μm fraction was separated by sedimentation and carbonates and organic matter were eliminated to ensure purity.

2.2. Sample pretreatment

Before the sorption experiments, sets of 0.2 g of the bentonite samples were incubated in sealed tubes with 0.07 g of metallic iron powder (99.98%, Merck) for 90 days at either 20 or 80^{o}C in the presence of 5 mL of the aqueous phase in which the subsequent sorption would take place (deionized water or Ca solution). The pH during the incubation period was neutral or slightly basic, accordingly to the smectite initial pH (see Table 1). Oxygen was displaced by N_2 both in the solutions and in the resulting suspensions in the beginning of the incubation period. The temperatures and clay/Fe mass ratios used were assumed to simulate conditions in a DGR (Lantenois, 2003; Perronet et al., 2007).

2.3. Sorption/desorption experiments

Batch sorption tests were carried out in 50 mL centrifuge tubes by adding 30 mL solution containing mixtures of lanthanides with various ratios in two different ionic media to the previously incubated bentonites. The ionic media were either deionized water (Milli-Q Reagent Water System from Millipore, resistivity of >18 MΩ cm^{-1}) or 0.02 mol L^{-1} $Ca(NO_3)_2$ aqueous solution (Prolabo, RP Normapur, analytical grade) at an initial pH of 7, and the concentrations of the theoretical initial La and Lu concentrations used in the solutions are shown in Table 2. The lanthanide solutions were prepared from $La(NO_3)_3$ and $Lu(NO_3)_3$ (99.9%, Aldrich). The experimental design provided sorption isotherms of the primary lanthanide with a fixed concentration of the competitive lanthanide. The suspensions were shaken end-over-end at 30 rpm at room temperature for 24 h and subsequently were centrifuged at 10,000 rpm for 25 min (Hettich Universal 30 F with an E1174 rotor) and filtered (Whatman 41, 0.22 μm). The supernatants were collected in polyethylene bottles, diluted with 1% HNO_3 and stored at 4ºC for analysis.

Batch desorption tests were performed the day after the sorption tests by bringing the clay residues from the sorption tests into contact with the two ionic media mentioned above, but without the lanthanides. The other experimental conditions were identical to those described for the sorption tests.

2.4. Structural characterization methods

2.4.1. X-Ray Diffraction (XRD).

Powder X-ray diffraction data were collected with a Bruker D8 Advance diffractometer with CuKα1 radiation (λ=1.5405 Å) and a Ni filter. The diffractograms were obtained from 3º to 70º 2θ with a step of 0.05º and a counting time of 3 s. Before carrying out the measurements, the zero of the instrument was calibrated following equipment recommendations. Peak positions were controlled with Rietveld fitting using corundum as reference sample. The crystalline phases were identified using the computer program X´Pert HighScore (Philips Analytical B.V. Almelo, The Netherlands).

2.4.2. Scanning electron microscopy (SEM) and energy dispersion X-ray (EDX) analyses.

The morphology of the samples was analyzed by SEM (JEOL, Model JSM 5400) at 20 kV. An EDX system (Oxford Link ISIS) was fitted to the SEM equipment to perform chemical analyses of the samples using a Si/Li detector with a Be window.

2.5. Determination of La and Lu in the solutions derived from sorption/desorption experiments

Lanthanide concentrations in the initial solutions and in the supernatants obtained after the sorption/desorption experiments were analyzed by Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) (Perkin-Elmer Optima-3200RL). The wavelengths (nm) used in the ICP-OES measurements were 384.902 (La), 261.542 (Lu), 259.939 (Fe) and 317.933 (Ca).

Concentration ranges of the standards were 0.05–100 mg L^{-1} for La and 0.01–100 mg L^{-1} for Lu. The detection limits for the ICP-OES are 50 µg L^{-1} for La, 10 µg L^{-1} for Lu and Fe and 200 µg L^{-1} for Ca.

2.6. Calculation of sorption/desorption parameters

Following ICP-OES measurements, the initial lanthanide concentration (C_{init}, meq L^{-1}), the equilibrium concentration in the supernatant after sorption experiments (C_{eq}, meq L^{-1}) and the equilibrium concentration in the supernatant after desorption experiments ($C_{eq,des}$, meq L^{-1}) were determined. Based on these data, the following parameters were calculated.

a) The sorption distribution coefficient (K_d, L kg^{-1}) (equation 1):

$$K_d = \frac{(C_{init} - C_{eq})V}{C_{eq}\, m} \tag{1}$$

where V is the liquid phase volume in L and m is the clay sample weight in kg.

b) The desorption distribution coefficient ($K_{d,des}$, L kg^{-1}) (equation 2):

$$K_{d,des} = \frac{(C_{init} - C_{eq} - C_{eq,des})V}{C_{eq,des}\, m} \tag{2}$$

c) The desorption rate (R_{des}, %) (equation 3):

$$R_{des} = \frac{C_{eq,des}}{C_{init} - C_{eq}}\, 100 \tag{3}$$

2.7. Use of the two-solute Langmuir equation to fit sorption data

The Langmuir model was chosen to fit the sorption data. This model assumes that sorption takes place at specific homogeneous sites, that the sorbent forms a monolayer, that interactions between sorbed species do not take place, and that the sorption energy is constant over the entire surface (Do, 1998). An extended form of the Langmuir model, shown in equation (4), was used to analyze the two-solute sorption (Srivastava et al., 2006; Sanghwa et al., 2009). This equation predicts the concentration of solute i sorbed ($C_{sorb,i}$) in the presence of sorption-competitive solutes.

$$C_{sorb,i} = \frac{b_i \; K_i \; C_{eq,i}}{1 + \sum_{j=1}^{N} K_j \; C_{eq,j}} \qquad (4)$$

In equation (4), $C_{eq,i}$ is the equilibrium concentration of solute i in a mixture of N solutes, and b_i and K_i are empirical sorption parameters obtained from the fitting of the isotherms. The former represents the maximum sorption capacity determined by the reactive surface sites in an ideal monolayer system, and the latter represents the bonding energy associated with a pH-dependent equilibrium constant. In addition, we plotted the sorption data in three-dimensional space, because the three-dimensional fitting added information to that of the two-dimensional fitting (Yan et al., 2010).

2.8. Data handling

The sorption/desorption tests were performed in 3-6 replicates, which allowed the calculation of the mean and standard deviations of the derived parameters. The sorption data fittings were made using *sftool* (an interactive environment for fitting curves to n-dimensional data), which is included in the mathematical software Matlab 7.10.0 (Mathworks, 2010). The fitting coefficients were taken for positive values with confidence limits ≥ 95% using non-linear least squares fitting with the Trust-region or Levenberg-Marquardt algorithm option. In all fittings, the fit values (R^2) were close to 1 with low residual mean square error (RMSE).

3. Results and Discussion

3.1. Structural analyses of samples resulting from sorption experiments

The XRD patterns of the FEBEX and MX-80 samples are shown in Figs. 1 and 2. Two sets of reflections could be distinguished in the Fe-treated bentonites, one because of the iron phases and one a result of the modified bentonites. Crystalline Fe is the most abundant iron phases phase in all samples (F in the XRD patterns). Small amounts of goethite were also observed (Bildstein, 2006; Carlson, 2007). It is considered that amorphous Fe oxyhydroxides may also be present and may contribute to the observed increase of background.

Swelling of the bentonite layers was observed in the two bentonites. Specifically, the 001 space increased from 14.7 Å to 15.5 Å in FEBEX and from 12.0 Å to 15.4 Å in MX-80, suggesting sorption of hydrated M^{3+} cations in the interlayer space (Alba et al., 2001). The 060 reflection of Fe-treated FEBEX shifted to higher 2θ values, which indicated lower b-spacing due to the creation of a vacant site in the octahedral sheet and the subsequent leaching of the octahedral cations (Grim, 1968). Additionally, high background was observed in both bentonites due to amorphous phases and clay collapse (d_{001} ca. 9 Å marked with an asterisk in the XRD patterns) or due to fluorescence from Fe, which was evident when Cu radiation was used. Lantenois et al. (2005) had already assessed the destabilization of trioctahedral smectites at pH higher than 7 in contact with metallic Fe at representative temperatures of nuclear waste disposal (i.e., 80°C). Similarly, dioctahedral smectites were destabilized under such conditions and exhibited lower swelling pressures and reduced CEC (Carlson et al., 2007; Sanders et al., 2010). The bentonites tested here were mainly constituted by dioctahedral smectites, which have already been observed as being less stable than the trioctahedral members (Alba et al., 2001; Alba et al., 2010).

The SEM micrograph of FEBEX after Fe pretreatment is shown in Fig. 3a. Both lamellar and spherical particles were observed, which are characteristic of smectites and metallic iron, respectively (SEM micrograph of the initial metallic iron powder not shown). The presence of spherical iron particles was confirmed by X-ray mapping (Fig. 3b). Finally, the La and Lu EDX mapping (Figs. 3c and 3d) displayed a homogeneous distribution of La and Lu. Similar behavior was observed for the rest of the scenarios examined.

The EDX spectra of the lamellar FEBEX and MX80 bentonite particles from samples which were not submitted to Fe incubation (Figs. 4a and 6a) are typical of smectites. New lines were observed in Figs. 4b-e and 6b-e, and they were due to the Lα and Lβ lines of La and Lu with relative intensities consistent with their initial concentrations, which confirmed their sorption at smectite sites. Finally, Figs. 4d-e and 6d-e showed a high intensity of the Ca-line that indicated a competitive sorption of Ca when it was present in the sorption medium. The EDX spectra of the spherical particles (Figs. 5 and 7) generally showed signals corresponding to the Fe Kα and Kβ, which did not indicate significant sorption of La and/or Lu in those particles. However in goethite bearing samples (Bildstein, 2006; Carlson, 2007) (i.e., FEBEX incubated at 80ºC with La/Lu ratio 0.09/3.0 in the Ca medium, or MX80 incubated at 80ºC with La/Lu ratio 0.09/3.0 in water medium), the EDX spectra (Figs. 5c and 7a, respectively) displayed spectral lines of La and Lu, thus demonstrating that lanthanides were also sorbed at the new Fe phases formed by Fe oxidation. This was consistent with reported data that showed that the amorphous species of oxidized iron were able to sorb lanthanides onto their surface, and that the equilibrium constant for sorption depended on the nature of the lanthanide (Quinn et al 2006).

3.2. Examination of lanthanide sorption data

The sorption data for La and Lu in the two media for FEBEX and MX80 bentonites, including the lanthanide initial (C_{init} (La), C_{init} (Lu)) and sorbed concentrations (C_{sorb} (La), C_{sorb} (Lu)) and the resulting pH in the supernatants following sorption are summarized in Tables 3 and 4. The Fe concentration in the equilibrium solution following sorption experiments varied within a range of 0.01 – 0.16 meq L^{-1} for samples incubated at 20°C. For samples incubated at 80°C, Fe concentrations were generally similar, although the Fe concentration in the water medium occasionally exceeded 1 meq L^{-1}.

Lanthanide sorption was systematically higher in the FEBEX than in the MX80 bentonite in the water medium, especially at the low-medium concentration range, whereas this effect was not statistically significant in the Ca medium. Since the smectites in the two bentonites are dioctahedral, other factors such as the smectite CEC, the sorption pH and the type of isomorphic substitutions may be considered to affect lanthanide sorption. Previous studies that examined lanthanide sorption in set of six smectites showed that, for smectites with similar structure, the type of isomorphic substitutions and, especially, sorption pH controlled the sequence of lanthanide sorption (higher sorption at higher pH values), as these two latter factors affect the availability of sorption specific sites in the smectites (Galunin et al., 2010). In contrast the CEC affected basically the ionic exchange process, which is the driving force mechanism in the medium-large concentration range in the water medium and in the whole range of lanthanide concentrations in the Ca medium (Galunin et al., 2010). As the CEC values were sufficiently large, differences in sorption were not observed here between smectites in the latter experimental setup. Regarding the role of pH, in the Ca medium, since the initial pH was 7 to ensure that there were not solubility problems in the lanthanide higher-concentration range, the final pH after the sorption experiments was similar for both bentonites, within a narrow range of 6.1-6.4. In the case of the water medium, the pH of the sorption experiments with the FEBEX bentonite was 6.2-7.5, depending of the final equilibrium lanthanide concentration, whereas the pH with the MX80 bentonite experiments was lower (4.7-6.9).

In experiments with the water medium, there was a general decrease in the K_d values of a given lanthanide with increasing initial concentrations in the range tested (from around 0.1 to 9 meq L^{-1}) at a constant concentration of the competitive lanthanide. The decrease observed was sometimes greater by two orders of magnitude, as was the case with La in the FEBEX smectite after incubation at 80°C. This finding was similar to what was previously observed in these bentonites without Fe pretreatment (Galunin et al., 2010, 2011). Changes in K_d due to the variation of the initial lanthanide concentration were higher than previously reported as a result of changes in the two clays tested and because of the incubation temperature. In addition, effects from the presence of a competitive solute were also observed. At a constant concentration of a primary lanthanide, the increase in concentration of the competitive lanthanide decreased the K_d of the primary lanthanide by as much as two orders of magnitude. Again, this effect was stronger for La than for Lu, especially in the FEBEX bentonite, suggesting a higher competitive effect of Lu over La as was observed in previous reported experiments (Galunin et al., 2011).

The composition of the medium influenced K_d. Specifically, the K_d values in the Ca medium were systematically lower compared to the water medium and also exhibited very little variance, regardless of the initial concentration of lanthanide or clay. The decrease in K_d values from the water to the Ca medium were nearly two orders of magnitude, especially in the FEBEX bentonite when La was the target solute. The results corroborated previous data reported for the sorption of mixtures of La and Lu in the absence of Fe (Galunin et al., 2011). The effect of Ca on the quantification of K_d was explained in terms of the potential competitive influence of the Ca ions, which were sorbed at the interlayer space and displaced the lanthanides to less specific sites because the sorbed concentration of Ca was much higher than that of the two lanthanides (Galunin et al., 2011).

As discussed above, the main sorption patterns observed in samples subjected to incubation with Fe were similar to those already observed with smectites without Fe pretreatment. This suggests that the main sorption mechanisms were similar, although the presence of Fe might quantitatively affect the lanthanide sorption. On the one hand, the formation of oxidized iron species, such as goethite, which has high sorption affinity (Dong et al., 2001; Quinn et al., 2006), could contribute to a measurable increase in the K_d of the lanthanides. On the other hand, the likely loss of efficacy in the bentonite performance due to the destabilization induced by Fe treatment, as deduced from the structural analyses, could lead to a decrease in sorption sites with a high affinity for lanthanides and thus to a decrease in K_d in certain scenarios. Therefore, the ratios of the K_d values of the two lanthanides measured in the samples subjected to Fe treatment at both temperatures versus the values determined under the same conditions but without Fe pretreatment, were calculated to allow analysis of the effects of Fe incubation. The data used to calculate the ratios were taken from previously reported experiments (Galunin et al., 2011). The K_d (La) for the FEBEX bentonite samples incubated with Fe at 20^{o}C in the water medium were higher than for samples that had not been incubated with Fe in all the experiments with single La solutions and in those within the low concentration range when Lu was also present. This indicates that further increase in K_d was observed for the cases already having the highest K_d values. For the remaining experimental setups K_d (La) decreased when the concentration of the competitive element increased or was similar to K_d in the absence of Fe pretreatment. For Lu, although K_d (Lu) did not increase after the Fe treatment, a similar decrease in K_d (Lu) was observed when the La concentration increased. In all cases, the K_d values did not change after Fe treatment if the K_d of the lanthanides was already low. These results indicate that when the number of high-affinity sorption sites was high enough to specifically sorb the lanthanide present in the system (as was the case for experiments with single lanthanide solutions or with low concentrations of either the primary or secondary lanthanide), the Fe treatment led to an increase in K_d (Ln) due to the formation of Fe oxides able to specifically sorb lanthanides. This potentially beneficial effect was discovered by Viany et al., (1997) who suggested that the new Fe oxide phase could be an additional sorptive phase for radionuclides. In our study, the formation of Fe oxides was minimal and the appearance of new crystalline Fe oxide phases was observed in only a few samples, most likely because of the short incubation time, although new amorphous phases were observed in all samples. Therefore, because the formation of Fe oxides was low in our experiments, these sites became rapidly saturated when the lanthanide concentration increased, and sorption was then limited by the smectite sites. As Fe pretreatment caused smectite degradation when the lanthanide concentration increased, K_d decreased following the saturation of specific sites, which were fewer than in the untreated bentonites. In cases that were already governed by low affinity sites (e.g., at high initial concentrations), Fe treatment did not affect lanthanide sorption.

These findings were also observed for the FEBEX samples treated at 80°C and in the MX80 bentonite at both temperatures. Notably, in the MX80 bentonite, the K_d ratios for Lu showed a higher increase in K_d (Lu) at the lowest initial concentration range than that observed for the FEBEX samples. In cases where sorption was completely or partially governed by the specific sites in the bentonites, the K_d of the lanthanides tended to decrease after Fe pretreatment. However, in those cases in which sorption was primarily controlled by low affinity sites, the K_d remained relatively constant. Finally, the same trend was observed in the Ca medium. As Ca already acted as a strong competitive solute for sorption, K_d values were low regardless of the Fe treatment. However, there were significant K_d decrease that was not related to the lanthanide concentration. Thus, it was suggested that in the Ca medium, because of the strong competitive effect of Ca and the partial elimination of high affinity sites in the smectites, the low affinity sites were the only ones responsible for lanthanide sorption, thus leading to a further general decrease in K_d.

3.3. Use of a modified, two-solute Langmuir equation for the fitting of the sorption data

A three-dimensional, two-solute Langmuir equation was applied to fit the sorption data. An example of the 3-D Langmuir fitting was shown in Fig. 8, and the fitting parameters are summarized in Table 5.

The values of the b parameter were similar to or slightly higher for Lu than for La in both the water and Ca media, except in the case of the MX80 bentonite pretreated at 80°C in water medium. The temperature of the Fe treatment did not have measurable effect on the b values. Thus, the b values were consistent with the C_{sorb} values included in Tables 3 and 4 for the two lanthanides. The b values were always lower than the CEC values of the bentonites, except in the case of MX80 bentonite pretreated at 80°C in the Ca medium. In this last case, the sorption isotherms in the Ca medium did not indicate a maximum sorption capacity of the clays, thus they did not follow the Langmuir sorption isotherm and the estimated b values were anomaly high and they exceeded the CEC values of the bentonite.

The K parameters were much higher in the water than in the Ca medium, which was consistent with higher K_d values found in the water medium. At both temperatures, K_l(Lu) was higher than K_l(Lu) in the FEBEX bentonite in the water medium, whereas the opposite was observed in the MX80 bentonite. This result was fully consistent with the K_d values measured because K_d (La) was higher than K_d (Lu) in the FEBEX, but the opposite was true in the MX80 bentonite.

Assuming that a main objective of the Langmuir fitting is to allow comparisons with similar systems, the obtained b and K_l parameters were compared to those obtained from the sorption fitting of samples not subjected to Fe pretreatment (Galunin et al., 2011). Ratios could not be calculated because the b and K_i of the untreated samples originated from a more complete dataset, but the b values obtained here were generally similar or lower than those obtained with the untreated samples, thus indicating that the-Fe incubation seemed to provoke a decrease in the sorption capacity of the Fe-incubated bentonites. In addition, although changes in the K_l values obtained in the Ca medium were hardly noticeable, the K_l (La) values obtained in the water medium in the FEBEX bentonite were higher than in the untreated samples. This can be explained by the influence of the K_l(La) in those cases where an increase in K_d (La) was measured (with K_d ratios higher than 2) because they corresponded to experiments with the highest K_d (La). Instead, the K_l (Lu) in the FEBEX samples decreased in the Fe-treated samples, consistent with the K_d (La) values. Regarding the MX80 samples, the K_l values for La decreased. However, the K_l values for Lu increased; in accordance with the higher K_d ratios measured for Lu in the Fe-treated MX80 samples.

3.4. Lanthanide sorption reversibility

The desorption K_d values ($K_{d,des}$) and the desorption rates (R_{des}) for both lanthanides in the Fe-treated bentonites are listed in Tables 6 and 7. As the two parameters are closely correlated ($\log R_{des} = 2.99 - 0.74 \times \log K_{d,des}$, $R^2 = 0.81$ for La; $\log R_{des} = 2.92 - 0.74 \times \log K_{d,des}$, $R^2 = 0.74$ for Lu), both parameters are equally valid to describe sorption reversibility. In the Fe-treated FEBEX samples in the water medium, the R_{des} values for both lanthanides were lower than 4% even at the highest initial concentrations, thus indicating that the sorption was virtually irreversible. In the MX80 samples, desorption rates were higher, with a few values between 5 and 10% or higher. This result indicates that lower K_d values are related to a higher sorption reversibility, thus confirming that these were the scenarios with the lowest lanthanide retention by the smectite. Examination of the values obtained in the Ca medium for the two bentonites confirmed this trend because the desorption rates were higher than in the water medium, by more than 30% in the Fe-treated MX80 samples. Therefore, the lanthanide sorption in the Ca medium was not only lower but also more reversible than in the water medium, as was also previously found for untreated samples (Galunin et al., 2010). The results were consistent with previous reports that predicted significant sorption reversibility due to the sorption of trivalent lanthanide cations at low affinity sites, in which the sorption mechanisms are based on outer sphere processes such as ion-interlayer exchange (Bonnot-Courtois and Jaffrezic-Renault, 1982; Coppin et al., 2003).

To confirm that the variations in R_{des}, and thus in $K_{d,des}$, were due to the same mechanisms affecting sorption, the correlation between the $K_{d,des}$ and K_d was examined. In general, the two parameters were correlated ($K_{d,des\ La} = 1.36 \times K_{d,La} + 510$, $R^2 = 0.96$; $K_{d,des\ Lu} = 1.10 \times K_{d,Lu} + 970$, $R^2 = 0.90$). The close correlation between the two variables suggested that $K_{d,des}$, and thus sorption reversibility, could accurately be predicted from the sorption data.

4. Conclusions

Although the FEBEX and MX80 bentonites were incubated in the presence of Fe(0) for a relatively short period, structural and sorption data indicated that changes in the solid phase occurred. The formation of either amorphous or crystalline iron oxyhydroxides (goethite), could increase K_d in Fe-treated samples in the low lanthanide concentration scenarios, due to the increase in high affinity sites in the resulting samples. In the presence of goethite lanthanides not only sorbed on smectite sites, but also at the Fe oxide phases. For scenarios with higher lanthanide concentration, the positive effect on the increase in the lanthanide sorption was overcome by the smectite degradation induced by the presence of Fe. This pattern was generally more significant in the Ca than in the water medium.

Although corrosion of metal canisters and the presence of alkaline Ca-enriched fluids from the leachates of the surrounding concrete barriers would lead to potential degradation of the clay-engineered barrier in a DGR, whose performance could be at risk because a decrease in their retention capacity could be expected. However, in situ formation of Fe oxyhydroxides with a high-sorption capacity should also be assessed for a better prediction of the changes in the retention capacity of the barrier.

Acknowledgements

This research was supported by grants from the Ministry of Education and Science of Spain (projects CTM2008-01147/TECNO and CTM2011-27211), Generalitat de Catalunya (AGAUR 2009SGR1188), DGICYT and FEDER funds (project CTQ2010-14874) and from EC funded project within the 6th Framework Programme as the HRM Activity under the Contract MRTN-CT-2006-035957. Additionally, the authors would like to thank Dr. A. Padró for his technical help and assistance in the ICP-OES analyses. XRD measurements were carried out at the CITIUS X-Ray laboratory (Universidad de Sevilla), and SEM/EXD analyses were carried out at the Instituto Ciencia de los Materiales de Sevilla (CICIC).

References

Alba, M.D., Becerro, A.I., Castro, M.A., Perdigón, A.C., 2001. Hydrothermal reactivity of Lu-saturated smectites: Part I. A long-range order study. Am. Mineral. 86, 115-123.

Alba, M.D., Castro, M.A., Chain, P., Orta, M.M., Pazos, M.C., Pavon, E, 2010. Hydrothermal stability of layered silicates in neutral and acidic media: effect on engineered-barrier safety. Clay Clay Mineral. 58, 501-514

Anastácio, A.S., Aouad, A., Sellin, P., Domingos Fabris, J., Bergaya, F., Stucki, J.W., 2008. Characterization of a redox-modified clay mineral with respect to its suitability as a barrier in radioactive waste confinement. Appl. Clay Sci. 39, 172-179.

Astudillo, J., 2001. El almacenamiento geológico profundo de los residuos radiactivos de alta actividad. Principios básicos y tecnología. ENRESA, Madrid.

Bennett, D.G., Gens, R., 2008. Overview of European concepts for high-level waste and spent fuel disposal with special reference waste container corrosion. J. Nucl. Mater. 379, 1-8.

Bildstein, O., Trotignon, L., Perronnet, M., Jullien, M., 2006. Modelling iron-clay interactions in deep geological disposal conditions. Phys. Chem. Earth 31, 618-625.

Bonnot-Courtois, C., Jaffrezic-Renault, N., 1982. Étude des echanges entre terres rares et cations interfoliares de deux argiles. Clay Miner. 17, 409-420.

Bradbury, M., Baeyens, B., 2005. Modelling the sorption of Mn(II), Co(II), Ni(II), Cd(II), Eu(III), Am(III), Sn(IV), Th(IV), Np(V) and U(VI) on montmorillonites: Linear free energy relationships and estimates of surface binding constants for some selected heavy metals and actinides. Geochim. Cosmochim. Acta. 69, 875-892.

Buil, B., Gomez, P., Garralon, A., Turrero, M.J., 2007. Rare-earth elements: a tool for understanding the behavior of trivalent actinides in the geosphere. Mater. Res. Soc. Symp. Proc. 985, 437-442.

Carlson, L., Karnland, O., Oversby, V.M., Rance, A.P., Smart, N.R., Snellma, M., Vähänen, M., Werme, L.O., 2007. Experimental studies of the interactions between anaerobically corroding iron and bentonite. Phys. Chem. Earth. 32, 334-345.

Chapman, N., 2006. Geological disposal of radioactive waste – concept, status and trends. J. Iber. Geol. 32, 7-14.

Chapman, N., Smellie, J., 1986. Introduction and summary of the workshop: natural analogues to the conditions around a final repository for high-level radioactive waste. Chem. Geol. 55, 167-173.

Coppin, F., Berger, G., Bauer, A., Castet, S., Loubet, M., 2002. Sorption of lanthanides on smectite and kaolinite. Chem. Geol. 182, 57-68.

Coppin, F., Castet, S., Berger, G., Loubet, M., 2003. Microscopic reversibility of Sm and Yb sorption onto smectite and kaolinite: experimental evidence. Geochim. Cosmochim. Acta. 67, 2515-2527.

Do, D., 1998. In *Adsorption analysis: equilibria and kinetics*, vol. 2. Imperial College Press-ICP, London.

Dong, W., Wang, X., Bian, X., Wang, A., Du, J., Tao, Z., 2001. Comparative study on sorption/desorption of radioeuropium on alumina, bentonite and red earth: effects of pH, ionic strength, fulvic acid, and iron oxides in red earth. Appl. Rad. Isot. 54, 603-610.

Fernandez, A., Baeyens, B., Bradbury, M., Rivas, P., 2004. Analysis of the porewater chemical composition of a Spanish compacted bentonite used in an engineered barrier. Phys. Chem. Earth. 29, 105-118.

Galunin, E., Alba, M.D., Santos, M.J., Abrão, T., Vidal, M., 2010. Lanthanide sorption on smectitic clays in presence of cement leachates. Geochim. Cosmochim. Acta. 74, 862-875.

Galunin, E., Alba, M.D., Santos, M.J., Abrão, T., Vidal, M., 2011. Examination of competitive lanthanide sorption onto smectites and its significance in the management of radioactive waste. J. Hazard. Mater. 186, 1930-1941.

Gaudin, A., Gaboreau, S., Tinseau, E., Bartier, D., Petit, S., Grauby, O., Foct, F., Beaufort, D., 2009. Mineralogical reactions in the Tournemire argillite after in-situ interaction with steels. Appl. Clay Sci. 43, 196-207.

Grim, R.E., 1968. Clay Mineralogy. McGraw-Hill Book Company, New York.

Kumpulainen, S., Carlson, T., Muurinen, A., Svensson, D., Sasamoto, H., Yui, M., Wersin, P., Snellman, M., 2010. Long-term (8-10 y) alteration of bentonite in the presence of metallic iron. Abstracts of the 4rd International Meeting "Clays in Natural and Engineered Barriers for Radioactive waste Confinement", Nantes, France, March 29 – April 1, 97-98.

Landais, P., 2006. Advances in geochemical research for the underground disposal of high-level, long-lived radioactive waste in a clay formation. J. Geochem. Explor. 88, 32-36.

Lantenois, S., 2003. Réactivité fer métal/smectites en milieu hydraté à 80°C. PhD thesis, Université d'Orléans, Orléans, France, 188 pp.

Lantenois, S., Lanson, B., Muller, F., Bauer, A., Jullien, M., Plançon, A., 2005. Experimental study of smectite interaction with metal Fe at low temperature: 1. Smectite destabilization, Clays Clay Miner. 53, 597-612.

McCombie, C., Pentz, D.L., Kurzeme, M., Miller, I., 2000. Deep geological repositories: a safe and secure solution to disposal of nuclear wastes. In *GeoEng2000 – An international conference on geotechnical & geological engineering*, *19-24 November 2000*. Melbourne, Australia. Lancaster, Technomic.

Metcalfe, R., Walker, C., 2004. Proceedings of the international workshop on bentonite-cement interactions in repository environment. NUMO-TR-04-05, Nuclear Waste Management Organization of Japan (NUMO).

Meunier, A., Velde, B., Griffault, L., 1998. The reactivity of bentonites: a review. An application to clay barrier stability for nuclear waste storage. Clays Clay Miner. 33, 187-196.

Montes, H.G., Fritz, B., Clement, A., Michau, N., 2007. Modelling of geochemical reactions and experimental cation exchange in MX-80 bentonite. J. Environ. Manage. 77, 35-46.

Oh, S., Kwak, M.Y., Shin, W.S., 2009. Competitive sorption of lead and cadmium onto sediments. Chem. Eng. J. 152, 376–388.

Perronnet, M., Villiéras, F., Jullien, M., Razafitianamaharavo, A., Raynal, J., Bonnin, D., 2007. Towards a link between the energetic heterogeneities of the edge faces of smectites and their stability in the context of metallic corrosion. Geochim. Cosmochim. Acta 71, 1463-1479.

Pusch, R, 2006. Engineered Barriers. In *Disposal of hazardous waste in underground mines* (eds. V. Popov and R. Pusch). Wessex Institute of Technology, UK, pp. 35-40.

Quinn, K.A., Byrne, R.H., Schijf, J., 2006. Sorption of yttrium and rare earth elements by amorphous ferric hydroxide: Influence of solution complexation with carbonate. Geochim. Cosmochim. Acta 70, 4151-4165.

Sanders, D., Kaufhold, S., Hassel, A.W., Dohrmann, R., 2010. Smectite Alteration by anaerobic iron corrosion. Abstracts of the 4rd International Meeting “Clays in Natural and Engineered Barriers for Radioactive waste Confinement”, Nantes, France, March 29 – April 1, 95-96.

Savage, D., Watson, C., Benbow, S., Wilson, J., 2010. Modelling iron-bentonite interaction. Appl. Clay Sci. 47, 91-98.

Smart, N.R., Blackwood, D.J., Werme, L., 2002. Anaerobic corrosion of carbon steel and cast iron in artificial groundwaters: Part 1 – Gas generation. Corrosion 58, 627-637.

Srivastava, V.C., Mall, I.D., Mishra, I.M., 2006. Equilibrium modelling of single and binary adsorption of cadmium and nickel onto bagasse fly ash. Chem. Eng. J. 117, 79–91.

The Mathworks, Inc. (2010) *User Guide – Matlab 7.10.0 (R2010a).* Apple Hill Drive, Natick, MA 01760-2098, USA.

Tripathy, S., Sriharan, A., Schanz, T., 2004. Swelling pressure of compacted bentonites from diffuse double layer theory. Can. J. Geotech. 41, 437-450.

Viani, B.E., Torretto, P.C., Matzen, S.L., 1997. Radionuclide transport through engineered barrier system altered products. UCRL-ID-129281, LLNL, USA.

Wilson, J., Savage, D., Cuadros, J., Shibata, M., Ragnarsdottir, K.V., 2006a. The effect of iron on montmorillonite stability. (I) Background and thermodynamic considerations. Geochim. Cosmochim. Acta 70, 306-322.

Wilson, J., Cressey, G., Cressey, B., Cuadros, J., Ragnarsdottir, K.V., Savage, D., Shibata, M., 2006b. The effect of iron on montmorillonite stability. (II) Experimental investigation. Geochim. Cosmochim. Acta 70, 323-336.

Yan, Ch., Li, G., Xue, P., Wei, Q., Li, Q., 2010. Competitive effect of Cu(II) and Zn (II) on the biosorption of lead (II) by Myriophyllum spicatum. J. Hazard. Mater. 179, 721-728.