

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

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10

11 **ABSTRACT**

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

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

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

35 **1. Introduction**

36

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

49 Smectites, the main constituents of bentonite, react chemically with iron, which alters their  
50 properties (Lantenois et al., 2005; Wilson et al., 2006a, 2006b; Perronet et al., 2007; Anastácio et  
51 al., 2008; Bennett and Gens, 2008). Under the conditions expected in the repository, alteration of  
52 smectite would most likely increase hydraulic conductivity and porosity/permeability and decrease  
53 its swelling pressures and cation exchange capacity (CEC) (Bildstein et al., 2006; Carlson et al.,  
54 2007; Gaudin et al., 2009; Savage et al., 2010). The mineralogical changes leading to the  
55 destabilization of the smectite structure as a result of the formation of corrosion products such as  
56 magnetite, hematite, goethite and serpentine-like minerals have also been investigated (Smart et al.,  
57 2002; Lantenois et al., 2005; Bildstein et al., 2006; Carlson et al., 2007; Gaudin et al., 2009).  
58 However, corrosion products from metal canister degradation may also contribute to the retardation  
59 of radionuclide transport upon release from the waste canister (Viani et al., 1997).

60 Because there is still a lack of data concerning the direct effects of the presence of Fe on  
61 radionuclide sorption in smectites, here we study the effect of Fe(0) on the sorption/desorption  
62 pattern of a lanthanide mixture in two smectites that have previously been used in investigations  
63 dealing with clay-engineered barriers, the MX80 and FEBEX bentonites. Lanthanum and lutetium,  
64 were used as trivalent actinide analogues due to their chemical similarity (Chapman and Smellie,  
65 1986; Buil et al., 2007). Sorption experiments were carried out after incubation of the bentonites for  
66 90 days at two temperatures, 20 and 80°C (the latter simulating DGR conditions), in the presence of  
67 Fe(0) (Lantenois, 2003; Perronet et al., 2007). Sorption experiments were conducted in pure water  
68 and in a Ca-enriched aqueous solution, to simulate the role of cement leachates in lanthanide  
69 sorption. Sorption data were fitted with a two-solute Langmuir equation to facilitate the comparison  
70 of the scenarios examined. Last, sorption reversibility was estimated from desorption tests and was  
71 compared with the sorption pattern.

72

## 73 **2. Materials and Methods**

74

### 75 *2.1. Smectite samples*

76

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

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

86

87 *2.2. Sample pretreatment*

88

89 Before the sorption experiments, sets of 0.2 g of the bentonite samples were incubated in  
90 sealed tubes with 0.07 g of metallic iron powder (99.98%, Merck) for 90 days at either 20 or 80°C  
91 in the presence of 5 mL of the aqueous phase in which the subsequent sorption would take place  
92 (deionized water or Ca solution). The pH during the incubation period was neutral or slightly basic,  
93 accordingly to the smectite initial pH (see Table 1). Oxygen was displaced by N<sub>2</sub> both in the  
94 solutions and in the resulting suspensions in the beginning of the incubation period. The  
95 temperatures and clay/Fe mass ratios used were assumed to simulate conditions in a DGR  
96 (Lantenois, 2003; Perronet et al., 2007).

97

98 *2.3. Sorption/desorption experiments*

99

100 Batch sorption tests were carried out in 50 mL centrifuge tubes by adding 30 mL solution  
101 containing mixtures of lanthanides with various ratios in two different ionic media to the previously  
102 incubated bentonites. The ionic media were either deionized water (Milli-Q Reagent Water System  
103 from Millipore, resistivity of >18 MΩ cm<sup>-1</sup>) or 0.02 mol L<sup>-1</sup> Ca(NO<sub>3</sub>)<sub>2</sub> aqueous solution (Prolabo,  
104 RP Normapur, analytical grade) at an initial pH of 7, and the concentrations of the theoretical initial  
105 La and Lu concentrations used in the solutions are shown in Table 2. The lanthanide solutions were  
106 prepared from La(NO<sub>3</sub>)<sub>3</sub> and Lu(NO<sub>3</sub>)<sub>3</sub> (99.9%, Aldrich). The experimental design provided  
107 sorption isotherms of the primary lanthanide with a fixed concentration of the competitive  
108 lanthanide. The suspensions were shaken end-over-end at 30 rpm at room temperature for 24 h and  
109 subsequently were centrifuged at 10,000 rpm for 25 min (Hettich Universal 30 F with an E1174  
110 rotor) and filtered (Whatman 41, 0.22 μm). The supernatants were collected in polyethylene bottles,  
111 diluted with 1% HNO<sub>3</sub> and stored at 4°C for analysis.

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

116

## 117 *2.4. Structural characterization methods*

### 118 *2.4.1. X-Ray Diffraction (XRD).*

119 Powder X-ray diffraction data were collected with a Bruker D8 Advance diffractometer with  
120 CuK $\alpha$ 1 radiation ( $\lambda=1.5405 \text{ \AA}$ ) and a Ni filter. The diffractograms were obtained from  $3^\circ$  to  $70^\circ 2\theta$   
121 with a step of  $0.05^\circ$  and a counting time of 3 s. Before carrying out the measurements, the zero of  
122 the instrument was calibrated following equipment recommendations. Peak positions were  
123 controlled with Rietveld fitting using corundum as reference sample. The crystalline phases were  
124 identified using the computer program X'Pert HighScore (Philips Analytical B.V. Almelo, The  
125 Netherlands).

126

### 127 *2.4.2. Scanning electron microscopy (SEM) and energy dispersion X-ray (EDX) analyses.*

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

131

## 132 *2.5. Determination of La and Lu in the solutions derived from sorption/desorption experiments*

133

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

138 Concentration ranges of the standards were 0.05–100 mg L<sup>-1</sup> for La and 0.01–100 mg L<sup>-1</sup> for Lu.  
139 The detection limits for the ICP-OES are 50 µg L<sup>-1</sup> for La, 10 µg L<sup>-1</sup> for Lu and Fe and 200 µg L<sup>-1</sup>  
140 for Ca.

141

## 142 2.6. Calculation of sorption/desorption parameters

143

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

148

149 a) The sorption distribution coefficient ( $K_d$ , L kg<sup>-1</sup>) (equation 1):

$$150 \quad K_d = \frac{(C_{init} - C_{eq})V}{C_{eq} m} \quad (1)$$

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

152

153 b) The desorption distribution coefficient ( $K_{d,des}$ , L kg<sup>-1</sup>) (equation 2):

$$154 \quad K_{d,des} = \frac{(C_{init} - C_{eq} - C_{eq,des})V}{C_{eq,des} m} \quad (2)$$

155

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

$$157 \quad R_{des} = \frac{C_{eq,des}}{C_{init} - C_{eq}} 100 \quad (3)$$

158

## 159 2.7. Use of the two-solute Langmuir equation to fit sorption data

160

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

$$167 \quad C_{sorb,i} = \frac{b_i K_i C_{eq,i}}{1 + \sum_{j=1}^N K_j C_{eq,j}} \quad (4)$$

168 In equation (4),  $C_{eq,i}$  is the equilibrium concentration of solute i in a mixture of N solutes, and  $b_i$  and  
169  $K_i$  are empirical sorption parameters obtained from the fitting of the isotherms. The former  
170 represents the maximum sorption capacity determined by the reactive surface sites in an ideal  
171 monolayer system, and the latter represents the bonding energy associated with a pH-dependent  
172 equilibrium constant. In addition, we plotted the sorption data in three-dimensional space, because  
173 the three-dimensional fitting added information to that of the two-dimensional fitting (Yan et al.,  
174 2010).

175

## 176 2.8. Data handling

177

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

185



186 **3. Results and Discussion**

187  
188 *3.1. Structural analyses of samples resulting from sorption experiments*

189  
190 The XRD patterns of the FEBEX and MX-80 samples are shown in Figs. 1 and 2. Two sets  
191 of reflections could be distinguished in the Fe-treated bentonites, one because of the iron phases and  
192 one a result of the modified bentonites. Crystalline Fe is the most abundant iron phases phase in all  
193 samples ( F in the XRD patterns). Small amounts of goethite were also observed (Bildstein, 2006;  
194 Carlson, 2007). It is considered that amorphous Fe oxyhydroxides may also be present and may  
195 contribute to the observed increase of background.

196 Swelling of the bentonite layers was observed in the two bentonites. Specifically, the 001  
197 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  
198 sorption of hydrated  $M^{3+}$  cations in the interlayer space (Alba et al., 2001). The 060 reflection of  
199 Fe-treated FEBEX shifted to higher  $2\theta$  values, which indicated lower b-spacing due to the creation  
200 of a vacant site in the octahedral sheet and the subsequent leaching of the octahedral cations (Grim,  
201 1968). Additionally, high background was observed in both bentonites due to amorphous phases  
202 and clay collapse ( $d_{001}$  ca. 9 Å marked with an asterisk in the XRD patterns) or due to fluorescence  
203 from Fe, which was evident when Cu radiation was used. Lantenois et al. (2005) had already  
204 assessed the destabilization of trioctahedral smectites at pH higher than 7 in contact with metallic  
205 Fe at representative temperatures of nuclear waste disposal (i.e., 80°C). Similarly, dioctahedral  
206 smectites were destabilized under such conditions and exhibited lower swelling pressures and  
207 reduced CEC (Carlson et al., 2007; Sanders et al., 2010). The bentonites tested here were mainly  
208 constituted by dioctahedral smectites, which have already been observed as being less stable than  
209 the trioctahedral members (Alba et al., 2001; Alba et al., 2010).

210 The SEM micrograph of FEBEX after Fe pretreatment is shown in Fig. 3a. Both lamellar  
211 and spherical particles were observed, which are characteristic of smectites and metallic iron,

212 respectively (SEM micrograph of the initial metallic iron powder not shown). The presence of  
213 spherical iron particles was confirmed by X-ray mapping (Fig. 3b). Finally, the La and Lu EDX  
214 mapping (Figs. 3c and 3d) displayed a homogeneous distribution of La and Lu. Similar behavior  
215 was observed for the rest of the scenarios examined.

216 The EDX spectra of the lamellar FEBEX and MX80 bentonite particles from samples which  
217 were not submitted to Fe incubation (Figs. 4a and 6a) are typical of smectites. New lines were  
218 observed in Figs. 4b-e and 6b-e, and they were due to the  $L\alpha$  and  $L\beta$  lines of La and Lu with  
219 relative intensities consistent with their initial concentrations, which confirmed their sorption at  
220 smectite sites. Finally, Figs. 4d-e and 6d-e showed a high intensity of the Ca-line that indicated a  
221 competitive sorption of Ca when it was present in the sorption medium. The EDX spectra of the  
222 spherical particles (Figs. 5 and 7) generally showed signals corresponding to the Fe  $K\alpha$  and  $K\beta$ ,  
223 which did not indicate significant sorption of La and/or Lu in those particles. However in goethite  
224 bearing samples (Bildstein, 2006; Carlson, 2007) (i.e., FEBEX incubated at 80°C with La/Lu ratio  
225 0.09/3.0 in the Ca medium, or MX80 incubated at 80°C with La/Lu ratio 0.09/3.0 in water medium),  
226 the EDX spectra (Figs. 5c and 7a, respectively) displayed spectral lines of La and Lu, thus  
227 demonstrating that lanthanides were also sorbed at the new Fe phases formed by Fe oxidation. This  
228 was consistent with reported data that showed that the amorphous species of oxidized iron were  
229 able to sorb lanthanides onto their surface, and that the equilibrium constant for sorption depended  
230 on the nature of the lanthanide (Quinn et al 2006).

231

### 232 3.2. Examination of lanthanide sorption data

233

234 The sorption data for La and Lu in the two media for FEBEX and MX80 bentonites,  
235 including the lanthanide initial ( $C_{init}$  (La),  $C_{init}$  (Lu)) and sorbed concentrations ( $C_{sorb}$  (La),  $C_{sorb}$   
236 (Lu)) and the resulting pH in the supernatants following sorption are summarized in Tables 3 and 4.  
237 The Fe concentration in the equilibrium solution following sorption experiments varied within a

238 range of 0.01 – 0.16 meq L<sup>-1</sup> for samples incubated at 20°C. For samples incubated at 80°C, Fe  
239 concentrations were generally similar, although the Fe concentration in the water medium  
240 occasionally exceeded 1 meq L<sup>-1</sup>.

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

259 In experiments with the water medium, there was a general decrease in the  $K_d$  values of a  
260 given lanthanide with increasing initial concentrations in the range tested (from around 0.1 to 9 meq  
261 L<sup>-1</sup>) at a constant concentration of the competitive lanthanide. The decrease observed was  
262 sometimes greater by two orders of magnitude, as was the case with La in the FEBEX smectite after  
263 incubation at 80°C. This finding was similar to what was previously observed in these bentonites

264 without Fe pretreatment (Galunin et al., 2010, 2011). Changes in  $K_d$  due to the variation of the  
265 initial lanthanide concentration were higher than previously reported as a result of changes in the  
266 two clays tested and because of the incubation temperature. In addition, effects from the presence of  
267 a competitive solute were also observed. At a constant concentration of a primary lanthanide, the  
268 increase in concentration of the competitive lanthanide decreased the  $K_d$  of the primary lanthanide  
269 by as much as two orders of magnitude. Again, this effect was stronger for La than for Lu,  
270 especially in the FEBEX bentonite, suggesting a higher competitive effect of Lu over La as was  
271 observed in previous reported experiments (Galunin et al., 2011).

272 The composition of the medium influenced  $K_d$ . Specifically, the  $K_d$  values in the Ca medium  
273 were systematically lower compared to the water medium and also exhibited very little variance,  
274 regardless of the initial concentration of lanthanide or clay. The decrease in  $K_d$  values from the  
275 water to the Ca medium were nearly two orders of magnitude, especially in the FEBEX bentonite  
276 when La was the target solute. The results corroborated previous data reported for the sorption of  
277 mixtures of La and Lu in the absence of Fe (Galunin et al., 2011). The effect of Ca on the  
278 quantification of  $K_d$  was explained in terms of the potential competitive influence of the Ca ions,  
279 which were sorbed at the interlayer space and displaced the lanthanides to less specific sites because  
280 the sorbed concentration of Ca was much higher than that of the two lanthanides (Galunin et al.,  
281 2011).

282 As discussed above, the main sorption patterns observed in samples subjected to incubation  
283 with Fe were similar to those already observed with smectites without Fe pretreatment. This  
284 suggests that the main sorption mechanisms were similar, although the presence of Fe might  
285 quantitatively affect the lanthanide sorption. On the one hand, the formation of oxidized iron  
286 species, such as goethite, which has high sorption affinity (Dong et al., 2001; Quinn et al., 2006),  
287 could contribute to a measurable increase in the  $K_d$  of the lanthanides. On the other hand, the likely  
288 loss of efficacy in the bentonite performance due to the destabilization induced by Fe treatment, as  
289 deduced from the structural analyses, could lead to a decrease in sorption sites with a high affinity

290 for lanthanides and thus to a decrease in  $K_d$  in certain scenarios. Therefore, the ratios of the  $K_d$   
291 values of the two lanthanides measured in the samples subjected to Fe treatment at both  
292 temperatures versus the values determined under the same conditions but without Fe pretreatment,  
293 were calculated to allow analysis of the effects of Fe incubation. The data used to calculate the  
294 ratios were taken from previously reported experiments (Galunin et al., 2011). The  $K_d$  (La) for the  
295 FEBEX bentonite samples incubated with Fe at 20°C in the water medium were higher than for  
296 samples that had not been incubated with Fe in all the experiments with single La solutions and in  
297 those within the low concentration range when Lu was also present. This indicates that further  
298 increase in  $K_d$  was observed for the cases already having the highest  $K_d$  values. For the remaining  
299 experimental setups  $K_d$  (La) decreased when the concentration of the competitive element increased  
300 or was similar to  $K_d$  in the absence of Fe pretreatment. For Lu, although  $K_d$  (Lu) did not increase  
301 after the Fe treatment, a similar decrease in  $K_d$  (Lu) was observed when the La concentration  
302 increased. In all cases, the  $K_d$  values did not change after Fe treatment if the  $K_d$  of the lanthanides  
303 was already low. These results indicate that when the number of high-affinity sorption sites was  
304 high enough to specifically sorb the lanthanide present in the system (as was the case for  
305 experiments with single lanthanide solutions or with low concentrations of either the primary or  
306 secondary lanthanide), the Fe treatment led to an increase in  $K_d$  (Ln) due to the formation of Fe  
307 oxides able to specifically sorb lanthanides. This potentially beneficial effect was discovered by  
308 Viany et al., (1997) who suggested that the new Fe oxide phase could be an additional sorptive  
309 phase for radionuclides. In our study, the formation of Fe oxides was minimal and the appearance of  
310 new crystalline Fe oxide phases was observed in only a few samples, most likely because of the  
311 short incubation time, although new amorphous phases were observed in all samples. Therefore,  
312 because the formation of Fe oxides was low in our experiments, these sites became rapidly saturated  
313 when the lanthanide concentration increased, and sorption was then limited by the smectite sites. As  
314 Fe pretreatment caused smectite degradation when the lanthanide concentration increased,  $K_d$   
315 decreased following the saturation of specific sites, which were fewer than in the untreated

316 bentonites. In cases that were already governed by low affinity sites (e.g., at high initial  
317 concentrations), Fe treatment did not affect lanthanide sorption.

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

330

### 331 *3.3. Use of a modified, two-solute Langmuir equation for the fitting of the sorption data*

332

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

336         The values of the b parameter were similar to or slightly higher for Lu than for La in both  
337 the water and Ca media, except in the case of the MX80 bentonite pretreated at 80°C in water  
338 medium. The temperature of the Fe treatment did not have measurable effect on the b values. Thus,  
339 the b values were consistent with the  $C_{sorb}$  values included in Tables 3 and 4 for the two lanthanides.  
340 The b values were always lower than the CEC values of the bentonites, except in the case of MX80  
341 bentonite pretreated at 80°C in the Ca medium. In this last case, the sorption isotherms in the Ca

342 medium did not indicate a maximum sorption capacity of the clays, thus they did not follow the  
343 Langmuir sorption isotherm and the estimated  $b$  values were anomaly high and they exceeded the  
344 CEC values of the bentonite.

345 The  $K$  parameters were much higher in the water than in the Ca medium, which was  
346 consistent with higher  $K_d$  values found in the water medium. At both temperatures,  $K_1(\text{Lu})$  was  
347 higher than  $K_1(\text{Lu})$  in the FEBEX bentonite in the water medium, whereas the opposite was  
348 observed in the MX80 bentonite. This result was fully consistent with the  $K_d$  values measured  
349 because  $K_d(\text{La})$  was higher than  $K_d(\text{Lu})$  in the FEBEX, but the opposite was true in the MX80  
350 bentonite.

351 Assuming that a main objective of the Langmuir fitting is to allow comparisons with similar  
352 systems, the obtained  $b$  and  $K_1$  parameters were compared to those obtained from the sorption  
353 fitting of samples not subjected to Fe pretreatment (Galunin et al., 2011). Ratios could not be  
354 calculated because the  $b$  and  $K_i$  of the untreated samples originated from a more complete dataset,  
355 but the  $b$  values obtained here were generally similar or lower than those obtained with the  
356 untreated samples, thus indicating that the-Fe incubation seemed to provoke a decrease in the  
357 sorption capacity of the Fe-incubated bentonites. In addition, although changes in the  $K_1$  values  
358 obtained in the Ca medium were hardly noticeable, the  $K_1(\text{La})$  values obtained in the water  
359 medium in the FEBEX bentonite were higher than in the untreated samples. This can be explained  
360 by the influence of the  $K_1(\text{La})$  in those cases where an increase in  $K_d(\text{La})$  was measured (with  $K_d$   
361 ratios higher than 2) because they corresponded to experiments with the highest  $K_d(\text{La})$ . Instead,  
362 the  $K_1(\text{Lu})$  in the FEBEX samples decreased in the Fe-treated samples, consistent with the  $K_d(\text{La})$   
363 values. Regarding the MX80 samples, the  $K_1$  values for La decreased. However, the  $K_1$  values for  
364 Lu increased; in accordance with the higher  $K_d$  ratios measured for Lu in the Fe-treated MX80  
365 samples.

366

367 *3.4. Lanthanide sorption reversibility*

368

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

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

391

#### 392 **4. Conclusions**

393



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

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

409

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419

420

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