1 # Effects of the presence of Fe(0) on the sorption of lanthanum and lutetium

2 ## mixtures in smectites

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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^oC 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^{-1} 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_d 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_d 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_d 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_d values correlated well with desorption data, which showed that the larger the

32   decrease in K_d, 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.

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).

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 a., 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.

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73   **2. Materials and Methods**

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75   *2.1. Smectite samples*

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77   The FEBEX and MX80 bentonites which were used in this study have been extensively

78   investigated in the recent past in many countries (Triphaty 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

2.2. Sample pretreatment

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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_2 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).

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2.3. Sorption/desorption experiments

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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^{-1}) or 0.02 mol L^{-1} Ca(NO$_3$)$_2$ 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$_3$)$_3$ and Lu(NO$_3$)$_3$ (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$_3$ 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.

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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   CuKα1 radiation (λ=1.5405 Å) and a Ni filter. The diffractograms were obtained from 3º to 70º 2θ

121   with a step of 0.05º 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*

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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^{-1} for La and 0.01–100 mg L^{-1} for Lu.

139 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}

140 for Ca.

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142 *2.6. Calculation of sorption/desorption parameters*

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144 Following ICP-OES measurements, the initial lanthanide concentration (C_{init}, meq L^{-1}), the

145 equilibrium concentration in the supernatant after sorption experiments (C_{eq}, meq L^{-1}) and the

146 equilibrium concentration in the supernatant after desorption experiments ($C_{eq,des}$, meq L^{-1}) were

147 determined. Based on these data, the following parameters were calculated.

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

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

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

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

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

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

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

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

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

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).

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176 *2.8. Data handling*

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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).

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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,

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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 Lα and Lβ 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 Kα and Kβ,

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 80ºC with La/Lu ratio

225   0.09/3.0 in the Ca medium, or MX80 incubated at 80ºC 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).

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232   *3.2. Examination of lanthanide sorption data*

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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^{-1} 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^{-1}.

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^{-1}) 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 $20^{o}C$ 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.

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

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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

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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, $K_1(Lu)$ was

347   higher than $K_1(Lu)$ 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 (La) was higher than K_d (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 (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 $K_1(La)$ in those cases where an increase in K_d (La) was measured (with K_d

361   ratios higher than 2) because they corresponded to experiments with the highest K_d (La). Instead,

362   the K_1 (Lu) in the FEBEX samples decreased in the Fe-treated samples, consistent with the K_d (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   ($logR_{des} = 2.99 - 0.74$ x $logK_{d,des}$, $R^2 = 0.81$ for La; $logR_{des} = 2.92 - 0.74$ x $logK_{d,des}$, $R^2 = 0.74$ 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 ($K_{d,des\ La} = 1.36$ x $K_{d,La} + 510$, $R^2 = 0.96$; $K_{d,des\ Lu} = 1.10$ x $K_{d,Lu} + 970$,

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.

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421   **References**

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