

# 1 Uranium immobilization by FEBEX bentonite and steel barriers in 2 hydrothermal conditions

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12

## 13 14 **Abstract**

15 FEBEX clay is considered a reference material in engineered barriers for safe storage of nuclear  
16 waste and uranium is a minor component of high-level radioactive waste (HLRW) and a main  
17 component of the spent nuclear fuel (SNF). Here, the kinetics of reaction of uranium with FEBEX  
18 was investigated in addition to the uranium immobilisation ability and the structural analysis of  
19 the reaction products. Hydrothermal treatments were accomplished with  $\text{UO}_2^{2+}$  and tetravalent  
20 actinide simulator  $\text{ZrO}^{2+}$ , also present in HLRW. The quantification of the reaction was performed  
21 through gamma spectrometry of uranium. Two mechanisms for  $\text{UO}_2^{2+}$  retention by FEBEX were  
22 detected: adsorption and formation of stable and insoluble new phases. The structural analyses  
23 performed using  $\text{ZrO}^{2+}$ , confirmed the uranium adsorption and the presence of new phases,  $\text{ZrO}_2$   
24 and  $\text{Zr}(\text{SiO}_4)$ , that emphasise the existence of a chemical reaction with the bentonite. The analysis  
25 of the velocity of reaction uranium-clay minerals revealed temperature dependence. An

26 exponential fitting suggested that the removal of uranium from solution at temperatures over 200  
27 °C could be completed in less than a year. For lower temperatures, several years are needed.  
28 Milliequivalents of  $\text{UO}_2^{2+}$  immobilised by the clay depended on temperature and time and were  
29 over cation exchange capacity (CEC) of FEBEX even at 100 °C (reaching 600% of CEC). The  
30 reaction with steel, also temperature dependent, was finally analysed. At 200 °C 40% -70% of  
31 uranium reacted with steel. But only 30%-15% reacted at 300°C and 100°C. The reactions provide  
32 a stable immobilisation mechanism for uranium even when its sorption and swelling capacities  
33 fail. Our experiments will be of particular interest for very deep borehole disposals where higher  
34 temperatures and pressures are expected.

35

36 **Key Words:** Bentonite, smectite, disilicates, steel, uranium, radioactive waste.

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## 39 **1. Introduction**

40 In many countries, the development of Deep Geological Repositories (DGR), for the storage  
41 of high-level radioactive waste (HLRW) and spent nuclear fuel (SNF), is based on a multiple  
42 barriers system. Most of the safety of the repositories relies on the engineered barrier which is  
43 mainly constituted by clay minerals [1]. Clay minerals have low permeability, high sorption and  
44 swelling capacity, which makes them ideal materials for natural and engineered barriers for  
45 nuclear waste isolation [2, 3]. Under specific experimental conditions a clay minerals barrier is  
46 able to delay the diffusion and immobilise radionuclides through mechanisms such as adsorption  
47 [4]. At the present time, bentonite is accepted as the most suitable clay mineral for the engineered  
48 barrier in DGRs [5]. Furthermore, very deep borehole disposal (DBD), are now emerging as a  
49 realistic alternative to mined repositories for spent nuclear fuel, reprocessing waste and plutonium  
50 [6]. Many different variants of the basic DBD concept have been proposed and, essentially, these

51 fall into two main categories that can be referred to as ‘high temperature’ (> ~700°C) and ‘low  
52 temperature (250 °C) [7].

53 Regarding the adsorption properties of the clay mineral [8], recent studies highlight the  
54 existence of an additional retention mechanism [9, 10]. The systematic study of the interaction of  
55 the rare earths cations (REE), such as La, Lu, Nd, Sm - as actinides chemical analogues, with  
56 natural and artificial clay minerals - revealed a reaction mechanism, based on the interaction  
57 between the lanthanide cations and the orthosilicate anions of the lamellar structure [11, 12]. At  
58 subcritical conditions (temperature and pressure), an insoluble and chemically stable phase,  
59 REE<sub>2</sub>Si<sub>2</sub>O<sub>7</sub>, is generated [13]. This might provide a stable immobilisation mechanism if the  
60 sorption and swelling capacities of the bentonite fail [14].

61 Initially, the studies focused on the structural analysis of REE<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> after the hydrothermal  
62 reaction between REE cations and clay minerals [9, 12, 14]. More recently, Alba et al., [11]  
63 quantified the Eu<sup>3+</sup> immobilization by a standard saponite and Villa-Alfageme et al. [15] studied  
64 Eu<sup>3+</sup> retention mechanisms by FEBEX and MX-80 bentonites, two of the recommended bentonites  
65 for the construction of barriers. Results proved that two mechanisms were involved in Eu<sup>3+</sup>  
66 retention by the bentonites: adsorption in specific and unspecific sites and a chemical reaction  
67 consisting on the formation of europium disilicates.

68 Uranium is the major component of HLRW and SNF from nuclear power plants, for this  
69 reason it is essential to analyse the role that silicates play in the retention of uranium. The previous  
70 hydrothermal treatment experiments analysed the retention of HLRW using actinides simulators.  
71 Uranium interaction properties should be evaluated, as well as its influence on the retention  
72 capacity of bentonites for the REE and other radionuclides from HLRW and SNF.

73 Previous experiments were not undertaken using uranium, on the contrary REE were the major  
74 components. This work is focused on the analysis of uranium and zirconium retention by FEBEX

75 bentonite and the quantification of the immobilisation mechanisms through hydrothermal  
76 treatments with uranium and zirconium.

77 The HLRW containers are one of the barriers that should be able to protect the repository  
78 systems. As such, container corrosion and the chemical interactions of corrosion products with the  
79 clay buffer are of great interest for the long-term performance of a repository [16, 17]. Several  
80 studies concerning the corrosion of candidate metals for the container, as well as the interaction of  
81 their corrosion products with bentonite, have been reported in the literature [18-20]. Regarding the  
82 steel-bentonite interactions, the transformation of bentonite into other minerals as a result of its  
83 interaction with the corrosion products of the metallic container has been observed [21, 22]. The  
84 effect of container corrosion on the stability of clay mineral depends mainly on factors such as pH,  
85 temperature, the crystal chemistry of the clay, the water/solid ratio and the iron/clay mass [23].

86 In previous studies we observed that during hydrothermal treatments in a steel reactor, the  
87 cations  $\text{Eu}^{3+}$ ,  $\text{Sm}^{3+}$  and  $\text{ZrO}^{2+}$  reacted not only with clay minerals, but also with the steel [11, 24,  
88 25]. Furthermore, it was found that both reactions compete. Here, we expand our analysis to the  
89 retention of uranium by steel containers. Few studies to study the role of the backfill material in  
90 the kinetics and the corrosion mechanisms of steel containers have been conducted to date. An  
91 understanding of the sorption/retention of radionuclides on the materials used to construct the  
92 engineered barrier (clay and container waste) is necessary to adequately predict the long-term  
93 performance of radioactive waste disposal facilities.

94 Concerning the hydrothermal conditions conducted in our experiments, it should be noted that  
95 they are not completely expected in the geological repositories currently under consideration:  
96 initial storage temperatures in DGR are expected to be greater than 200 °C, with temperatures  
97 falling below 150 °C several hundred years after emplacement [26]. But most important, pressure  
98 in DGR is expected to be below the maximum subcritical pressure conditions used in the  
99 hydrothermal treatments, ~ 100 atm. Nevertheless, the studies described here have practical

100 interest firstly because the hydrothermal conditions of high pressure and temperature are used to  
101 measure in reasonable times the reactions, many studies have been carried out by simulating the  
102 deep geological disposal at temperatures up to 350 °C to increase the reaction rate [1, 14, 27].  
103 Besides, experiments will be of particular interest for DBD repositories were higher temperatures  
104 and pressures are expected [6, 7, 28].

105 The aims of this work are, i) to quantify the retention of uranium and zirconium by FEBEX  
106 bentonite, i.e., reaction velocities, retention levels, dependence with temperature, etc, ii) to  
107 characterise the chemical reaction of uranium and zirconium with bentonites; and finally; iii) to  
108 estimate the role of steel in the retention of uranium, and its competition with the bentonites.

109

## 110 **2. Materials and methods**

### 111 *2.1. Bentonite.*

112 The FEBEX bentonite was extracted from the Cortijo de Archidona deposit (Almería, Spain).  
113 The processing at the factory consisted of disaggregation and gently grinding, drying at 60 °C and  
114 sieving by 5mm [29, 30]. The montmorillonite content of the FEBEX bentonite was above 90%  
115 (92±3%) [31]. The main characteristics of FEBEX bentonite are the following:  
116  $(\text{Ca}_{0.5}\text{Na}_{0.08}\text{K}_{0.11})(\text{Si}_{7.78}\text{Al}_{0.22})(\text{Al}_{2.78}\text{Fe}^{\text{III}}_{0.33}\text{Fe}^{\text{II}}_{0.02}\text{Mg}_{0.81})\text{O}_{20}(\text{OH})_4$  is the structural formula, total  
117 charge/u.c. is 1.19 and the theoretical cation exchange capacity (CEC) value, deduced from the  
118 molecular formula, is 158.2 meq/g [32].

119

### 120 *2.2. U and Zr solutions*

121 Two sets of reaction solutions were prepared. In order to make the structural characterisation  
122 of the sample after the hydrothermal reactions, a first set was prepared containing only the  
123 tetravalent actinide simulator  $\text{ZrO}^{2+}$  [33]. 1.382 g of  $\text{ZrO}(\text{NO}_3)_2 \cdot 7\text{H}_2\text{O}$ , were used to get 3.09  
124 mmol  $\text{ZrO}^{2+}$ , that were dissolved in 40 ml distillate water.

125 A second set was prepared using 0.016 mmol  $^{238}\text{U}$  and completed with 1.103 g of  
126  $\text{ZrO}(\text{NO}_3)_2 \cdot 7\text{H}_2\text{O}$  (Sigma-Aldrich). The stable analogous,  $\text{ZrO}^{2+}$ , was added to the uranium to  
127 obtain higher concentrations of  $\text{U-ZrO}^{2+}$ . 3.09 mmol (\*) were dissolved in 40 ml distillate water.  
128  $^{238}\text{U}$  was obtained from solid 6-hydrated uranyl nitrate,  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (Panreac). Initial  
129 activity of the prepared solution was approximately 50 Bq. Since uranium is radioactive, it is  
130 possible to directly quantify the reaction measuring the uranium activity before and after the  
131 hydrothermal treatment.

132

### 133 *2.3. Hydrothermal treatments*

134 Three hundred milligrams of powdered sample (FEBEX bentonite) and 40 ml of the solution  
135 with Zr or Zr-U were transferred into an 71 ml stainless steel T316SS hydrothermal reactor [34]  
136 and heated under autogenous pressure. Reaction products were collected by filtration using 0.45  
137  $\mu\text{m}$  Milipore filters and air-dried at 60°C.

138 In the DGR bentonite surrounds the steel and not the opposite; however, these experiments  
139 cannot be designed accordingly, given that the conditions of temperature and pressure needed for  
140 an hydrothermal treatment are actually attained when the bentonite is placed inside a sealed steel  
141 reactor that is placed in a stove.

142 Temperatures, vapour pressure and reaction times are summarized in Table 1.

143

### 144 *2.4. Structural characterization methods.*

145 The analysis of the hydration state of the interlayer space after the treatments and the detection  
146 of new crystalline phases were undertaken using X-ray diffraction (XRD) and a semiquantitative  
147 standard method ( $\Delta 2\theta=3-70^\circ$ ; step=0.015°; t=0.1s; tube conditions: 40 kV y 30 mA; divergence

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\*  $\text{ZrO}^{2+}$  is added to these set of experiments, and uranyl is not exclusively used, to get a concentration of reagents of the order of mmols. This will maintain the concentrations of the cations similar to the ones of the first set, were only Zr was used. Furthermore, this way uranium concentrations are kept below the legal limits of uranium for scientific purposes

148 slit: fixed 0.5°; sample with spin = 30 rpm; using nickel filter). A D8I powder diffractometer,  
149 located at Centro de Investigación, Tecnología e Innovación Universidad de Sevilla, CITIUS was  
150 used ( $\theta$ : $\theta$ , Bruker, D8 Advance A25 model, Cu anticathode, incidence slits variable or fixed, soller  
151 slits, Ni filter in the diffracted beam, linear detector).

152  $^{29}\text{Si}$  MAS-NMR spectra were recorded in a Bruker DRX 400 spectrometer with a  
153 multinuclear probe. Solid samples were packed in 4 mm zircon rotors and were spun under the  
154 magical angle to a frequency of 10 kHz. The spectra were registered at 79.49 MHz, 2.66  $\mu\text{s}$   
155 ( $\pi/2=7.98 \mu\text{s}$ ) of pulse length and 3s of delay time. The values of chemical shift were expressed in  
156 ppm, using tetramethylsilinate as external reference. Spectra were simulated using the DMFIT  
157 software [35] assuming infinite spinning speed. A Gaussian-Lorentzian model was used for all the  
158 peaks, and fitted parameters were: amplitude, position, linewidth and Gaussian-Lorentzian ratios.

159

## 160 *2.5. Radioactive measurements*

161 A Canberra hyper-pure germanium gamma detector (HPGe), from Radioisotope Service at  
162 CITIUS, was used to measure natural  $^{235}\text{U}$  activity in the sample, from which  $^{238}\text{U}$  activity was  
163 calculated. Counting efficiency was experimentally determined using  $^{235}\text{U}$  spiked standards so  
164 natural uranyl was added to the two standards of the geometries used: a 0.45  $\mu\text{m}$  Millipore filter  
165 and a 100 ml cylindrical beaker. Efficiency was verified for both geometries through Montecarlo  
166 simulations using LABSOCS program [36].

167 A calibration fitting (Figure 1) using diluted uranium standards is applied to calculate  $^{238}\text{U}$   
168 concentration in the sample from the  $^{235}\text{U}$  gamma measurement. Measured  $^{235}\text{U}$  cps were linearly  
169 related to  $^{238}\text{U}$  concentration in the sample.

170

## 171 **3. Results and discussion**

### 172 *3.1. Structural characterization*

173 The study of the evolution of the crystalline phases after the hydrothermal treatment with  
174  $\text{ZrO}^{2+}$  was carried out by XRD (Figure 2). The diffractogram of the initial FEBEX is in agreement  
175 with a montmorillonite with hydrated cations  $\text{Na}^+$  and  $\text{Ca}^{2+}$  in the interlayer space [37].

176 The XRD after the hydrothermal treatment at 150 °C for 14 days, Figure 2a, caused a weak  
177 reflection of the FEBEX bentonite and an increase of the background due to the lamellar structure  
178 breakdown and the formation of amorphous phases. After 28 days, those weak FEBEX reflections  
179 still remained but new zirconium crystalline phases were formed. Among  $\text{ZrO}_2$ , a phase  
180 containing zirconium and silicate,  $\text{ZrSiO}_4$ , was observed, which implies a chemical reaction  
181 between  $\text{ZrO}^{2+}$  and FEBEX framework.

182 The FEBEX damage increased with temperature and reaction time, and after the treatment at  
183 300 °C for 2 days no FEBEX reflections were observed (Figure 2c). This might be due to the  
184 chemical reaction of  $\text{ZrO}^{2+}$  with the FEBEX bentonite and to the low pH values reached in the  
185 treatments (pH=1.0-1.5). At  $T > 150$  °C. Secondary phases were generated from the destruction of  
186 the bentonite, i.e. kaolinite, bayerite and  $(\text{Ca,Fe,Mg})\text{SiO}_3$  and from the steel reactor corrosion,  
187  $\text{Fe}_2\text{O}_3$ . With the increase of temperature the number of phases containing Zr increased and the  
188 number of secondary phases decreased.

189 The quantification of siliceous species in the hydrothermal treatment was performed through  
190  $^{29}\text{Si}$  MAS NMR, i.e. Figure 3 shows the spectra of the hydrothermal treatment at 300 °C. For  
191 lower temperatures spectra are qualitatively similar and the only differences are in the  
192 quantification.

193 The initial spectra of the sample showed a peak at -93.6 ppm due to  $\text{Q}^3(0\text{Al})$  environment  
194 associated to montmorillonite [38]. After the hydrothermal treatment at 300 °C, this signal  
195 decreased abruptly and ever more significantly with the reaction time. New signals are detected at  
196 -91.2 ppm, due to kaolinite [39], at -81.0 ppm, due to  $\text{ZrSiO}_4$  [40], and at -108 ppm, due to



197 Q<sup>4</sup>(0Al) of tridimite [41]. The amount of Si associated to those environments depends on both  
198 temperature and reaction time and were in good agreement with the XRD results.

199 The <sup>29</sup>Si MAS NMR spectra were deconvoluted and the percentage of Si environment of  
200 FEBEX (original sample), Kaolinite (secondary phase from FEBEX breakdown) and ZrSiO<sub>4</sub>  
201 (phase originated by chemical reaction between ZrO<sup>2+</sup> and FEBEX) were analysed as a function of  
202 temperature, Figure 4a, and time reaction, Figure 4b.

203 Figure 4a displays the evolution of the phases with temperature at the maximum time reaction.  
204 An increase of temperature causes a decrease on the Si signal intensity associated to a decrease in  
205 FEBEX content (phyllosilicate 2:1) and an increase of the Si signal intensity of kaolinite  
206 (phyllosilicate 1:1). However, the intensity of the Si signal of ZrSiO<sub>4</sub> remains almost constant,  
207 18%. Time effect is shown in Figure 4b and follows a similar trend. A progressive decrease of  
208 FEBEX and an increase of kaolinite were observed as reaction time increases. The ZrSiO<sub>4</sub> phase  
209 remained also constant, ca. 18%, except for 5 days reaction time, where the phase decreased to ca.  
210 10%. The lowest pH in the final solution (pH=1.2) was obtained at 300 °C after five days reaction  
211 time.

212 The structural analysis has demonstrated that the hydrothermal treatment not only caused the  
213 adsorption of ZrO<sup>2+</sup> by FEBEX, but also two other mechanisms, the crystallization of ZrO<sub>2</sub> and  
214 the chemical interaction with the bentonite, were involved. At the lowest temperature, 150 °C, the  
215 kinetic of reaction allowed to detect that before the formation of ZrSiO<sub>4</sub>, the lamellar structure was  
216 broken-down and a reconstructive mechanism was followed.

217

### 218 3.2. *Quantification of the reactivity of bentonite with UO<sub>2</sub><sup>2+</sup>*

219 The structural analysis showed the existence of a chemical reaction with the clay mineral that  
220 includes the formation of new stable and insoluble phases of zirconium silicates. To quantify the

221 immobilisation, instead of using uniquely zirconium, as the trivalent stable element analogous to  
222 uranium, uranium was added to zirconium in the hydrothermal treatment (see section 2).

223 Hydrothermal treatments at 300 °C, 200 °C and 100 °C were performed as described in the  
224 methods section. The percentages of immobilised uranium measured after the treatments are  
225 shown in Table 2.

226 El Mrabet et al. [24, 25] observed that part of the initial zirconium was retained on the walls of  
227 steel reactors, as it reacts with bentonite, and both reaction mechanisms compete. For this reason,  
228 the percentage of retention by FEBEX bentonite had to be calculated considering that part of the  
229 uranium reacted with the steel. This percentage was calculated as uranium measured in the filter to  
230 total uranium; and total uranium was obtained as the uranium measured after the hydrothermal  
231 reaction in both filter and solution. This way, this percentage corresponds exclusively to the  
232 uranium immobilised in the solid phase, not in the steel, either due to adsorption onto the  
233 bentonite, precipitation or due to the formation of a new phase (silicates or oxides).

234 The general trend within uncertainties was an increase of the retention of uranium with  
235 temperature and time. This behavior was already reported for europium retention and several clay  
236 minerals (saponite, FEBEX and MX-80) [11, 15].

237 A second parameter to study was the amount of  $\text{UO}_2^{2+}$  -  $\text{ZrO}^{2+}$  retained by the bentonite; for  
238 that, the milliequivalents (meq) of  $\text{UO}_2^{2+}$  -  $\text{ZrO}^{2+}$  /100g bentonite were calculated and are shown in  
239 Figure 5. Meq were evaluated using the percentage of uranium retained by the bentonite and using  
240 a factor of conversion to correlate this percentage to the milliequivalents of uranium and zirconium  
241 per 100 g bentonite. Figure 5 shows the calculated milliequivalents versus reaction time, together  
242 with the amount of uranium necessary to satisfy the cation exchange capacity (CEC) of FEBEX  
243 bentonite (pointed line).

244 Cation Exchange capacity (CEC) for FEBEX bentonite is 158.8 meq/100 g. For hydrothermal  
245 treatments of two days ( $t=2$  days) and per 100 g of bentonite, only at 300 °C the  $\text{UO}_2^{2+}$  -  $\text{ZrO}^{2+}$

246 immobilised milliequivalents were over CEC,  $700 \pm 40$ . For reaction times longer than two days,  
247 the  $\text{UO}_2^{2+}$  -  $\text{ZrO}^{2+}$  immobilised milliequivalents were over CEC at 300°C, 200 °C and 100 °C. The  
248 highest amount of milliequivalents retained by 100 g of bentonite were found at 300°C for 26  
249 days,  $1200 \pm 70$ , and at 200°C for 28 days  $1150 \pm 70$ . Milliequivalents of retained uranium were  
250 over CEC even for short hydrothermal treatments; this result emphasises that processes of  
251 formation of new phases, additional to the adsorption, did occur. In the previous section the  
252 structural study revealed that the insoluble and stable phases detected were silicates and oxides.

253 The retained zirconium/uranium was directly compared to the CEC in order to quantify the  
254 immobilization ability of FEBEX due to chemical reaction. At 300 °C the retention was 440-770%  
255 over CEC, but it decreased progressively with temperature, 0-730% at 200 °C and 130-600% at  
256 100 °C. These percentages point out that the retention over CEC was significant for almost every  
257 analysed time and temperature.

258 Uranium-zircon immobilization ability was compared to that of europium from previous  
259 studies [11, 15]. The immobilization ability of FEBEX was considerably higher for uranium than  
260 for europium, since in the case of FEBEX the bentonite was only able to retain europium over  
261 CEC at 300 °C and below 300 °C the amount of retained europium was of the same order of CEC.

262 Here, regardless the reaction time, at 100 °C and higher temperatures, the mechanism of  
263 retention of uranium due to chemical reaction dominates over the immobilisation of the uranium  
264 through adsorption. This is an important conclusion in the study of the HLRW and SNF, because  
265 uranium is one of its major components and the formation of stable phases implies that the storage  
266 capacity of HLRW HLRW and SNF by the FEBEX bentonite might be higher than expected.  
267 Furthermore, our conclusions have direct impact in the study of DBD because they were obtained  
268 from hydrothermal experiments at subcritical pressure conditions (10 MPa), which are closer to  
269 the expected conditions in the DBD (200 °C- 700 °C and 40 - 150 MPa) [7].

270

271 3.3. Reaction rate of  $UO_2^{2+}$ -FEBEX bentonite interaction

272 Figure 6 presents the amount of uranium dissolved in the water after treatments at 300 °C, 200  
273 °C and 100 °C versus several reaction times. After the reaction, uranium was measured in the  
274 filtered bentonite (reacted) and in the remnant solution (dissolved). Total uranium involved in the  
275 reaction was obtained from the uranium in bentonite and solution (i.e. it was not considered the  
276 uranium reacted with steel). The percentage of unreacted uranium was calculated as the ratio  
277 uranium in the solution after the hydrothermal treatment to total uranium, calculated as described  
278 in section 3.2.

279 Roughly, the percentage of unreacted uranium decreased with temperature. The results were  
280 fitted to a decreasing exponential function with time (first order reaction) with good regression  
281 coefficients (Table 3). The exponent of the fitting provided the value of the reaction rate  
282 coefficient,  $k$ , following

$$283 \quad I = I_0 e^{-kt} \quad (1)$$

284 Where  $I$  is the percentage of unreacted uranium after the hydrothermal treatment and  $I_0$  is the  
285 initial uranium in the solution (100%). The values obtained from exponential fitting are displayed  
286 in Table 3 The half-life of the duration of the reaction,  $T_{1/2}$ , was deducted from  $k$  as

$$287 \quad T_{1/2} = \frac{\ln 2}{k} \quad (2)$$

288  $k$  value is the same order of magnitude for 300 °C ( $k = 14 \cdot 10^{-3} \text{ days}^{-1}$ ) and 200 °C ( $k = 27 \cdot 10^{-3}$   
289  $\text{days}^{-1}$ ) and their values are very close according to their uncertainties. To analyse the kinetic of  
290 reaction at 100 °C longer reaction times are needed to obtain a good precision for the reaction  
291 constant. For a hydrothermal treatment of two months, the associated uncertainty for  $k$  and its  
292 regression coefficient were unsatisfactory (Table 3). Thus, at 100 °C the reaction constant could  
293 only be obtained in order of magnitude ( $k \sim 2 \cdot 10^{-3} \text{ days}^{-1}$ ).

294 The value of the reaction constant,  $k$ , seems to be temperature dependent. Results from Table 3  
295 provided evidences of a change in the reaction rate with temperature. Thus, for temperatures  
296 ranged between 300-200 °C, corresponding half-live times had a mean value of ca. 1 month.  
297 However, the half-life is, in order of magnitude, longer than one year for 100 °C. That means that  
298 at 200-300 °C, the uranium could be completely removed from the solution in six months, when 5  
299 times the half-lives are completed; but six years would be needed for the total removal of uranium  
300 with FEBEX at 100 °C. It is remarkable that both periods of time are not significant in comparison  
301 to the half-life of the uranium isotope ( $4.47 \cdot 10^9$  years).

302 The kinetic study of the reaction of europium with saponite, FEBEX and MX-80 showed a  
303 similar behaviour [15]. For  $T \geq 200$  °C the time needed to remove completely the europium was  
304 always lower than one year ( $k \sim 10 \cdot 10^{-3} \text{ days}^{-1}$ ) for all the studied clay minerals. On the contrary,  
305 for  $T < 200$  °C, several years were required ( $k \sim 10^{-3} \text{ days}^{-1}$ ).

306  $k$  obtained for saponite, FEBEX and MX-80 in europium and uranium for any temperature is  
307 always between  $10^{-2}$  and  $10^{-3} \text{ days}^{-1}$  [15].

308 It is worth mentioning that the kinetic at 200 °C is especially fast, as the reaction constant  $k$   
309 was higher at 200 °C ( $k \sim 3 \cdot 10^{-2} \text{ days}^{-1}$ ) than at 300 °C ( $k \sim 10^{-2} \text{ days}^{-1}$ ). Besides, at 28 days the  
310 same amount of uranium reacted at 200 °C and at 300°C.

311

#### 312 3.4. Reaction of Uranium with the steel

313 The immobilisation of uranium with steel was also analysed and the results are plotted on  
314 Figure 7. This figure shows the ratio of uranium immobilised by the steel reactor to the spiked  
315 uranium. The uranium immobilised by the steel was calculated subtracting the uranium measured  
316 in filter and solution to spiked uranium. The retention by the steel depends on temperature and, as  
317 for the bentonite, uranium retention by steel presents a singularity at 200 °C. At 200 °C, a strong

318 linear dependence ( $R^2 = 0.93$ ) with the reaction time is observed and the amount of immobilised  
319 uranium by the steel increases from 40%, at the beginning of the treatment, up to 70%. However,  
320 at 300 °C and 100 °C the uranium retention by steel is lower and remains constant: 30% and 15%  
321 of uranium is sorbed at 300 °C and 100 °C, respectively. The results are compatible with previous  
322 ones for  $\text{Eu}^{3+}$ ,  $\text{Sm}^{3+}$  and  $\text{ZrO}^{2+}$  [11, 24, 25].

323 After a first hydrothermal treatment, an unwashed steel reactor was reused for a new  
324 hydrothermal treatment using 40 ml water and 0.3 g of FEBEX, at 300 °C for seven days, with the  
325 purpose of evaluating the reversibility of the immobilisation of uranium by the steel. Final  
326 precipitate was filtered and no uranium traces were measured in filter and remnant solution. The  
327 uranium concentration in solid and liquid fraction after the desorption treatment was below the  
328 limit of detection and, therefore, the retention of uranium by steel does not seem to be reversible at  
329 subcritical conditions and neutral pH.

330 It is worth reminding that the reaction uranium-steel steel depends on many other parameters,  
331 such as the uranium concentration, the total amount of uranium, solid-to-liquid (clay-water)  
332 ratio... All this suggests that further studies should be performed to further constraint the  
333 mechanisms of this reaction.

334

#### 335 **4. Summary and conclusions**

336 The structural analysis has demonstrated that the hydrothermal treatment not only provoke the  
337 adsorption of  $\text{ZrO}_2^+$  (chemical analogous of uranium) by FEBEX, but also two other mechanisms,  
338 the crystallization of oxide and the chemical interaction with the bentonite, were involved. At  
339 150°C it was detected that before the formation of  $\text{ZrSiO}_4$ , the lamellar structure was broken-down  
340 and followed a reconstructive mechanism.

341 The kinetics of reaction uranium-clay minerals is a first-order reaction and exhibit Arrhenius  
342 dependence with temperature. Removal of uranium from solution by the bentonite at temperatures

343 over 200 °C would be completed in less than a year. When the temperature diminished below 200  
344 °C, several years would be needed for a complete removal. This reaction velocity was similar for  
345 europium and uranium.

346 The  $\text{UO}_2^{2+}$  immobilised by the clay were temperature and time dependent and it also depended  
347 on the reacted elements. Furthermore, the immobilised amount of  $\text{UO}_2^{2+}$  was systematically over  
348 the cation exchange capacity of FEBEX at all explored temperatures (and increases to up 600-  
349 700% for high reaction times).

350 The results confirmed the presence of a new chemical phase to immobilise uranium and  
351 showed that in the reaction uranium-FEBEX under subcritical conditions, two mechanisms were  
352 involved: i) adsorption in specific and unspecific sites, and, ii) a chemical reaction with the clay  
353 mineral that includes the formation of a new stable and insoluble phase of mainly uranium  
354 silicates.

355 Steel took active part in the sorption of uranium through irreversible adsorption of uranium in  
356 unspecific sites of the steel reactor. At 200°C 40%-90% of the uranium reacted with steel.  
357 However, at 300 °C and 100 °C only a maximum of 30% of the uranium reacted with steel.

358 These results have direct implications in our knowledge of the reaction mechanism of HLRW  
359 and SNF with the engineered barrier. The potential retention ability for one of the major  
360 radionuclides from the HLRW and SNF is higher than assuming exclusively adsorption by the  
361 clay minerals. In addition, the stability of the stored waste might be higher than expected, since  
362 uranium is immobilised by a new chemical phase, and not only by the clay minerals. The  
363 existence of a reaction with steel has important implications for the storage of HLRW when steel  
364 containers were used. Finally, this is of direct interest for very deep borehole disposals, DBD,  
365 where high temperatures (200 °C- 700 °C) and high pressures are expected (40-150 MPa).

366

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**Table 1.** Temperatures and times used in the hydrothermal treatments with FEBEX and  $\text{UO}_2^{2+}$  and  $\text{ZrO}^{2+}$ . Stripes correspond to solutions where no radioactive tracer was added.

T (°C)	$p^{[a]}$ (b)	Time (days)							
		2	5	7	14	26	28	63	84
100	1.01								
150	4.76								
200	15.54								
300	85.90								

[a] The maximum pressure corresponds to the water vapor pressure at this temperature

**Table 2.**  $^{238}\text{U}$  reacted with FEBEX bentonite (%) collected in the filter after the hydrothermal treatment at 300 °C, 200°C and 100°C. In the calculation of the percentage it has been excluded the amount of uranium reacted with the steel reacted. Uncertainties correspond to 1 sigma and were calculated by error propagation of the  $^{238}\text{U}$  counts per second detected by gamma spectrometry. Except for the 7 and 14 days treatments at 300°, that corresponds to the standard deviation of the results from two replicates.

Treatment time (days)	$^{238}\text{U}$ measured in bentonite (%)		
	300 °C	200 °C	100 °C
2	$29 \pm 2$	0	
5	$42 \pm 3$		
7	$39 \pm 6$	$14 \pm 1$	$9 \pm 1$
14	$51 \pm 3$	$33 \pm 2$	
26	$50 \pm 3$		
28		$49 \pm 3$	$9 \pm 1$
63			$35 \pm 2$
84			$40 \pm 3$

**Table 3.** Kinetic parameter of adsorption-reaction of uranium with FEBEX

T (°C)	$k \cdot 10^{-3}$ (days <sup>-1</sup> )	$T_{1/2}$ (days)	R <sup>2</sup>
300	14 ± 4	50 ± 10	0.693
200	28 ± 3	25 ± 2	0.9782
100	2 ± 2	418 ± 415	0.2302

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493 **Fig. 1.** Uranium concentration versus  $^{235}\text{U}$  counts per second (cps) measured through gamma  
494 spectrometry. Calibration has been performed for a) liquid solution after hydrothermal treatment  
495 b) filter containing solid phase after treatment.

496 **Fig. 2.** XRD of FEBEX bentonite after hydrothermal treatment at a) 150 °C, b) 200 °C, and, c) 300  
497 °C at different time reactions. \*= Zircon,  $\text{ZrSiO}_4$ , (PDF 00-06-0226), += Baddeleyite,  $\text{ZrO}_2$  (PDF  
498 00-3-515), ^= Hematite,  $\text{Fe}_2\text{O}_3$  (PDF 00-33-664), a=Bayerite,  $\text{Al}_2\text{O}_3\cdot\text{H}_2\text{O}$  (PDF 00-08-096),  
499 k=Kaolinite (PDF 00-01-527), and, s=(Ca,Fe,Mg) $\text{SiO}_3$  (PDF 00-03-623).

500 **Fig. 3.**  $^{29}\text{Si}$  MAS NMR of raw FEBEX and after the hydrothermal treatment at 300 °C at different  
501 times.

502 **Fig. 4.**  $^{29}\text{Si}$  MAS NMR environment evolution as a function of reaction conditions: a)  
503 temperature, and, b) time.

504 **Fig. 5.** Milliequivalents of  $\text{UO}_2^{2+}$  and  $\text{ZrO}^{2+}$  per 100g immobilized by FEBEX bentonite. Pointed  
505 line corresponds to CEC (Cationic Exchange Capacity) of FEBEX, 158.2 meq/100g. Uncertainties  
506 correspond to 1 sigma and were calculated by error propagation of the counts per second detected  
507 by gamma spectrometry. Uncertainties of the 7 and 14 days treatments at 300 °C, correspond to  
508 the standard deviation of the results from two replicates.

509 **Fig. 6.**  $^{238}\text{U}$  (%) collected in the solution after the hydrothermal treatment (unreacted uranium) at  
510 300 °C, 200 °C and 100 °C. In the calculation of the percentage it has been excluded the amount of  
511 uranium reacted with the steel reacted. Results have been fitted to an exponential function.

512 **Fig. 7.**  $^{238}\text{U}$  reacted with steel (%) after the hydrothermal treatment at 300 °C, 200 °C and 100 °C.  
513 The percentages of steel reacted uranium have been obtained subtracting uranium measured in  
514 solution and filter after the treatment to the total spiked uranium. Uncertainties correspond to 1  
515 sigma and were calculated by error propagation of the counts per second detected by gamma  
516 spectrometry. Uncertainties of the 7 and 14 days treatments at 300 °C, correspond to the standard  
517 deviation of the results from two treatments.