

1 **Quantification and comparison of the reaction properties of FEBEX**
2 **and MX-80 clays with saponite, as immobilizers of europium under**
3 **subcritical conditions.**

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10
11 **Abstract**

12 The evaluation of the retention mechanisms in FEBEX and MX-80 bentonites, selected as
13 reference materials to construct engineered barriers, carries major implications in the safe storage
14 of nuclear waste. The kinetics and reactivity of the reaction of Eu -as a lanthanide high-level
15 radioactive waste simulator- with FEBEX and MX-80 were investigated, in addition to their
16 immobilisation capacity through a recently discovered chemical retention mechanism and the
17 structural analysis of the reaction products. Hydrothermal treatments were accomplished with
18 $\text{Eu}(\text{NO}_3)_3$ (^{151}Eu and ^{153}Eu , with 52.2% ^{153}Eu) and spiked with radioactive ^{152}Eu for the
19 quantification of the reactions. Results were compared with saponite as the reference smectite.
20 The strong dependence of the reaction parameters with temperature and time was quantified and
21 the reaction velocity was evaluated. The velocity follows these trends: 240 days are needed for
22 the total retention of europium for temperatures over 200°C; below 150°C, significantly longer
23 reaction times, on the order of three years are required to complete the reaction. Clays do not

24 influence velocity rates, but the retention capacity of bentonites remains lower than for saponite.
25 At 300°C, the milliequivalents retained by the three clays are consistently over CEC. The
26 structural analyses reveal not only adsorption of europium but also the presence of $\text{Eu}(\text{OH})_3$
27 precipitation and Eu_2SiO_3 confirming the existence of a chemical reaction.

28 **Key Words:** Bentonite, smectite, disilicates, europium, hydrothermal treatment, radioactive
29 waste.

30

31 **1. Introduction**

32 In many countries, the development of Deep Geological Repositories (DGR), for the storage
33 of high-level radioactive waste (HLRW) is based on a system of multiple barriers. Most safety
34 within the repositories relies on the engineered barrier (Savage and Chapman, 1982). Clays
35 present low permeability, and high sorption and swelling capacity, which makes them ideal
36 materials for natural and engineered barriers for nuclear waste isolation (Pusch, 2006). A clay
37 barrier is able to delay the diffusion and immobilise, in certain experimental conditions, the
38 radioactive wastes through a physical-chemical mechanism, such as adsorption, desorption or
39 even a chemical reaction including the formation of secondary stable mineral phases. At the
40 present time, bentonite is accepted as the most suitable clay for the engineered barrier in DGRs
41 (Fernandes et al., 2012).

42 The performance of clay as the main component of the engineered barrier in the DGR has
43 been intensively studied, e.g. its response to intense irradiation (Sorieul et al., 2008), its sorption
44 properties (Fernandes et al., 2012; Stumpf et al., 2001), colloid formation reactions (Bouby et al.,
45 2011) and the connections between sorption chemistry and mechanical compaction (Miller and
46 Wang, 2012). Regarding the clay adsorption properties, recent studies highlight the existence of
47 an additional retention mechanism (Alba et al., 2009a; Trillo et al., 1994). The systematic study

48 of the interaction of the Rare Earth Element (REE) cations, such as La, Lu, Nd, Sm, as actinides
49 chemical analogues, with natural and artificial clay minerals, reveal a reaction mechanism, based
50 on the chemical interaction between the lanthanide cations and the orthosilicate anions of the
51 lamellar structure (Alba et al., 2011; Alba and Chain, 2005). At subcritical conditions,
52 (temperature and pressure), an insoluble and chemically stable phase, $\text{REE}_2\text{Si}_2\text{O}_7$, is generated
53 (Alba et al., 2009b). Therefore, the expected retention capacity of bentonite increases and can
54 provide a stable immobilisation mechanism even when its sorption and swelling capacities fail
55 (Alba and Chain, 2007).

56 These previous studies are focused on the structural analysis of $\text{REE}_2\text{Si}_2\text{O}_7$, after the
57 hydrothermal reaction between REE cations and clay minerals (Alba and Chain, 2005; Alba and
58 Chain, 2007; Alba et al., 2009a). More recently, Alba et al., (2011) have quantified the Eu^{3+}
59 immobilization by a standard saponite, and physical and chemical interactions are analysed.
60 However, the final motivation of these analyses is the study of bentonites, since they constitute
61 one of the most recommended materials for the construction of the engineered barrier.

62 In this work, an evaluation of the retention mechanisms in bentonites is performed. The
63 FEBEX and MX-80 clays are commonly selected as reference materials by various nuclear waste
64 management agencies in the construction of engineered barriers in a potential DGR (Villar et al.,
65 2012).

66 Therefore, the aims of this study are: i) quantification of the immobilisation power of the
67 bentonites FEBEX and MX-80 in comparison with the pure smectite saponite; ii) completion of a
68 kinetic analysis of the process and a structural analysis of the products of reaction; and iii)
69 verification of the mechanism in a wide range of temperatures, including those where the extent
70 of the reaction is so low that is not possible to detect structural changes.

71 In order to achieve these objectives, hydrothermal treatments of FEBEX and MX-80 with
72 stable europium are performed in the temperature range between 80°C and 300°C. Stable
73 europium was spiked with ^{152}Eu in order to quantitatively compare the reactivity and kinetics of
74 the bentonites to the saponite.

75

76 **2. Materials and methods**

77

78 *2.1. Clay samples.*

79 The FEBEX bentonite was extracted from the Cortijo de Archidona deposit (Almería, Spain).
80 The processing at the factory consisted of disaggregation and gently grinding, drying at 60 °C
81 and sieving by 5mm (ENRESA, 2000; ENRESA, 2006). The montmorillonite content of the
82 FEBEX bentonite was above 90% ($92\pm 3\%$)(Villar et al., 2012). The MX-80 bentonite was
83 extracted from Wyoming (USA) and was supplied in the form of powder homoionised with
84 sodium (Madsen, 1998). The MX-80 batch used in this investigation was mainly composed of
85 montmorillonite (83%)(Villar et al., 2012). As reference, a purified saponite from the Source
86 Clay Minerals Repository of the University of Missouri (Columbia) was used as reference
87 material (Alba et al., 2001). Table 1 summarizes the main clay characteristics (Galunin et al.,
88 2010).

89

90 *2.2. Eu^{3+} solutions.*

91 Two sets of starting solutions of $7.9\cdot 10^{-2}\text{M}$ $\text{Eu}(\text{NO}_3)_3$ (^{151}Eu and ^{153}Eu , with 52.2% ^{153}Eu)
92 were prepared: The first solution contained solely stable Eu isotopes; the second solution was
93 enriched with the radioisotope ^{152}Eu (with a half-life of 13.5 years). A volume of 1 ml from a
94 diluted standard solution up to a total activity of 9.8 Bq was added to 35 ml of the former

95 solution, as a compromise for safe radioactive handling and high counting rates for fast
96 measurements. That activity corresponded to 10^{-14} mol of ^{152}Eu . The pH of the two solutions was
97 adjusted to pH=6.0-6.5, by slowly adding 0.05 M ammonia solution while stirring.

98

99 *2.3. Hydrothermal treatments.*

100 Three hundred milligrams of the powdered samples (Saponite, FEBEX, MX-80) were
101 dispersed in the 40 ml of Eu^{3+} solutions and were heated in a stainless steel reactor (Perdigón,
102 2002), at the temperatures and times summarized in Table 2. The cells marked with vertical lines
103 correspond to the treatment with a starting solution of $7.9 \cdot 10^{-2}\text{M}$ $\text{Eu}(\text{NO}_3)_3$, while the grey cells
104 correspond to the treatment with a starting solution of $7.9 \cdot 10^{-2}\text{M}$ $\text{Eu}(\text{NO}_3)_3$ enriched with the
105 ^{152}Eu isotope. The reaction products were collected by filtering using a Millipore filter with 0.45
106 μm pore diameter, washed with distilled water, and dried in air at 60°C . The reaction solution and
107 the washing liquid were kept for quantitative analysis of europium by gamma spectroscopy. The
108 solid samples were collected either for gamma (^{152}Eu spiked), or for structural analysis by XRD
109 and SEM/EDX (not spiked with radioactive isotopes).

110

111 *2.4. Characterization methods.*

112 A Canberra, hyper-pure n-type germanium gamma detector (HPGe), was used for ^{152}Eu
113 gamma spectrometry measurements, in Radioisotopes Service at CITIUS laboratories
114 (Universidad de Sevilla). Counting efficiency was experimentally determined by means of
115 preparing standards spiked with ^{152}Eu for the two geometries analysed: filter and cylindrical
116 beaker. Efficiency was verified for both counting geometries using Monte Carlo simulations,
117 through an optimized LABSOCS program (Hurtado and Villa, 2010).

118 In the structural study, powered non-¹⁵²Eu spiked samples were analysed using a Bruker D8
119 to obtain an X-Ray diffraction diagram (XRD), also located at CITIUS laboratories (Universidad
120 de Sevilla). Radiation of Cu, K α , and Ni filters was chosen, whereby 40 kV, 40 mA, 0.05° 2 θ
121 step, and 3 s counting time were the operational parameters. Crystalline phase identification was
122 carried out using the DIFFRAC^{plus} Evaluation package (©2010 Bruker AXS GmbH, Karlsruhe,
123 Germany).

124 When crystalline phases could not be identified by XRD, scanning electron microscopy
125 (SEM/EDX) was chosen. Morphologies and chemical compositions were analysed in Microscopy
126 Service in ICMS (CSIC-Universidad de Sevilla) with a SEM-FEG HITACHI S- 4800; a scanning
127 electron microscope equipped with an Xflash 4010 (Bruker) for energy dispersive X-ray (EDX)
128 analysis.

129

130 **3. Results and discussion**

131

132 *3.1. Quantification of the reactivity of clays with Eu³⁺.*

133 Retention of europium in the bentonites was evaluated from the comparison of the initially
134 added radioactive europium with the measurement of the europium in the filter after
135 hydrothermal treatment. Subsequently, milliequivalents of europium per 100g clay retained in the
136 solid were calculated and displayed for every hydrothermal treatment in Fig. 1, where the amount
137 of europium that would be needed to satisfy the CEC (Cation Exchange Capacity) of the clays
138 (horizontal lines) is also shown.

139 Predominantly, when the reaction temperature increases, the amount of europium retained in
140 the solid phase increases. At the beginning of the reaction (t=0), the milliequivalents of europium
141 retained by the clays were within the range of the CEC for every temperature, that is, the

142 europium was retained exclusively due to cationic exchange, and no significant chemical reaction
143 took place. At 300°C, for longer reaction times, regardless of the clay, the milliequivalents of
144 retained europium were higher than the CEC, that is, immobilization was not only associated to
145 sorption in specific and non-specific sites, but also to the chemical reaction between europium
146 and the clay framework. For the FEBEX and MX-80 bentonites, the amount of europium
147 retained, although higher than CEC, was significantly lower than for saponite. At 150° C, only
148 saponite was able to retain europium above its CEC, and hence the immobilization of europium
149 in FEBEX and MX-80 is associated exclusively to CEC for the first two months of the reaction.
150 At 80°C, no clay was able to retain milliequivalents of europium above CEC.

151 One of the highlights of this work is that we have succeeded in quantitatively comparing
152 FEBEX and MX-80 in relation to the retention capacity of one key radionuclide. It was found
153 that the differences for the two clays were negligible in this respect, but their retention capacity,
154 either chemical or physical, was lower than that of the reference clay (saponite).

155 The immobilisation capacity of bentonites through the chemical retention mechanism is also
156 proved and quantified. This impact is highlighted at 300°C, since at that temperature, the
157 milliequivalents retained were consistently over the CEC. For saponite, the europium reaction is
158 400-1200% times higher. In FEBEX and MX-80, europium reacts from 130% to 600% (FEBEX),
159 and 130% to 1100% (MX-80) over the CEC. The chemical reaction failed to clearly increase with
160 time for every clay and every temperature. However, in the case of saponite, this increase did
161 remain clear. Since the retention of europium over CEC is a first order kinetical reaction (Alba et
162 al., 2011), it is expected that europium retention in the clays over their CEC capacities (formation
163 of new chemical phases) will be increased with longer reaction times (years).

164 These results could be critical in HLRW disposal within the engineered barrier, and carry
165 implications towards the stability of the radioactive wastes stored in bentonite since the formation

166 of chemical phases is expected to be more stable than the sorption in non-specific sites of the
167 clay.

168

169 3.2. Reaction rate of Eu^{3+} -clays.

170 The quantification of the reaction using radioactive ^{152}Eu supports previously found evidence
171 (Alba et al., 2011) that showed a strong dependence of the reacted europium and its reaction
172 velocity on temperature and time.

173 Figure 2 presents the results for the hydrothermal treatment with the clays at different
174 temperatures. The ratio in the ordinate of Figure 2 represents the ^{152}Eu measured in the solution,
175 (that is, unreacted ^{152}Eu), referring to the total ^{152}Eu collected after the treatment, and was shown
176 versus time. In other words, ^{152}Eu is measured in clay and solution, and the total represents the
177 ^{152}Eu involved in the reaction: reacted (^{152}Eu measured within the clay) and unreacted (^{152}Eu
178 measured in the remaining solution). The europium amount in the remaining solution decreased
179 with time and temperature. The ^{152}Eu concentration in the solution (Fig. 2), which is directly
180 related to europium reactivity, was fitted to an exponential (first order kinetic reaction) with a
181 good regression coefficient, especially for higher temperatures and/or long reaction times (Table
182 3). The exponent of the fitting provided the reaction velocity constant, k , according to

$$183 \quad I = I_0 e^{-kt} \quad (1)$$

184 The k values obtained from the exponential fitting for saponite, FEBEX, and for MX-80 at
185 various temperatures are displayed in Table 3. From the k value, and by taking into account a
186 first-order reaction, the half-life of the reaction ($T_{1/2} = \ln 2/k$) was calculated and shown in
187 Table 3.

188 The velocity rate (k) depends on the temperature. At $350^{\circ}\text{C} \leq T \leq 200^{\circ}\text{C}$, the velocity of the
189 reaction was relatively fast and the fitted exponentials showed steep slopes. Their reaction rate
190 constants, k , were also similar within the uncertainty (Table 3). k values displayed in Table 3, can
191 be used to calculate the half-life of the exponential decay. Which is 49.5 days in this case.
192 According to the definition of half-life at least 5 half-lives are needed to consider that the
193 exponential decay approached approximately zero, i.e. around 8 months would be needed for the
194 total retention of the europium by the saponite.

195 On the other hand, at 150°C and 80°C , the decay was slower and longer reaction times were
196 needed in order to evaluate the constant rate accurately; that is why the exponential fitting for
197 150°C and 80°C display poorer regression-fitting parameters (R^2 lower than 0.7). An estimation
198 of the reaction constant was obtained for both temperatures, and despite the higher uncertainties,
199 it remains clear that the constant of the exponential fitting was significantly lower. Calculated k
200 values were one order of magnitude lower than for $T \geq 200^{\circ}\text{C}$ (Table 3). Lower k values result in
201 longer reaction times (within three years) needed to complete the immobilisation of the
202 europium.

203 It is worth noticing that reaction velocities were classified in two groups of temperature ($350-$
204 200°C and $150-80^{\circ}\text{C}$) and provided two distinct k values for every group. Within the same
205 temperature, arranged k velocities were indistinguishable, in accordance with the uncertainty.

206 Moreover, k values quantified in Table 3 were equivalent for the three clays. Within
207 uncertainties, equivalent reaction velocities were observed for saponite, FEBEX and MX-80.
208 This implies that various types of clay affect the concentration of retained europium, but not their
209 reaction velocities. The time needed to complete the reaction is thus independent of the clay. To
210 immobilise all the europium at $300-350^{\circ}\text{C}$, approximately 8-9 months would be needed. The

211 reaction time increases for lower temperatures; to immobilise all the europium at 80-150°C,
212 several years would be needed.

213 In Alba et al. (2011) it is presented europium reaction with saponite (i.e. europium
214 immobilization by saponite) at 300°C, 200°C, 150°C, and 80°C. It increases with the temperature
215 and its reaction velocities are discriminated into two groups, according to the temperature. The
216 following relationship was found:

$$217 \quad \text{Eu}_{\text{reacted}}(350^{\circ}\text{C}) > \text{Eu}_{\text{reacted}}(200^{\circ}\text{C}) > \text{Eu}_{\text{reacted}}(150^{\circ}\text{C}) > \text{Eu}_{\text{reacted}}(80^{\circ}\text{C}).$$

218 Figure 2 shows that for the three clays, the amount of unreacted europium at 300-350°C was
219 lower than at 150°C and 80°C. Furthermore, at 300-350°C, the amount of retained europium
220 clearly depended on the clay used in the reaction. The following relationship is thereby inferred
221 in terms of capacity of immobilisation of europium at 300°C.

$$222 \quad \text{Eu}_{\text{reacted}}(\text{saponite}) \gg \text{Eu}_{\text{reacted}}(\text{FEBEX}) > \text{Eu}_{\text{reacted}}(\text{MX-80})$$

223 At 80°C and 150°C, the trend was similar. At 150°C, the points were scattered, although
224 saponite provided clearly higher reactivity values, and FEBEX and MX-80 provided
225 indistinguishable reactivity. Values seemed to be higher for MX-80, however this deduction
226 remains inconclusive due to the high uncertainties of the results. At 80°C, the reactivity was
227 almost equal for all three clays, but could not be verified due to the high dispersion of the results.

228

229 *3.3. Structural studies.*

230 The XRD patterns of the bentonites and those after reaction with $7.9 \cdot 10^{-2} \text{M}$ $\text{Eu}(\text{NO}_3)_3$ at
231 300°C are displayed in Figs. 3b and 4b. The pattern of the original bentonites (Figs. 3a and 4a)
232 show the general and basal reflections. The *hk* bands are composed of asymmetrical reflections
233 with the characteristic “saw-tooth” shape of the two-dimensional reflections (Warren, 1941). The
234 basal reflections are symmetrical. The 14.6 Å and 11.9 Å d_{001} values of unreacted FEBEX and

235 MX-80 bentonite, respectively, corresponded mainly to the bilayer hydrated Ca^{2+} in the FEBEX
236 interlayer and to the monolayer hydrated Na^+ in the MX-80 interlayer (Alba et al., 2001; Grim,
237 1968; Ravina and Low, 1977; Warren, 1941).

238 After the hydrothermal reaction at 300°C , (Figs. 3 and 4, b-f) the basal spacing of
239 bentonites was increased to 15.5 \AA , in agreement with data reported for smectites saturated with
240 multivalent cations (Ravina and Low, 1977). This increase agreed with a sorption of Eu^{3+}
241 equivalent to its CEC at 0 h (see Fig. 1). At reaction times longer than 0 h, where the sorption
242 was higher than the CEC, small reflections in the $10\text{-}55^\circ\ 2\theta$ range were observed as a
243 consequence of the generation of the new phases. In FEBEX, those small reflections
244 corresponded to Eu_2SiO_3 (PDF 35-297, marked with E), quartz (PDF 2-458, marked with q),
245 $\text{Na}_8(\text{AlSiO}_4)_6(\text{OH})_2$ (PDF 40-0100, marked with a), and $\text{Eu}(\text{OH})_3$ (PDF 83-2305, marked with
246 oh). In MX-80, only Eu_2SiO_3 and quartz were detected; the absence of $\text{Eu}(\text{OH})_3$ could be due to
247 the final pH value being below 3. The XRD patterns were noisy and showed a prominent
248 background, which indicated the partial disruption of the bentonite framework.

249 The treatments at 150°C and 80°C caused no crystallization of new phases and the unique
250 change in the XRD patterns was the shift of the 001 reflexion towards higher 2θ degree. Figure 5
251 shows the XRD pattern of both bentonites after hydrothermal treatment at 80°C for 63 days and
252 at 150°C for 56 days. In both cases, the 2θ position of the 001 reflection indicates the basal
253 spacing of bentonites, increased up to 15.5 \AA , in agreement with the sorption of Eu^{3+} at no
254 specific sites (Ravina and Low, 1977).

255 These results were corroborated through the compositional mapping by SEM/EDX of the
256 bentonites hydrothermally treated at 150°C (Fig. 6). In general, the morphology of most of the
257 particles were lamellar with amounts of Si, Al and Eu compatible with bentonites saturated with
258 Eu^{3+} (no specific site sorption), although other compacted particles were observed and were

259 enriched in Eu. The formation of phases, not observed by XRD, were compatible with $\text{Eu}(\text{OH})_3$
260 or Eu_2SiO_3 , and these same phases were observed at 300°C (specific site sorption and chemical
261 reaction).

262 Temperature played a greater role than time in the formation of the europium silicate, as
263 is predicted in thermodynamics and kinetics. However, long reaction times are expected to
264 increase the sorption by specific and chemical reaction mechanisms, even for low reaction
265 temperatures.

266

267 **4. Conclusions**

268

269 The results demonstrate that two mechanisms are involved in the Eu^{3+} (trivalent actinide
270 chemical analogue) retention by bentonites: sorption in specific and non-specific sites; and
271 chemical reaction within the bentonite framework. These findings have a direct and significant
272 implication in the mechanism of retention of HLRW by the engineered barrier of DGRs: Not
273 only does it increase the immobilisation capacity of the bentonite, but it also increases the
274 expected stability of the radioactive waste stored in bentonite.

275 Furthermore, the immobilization times can be quantified. The results pointed out that the
276 immobilization of europium by saponite, FEBEX and MX-80 would be completed in 8.5 months
277 at $350^\circ \leq T \leq 200^\circ\text{C}$, whereas several years will be needed at $200^\circ < T \leq 80^\circ\text{C}$.

278

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282

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340

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Table 1. Characteristics of the clays selected

Clays	Structural formula	Total charge/ u.c.	CEC ^d (meq/100g)
FEBEX ^a	$(\text{Ca}_{0.5}\text{Na}_{0.08}\text{K}_{0.11})(\text{Si}_{7.78}\text{Al}_{0.22})(\text{Al}_{2.78}\text{Fe}^{\text{III}}_{0.33}\text{Fe}^{\text{II}}_{0.02}\text{Mg}_{0.81})\text{O}_{20}(\text{OH})_4$	1.19	158.2
MX-80 ^b	$(\text{Na}_{0.36}\text{Ca}_{0.20})(\text{Si}_{7.96}\text{Al}_{0.04})(\text{Al}_{3.1}\text{Mg}_{0.56}\text{Fe}^{\text{III}}_{0.18}\text{Fe}^{\text{II}}_{0.16})\text{O}_{20}(\text{OH})_4$	0.76	102.1
Saponite ^c	$\text{Na}_{0.8}(\text{Si}_{7.2}\text{Al}_{0.8})(\text{Mg}_{5.79}\text{Fe}_{0.14})\text{O}_{20}(\text{OH})_4$	0.80	103.0

^a ENRESA, Spain^b CIEMAT, Spain^c Source Clays Repository of the Clay Minerals Society, University of Missouri, Columbia, USA^d theoretical cation exchange capacity value, mathematically deduced from clay molecular formula

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Table 2. Temperatures and times used in the hydrothermal treatments with FEBEX and MX-80 bentonite and europium. Stripes correspond to solutions where no radioactive tracer was added

T (°C)	Time (days)									
	0	2.2	4.5	9	28	35	56	63	120	
80	Stripe				Stripe		Stripe	Stripe	Stripe	Stripe
150					Stripe	Stripe	Stripe			
300	Stripe	Stripe	Stripe	Stripe	Stripe		Stripe			

Table 3. Kinetics parameters of the europium sorption by clays.

T (°C)	saponite	FEBEX	MX-80
	k · 10 ⁻³ (days ⁻¹)		
350	14 ± 5		
300		14 ± 3	11 ± 6
200	11.9 ± 0.1		
150	3.6 ± 1.5	3 ± 1	1.5 ± 1.2
80	2.4 ± 2.0	1.0 ± 0.1	2 ± 1
T(°C)	T _{1/2} (days)		
350	50 ± 2		
300		50 ± 10	60 ± 30
200	58.2 ± 0.5		
150	190 ± 80	230 ± 80	460 ± 300
80	290 ± 240	690 ± 70	350 ± 170
T(°C)	Regression coefficient (R ²)		
350	0.9959		
300		0.7669	0.6598
200	0.9951		
150	0.2912	0.9708	0.8770
80	0.4453	0.9826	0.0961

343
344 **Figure Captions**

345 **Fig. 1.** Amount of stable europium retained in the solid phase in FEBEX, MX-80 and saponite.
346 The solid line indicates the CEC of FEBEX, and the dashed line the CEC of MX-80 and saponite.
347 Red columns correspond to FEBEX results, blue columns correspond to MX-80 and the grid
348 pattern corresponds to saponite. Blank results mean that no experiment was performed for that
349 reaction time.
350

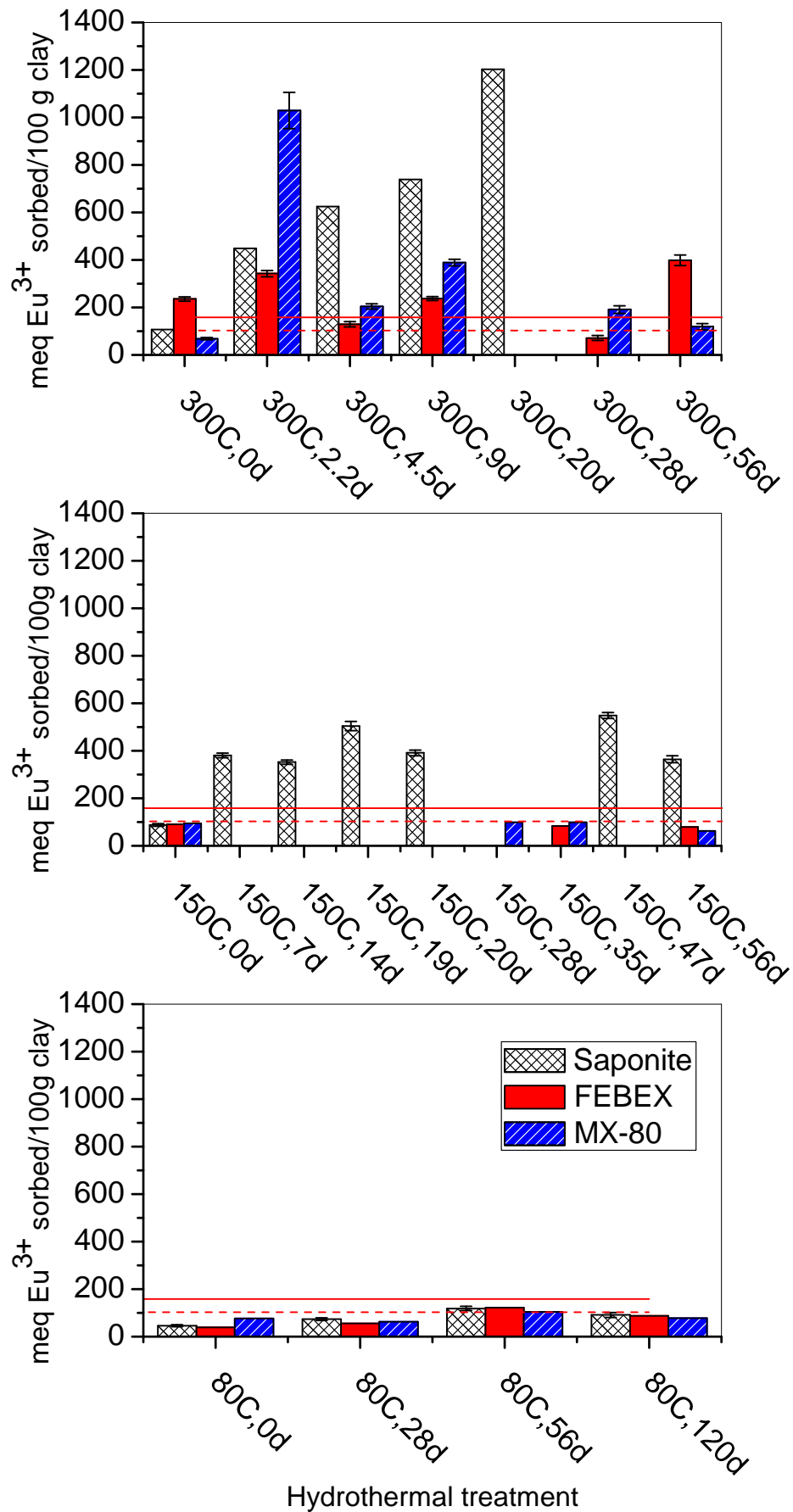
351 **Fig. 2.** ^{152}Eu (Bq) in the liquid phase after the hydrothermal treatment (unreacted ^{152}Eu) with
352 saponite, FEBEX and MX-80 versus time at (a) 300 °C, (b) 150 °C, and (c) 80 °C, data were
353 fitted to an exponential function. Initial ^{152}Eu added was 9 Bq. Red corresponds to FEBEX
354 results, blue to MX-80, and black to saponite.

355
356 **Fig. 3.** XRD diagrams of bentonite FEBEX: (a) before treatment; (b) after the hydrothermal
357 treatments at 300 °C for 0 h; (c) for 2.25 days; (d) for 4.5 days; (e) for 9 days; and (f) for 11
358 days. E= EuSiO_3 (PDF 35-297), oh= $\text{Eu}(\text{OH})_3$ (PDF 83-2305), a= $\text{Na}_8(\text{AlSiO}_4)_6(\text{OH})_2$ (PDF 40-
359 0100) and q=quartz (PDF 2-458).

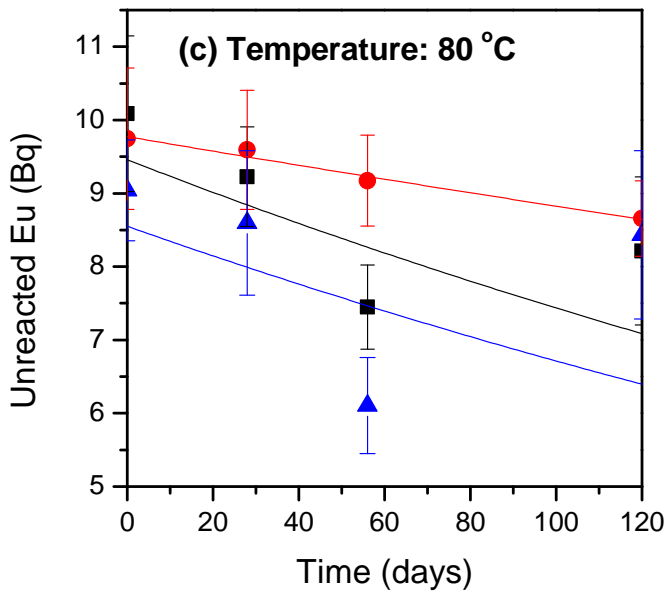
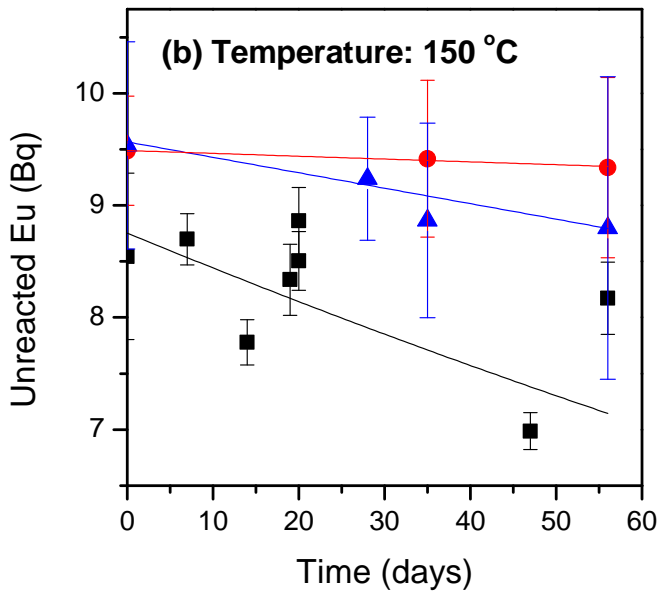
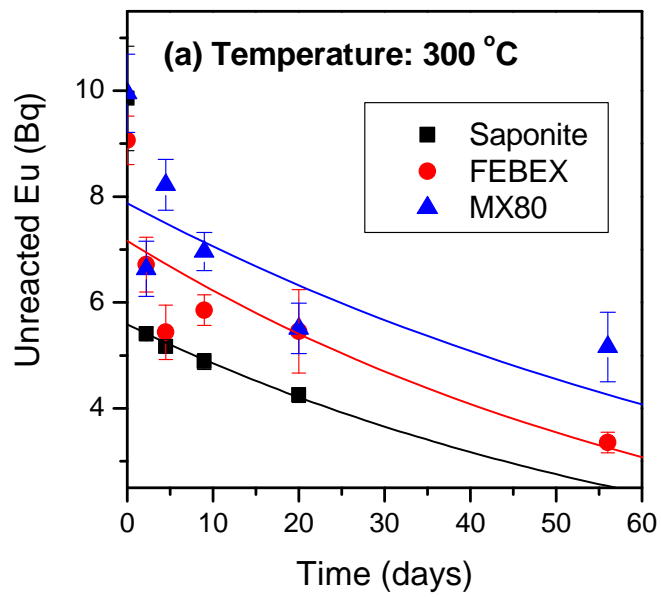
360
361 **Fig. 4.** XRD diagrams of bentonite MX-80: (a) before treatment; (b) after the hydrothermal
362 treatments at 300 °C for 0 h; (c) for 2.25 days; (d) for 4.5 days; and (e) for 9 days. E= EuSiO_3
363 (PDF 35-297) and q=quartz (PDF 2-458).

364
365 **Fig. 5.** XRD diagrams of bentonite FEBEX (left) and bentonite MX-80 (right): (a) before
366 treatment; (b) after the hydrothermal treatments at 80° C for 63 days; and (c) at 150° C for 56
367 days.

368
369 **Fig. 6.** SEM/EDX of bentonite FEBEX (left) and MX-80 (right) after hydrothermal treatment at
370 150° C for 28 days.

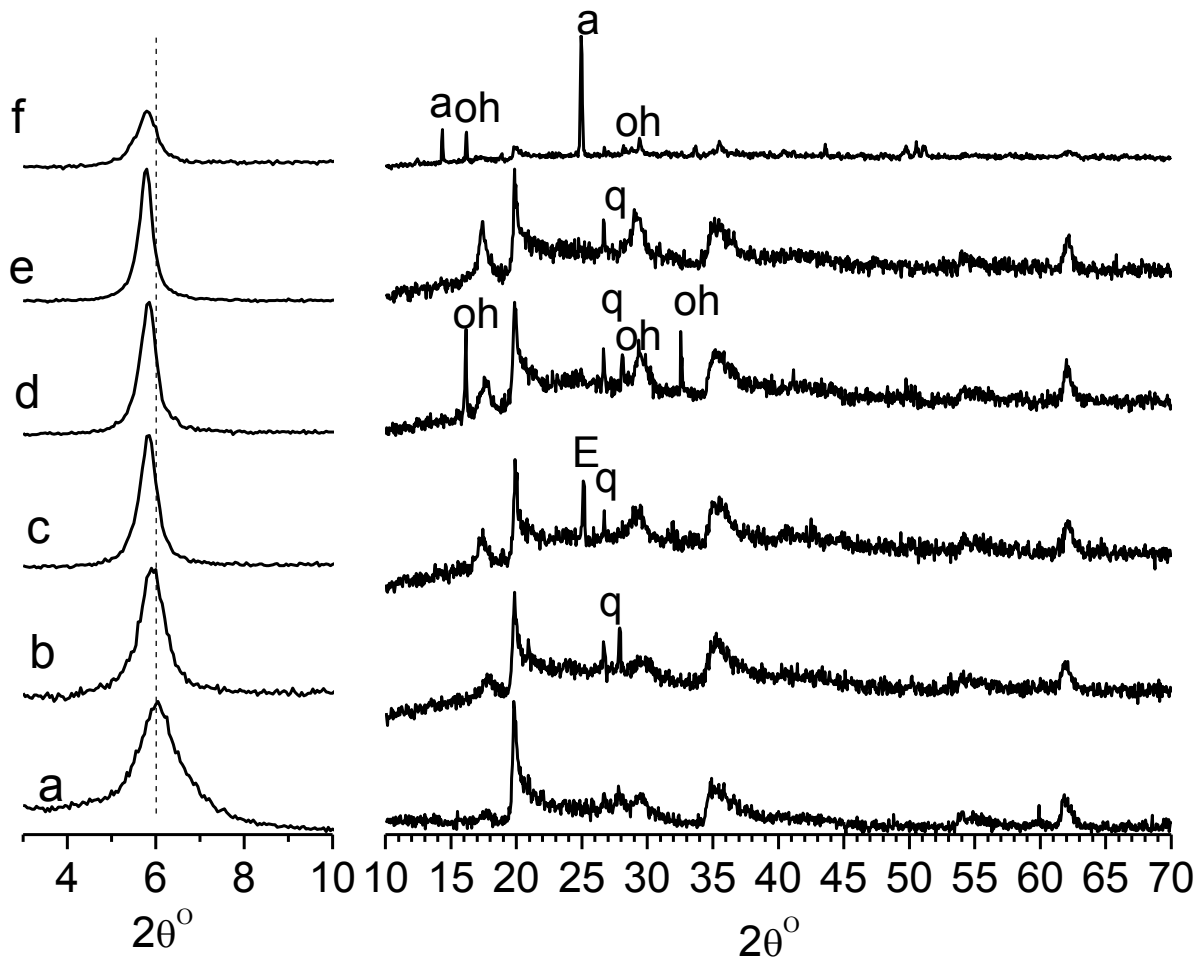


371 Figure 1



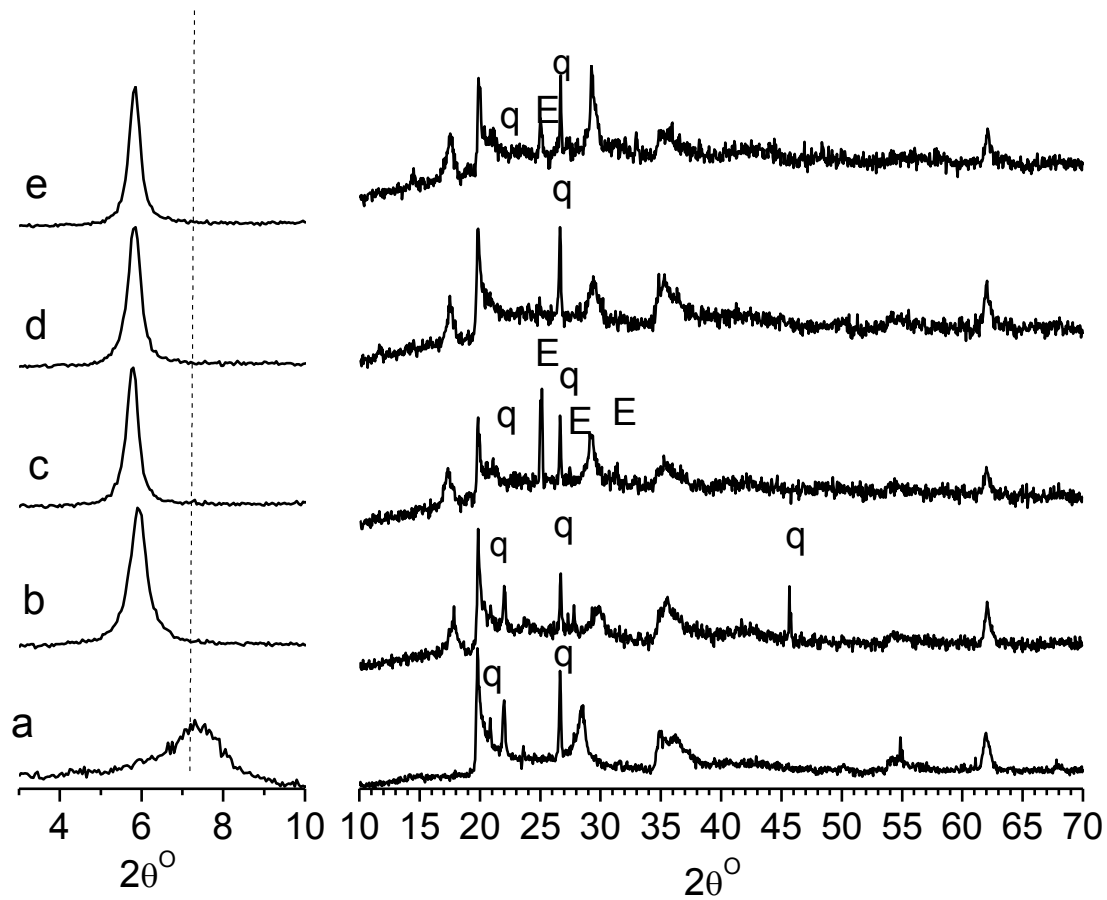
372 Figure 2

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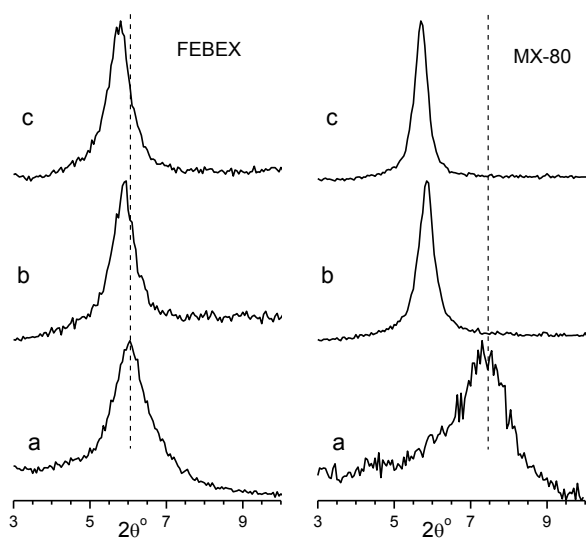
Figure 3



382

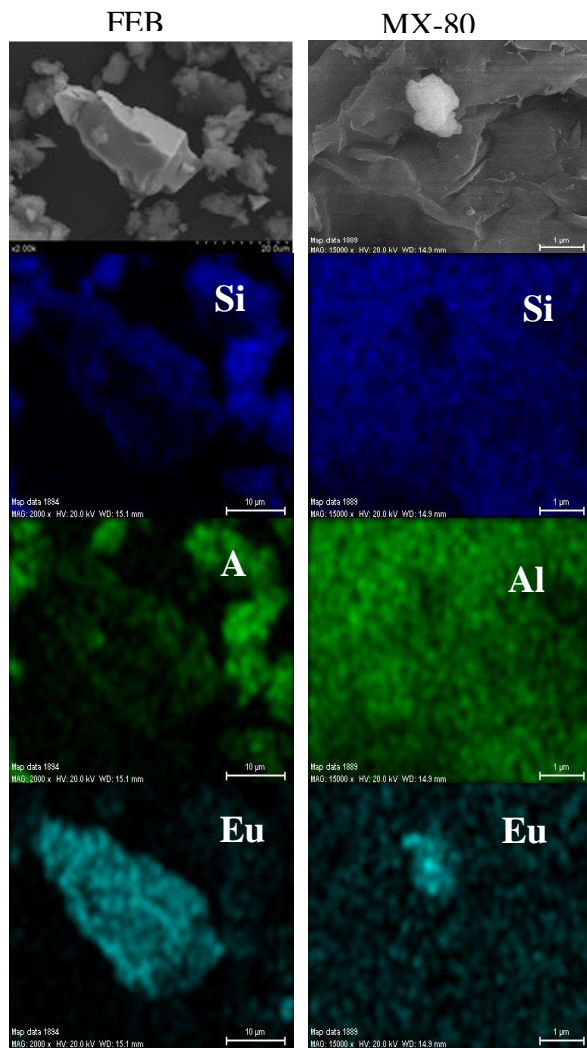
383

384 *Figure 4*



385 *Figure 5*

386



387

388

389 *Figure 6*

390