Uranium immobilization by FEBEX bentonite and steel barriers in hydrothermal conditions

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Abstract

FEBEX clay is considered a reference material in engineered barriers for safe storage of nuclear waste and uranium is a minor component of high-level radioactive waste (HLRW) and a main component of the spent nuclear fuel (SNF). Here, the kinetics of reaction of uranium with FEBEX was investigated in addition to the uranium immobilisation ability and the structural analysis of the reaction products. Hydrothermal treatments were accomplished with UO\(_2^{2+}\) and tetravalent actinide simulator ZrO\(_2^{2+}\), also present in HLRW. The quantification of the reaction was performed through gamma spectrometry of uranium. Two mechanisms for UO\(_2^{2+}\) retention by FEBEX were detected: adsorption and formation of stable and insoluble new phases. The structural analyses performed using ZrO\(_2^{2+}\), confirmed the uranium adsorption and the presence of new phases, ZrO\(_2\) and Zr(SiO\(_4\)), that emphasise the existence of a chemical reaction with the bentonite. The analysis of the velocity of reaction uranium-clay minerals revealed temperature dependence. An
exponential fitting suggested that the removal of uranium from solution at temperatures over 200 
ºC could be completed in less than a year. For lower temperatures, several years are needed. 
Milliequivalents of UO₂²⁺ immobilised by the clay depended on temperature and time and were 
over cation exchange capacity (CEC) of FEBEX even at 100 ºC (reaching 600% of CEC). The 
reaction with steel, also temperature dependent, was finally analysed. At 200 ºC 40% -70% of 
uranium reacted with steel. But only 30%-15% reacted at 300ºC and 100ºC. The reactions provide 
a stable immobilisation mechanism for uranium even when its sorption and swelling capacities 
fail. Our experiments will be of particular interest for very deep borehole disposals were higher 
temperatures and pressures are expected.

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

1. **Introduction**

   In many countries, the development of Deep Geological Repositories (DGR), for the storage 
of high-level radioactive waste (HLRW) and spent nuclear fuel (SNF), is based on a multiple 
barriers system. Most of the safety of the repositories relies on the engineered barrier which is 
mainly constituted by clay minerals [1]. Clay minerals have low permeability, high sorption and 
swelling capacity, which makes them ideal materials for natural and engineered barriers for 
nuclear waste isolation [2, 3]. Under specific experimental conditions a clay minerals barrier is 
able to delay the diffusion and immobilise radionuclides through mechanisms such as adsorption 
[4]. At the present time, bentonite is accepted as the most suitable clay mineral for the engineered 
barrier in DGRs [5]. Furthermore, very deep borehole disposal (DBD), are now emerging as a 
realistic alternative to mined repositories for spent nuclear fuel, reprocessing waste and plutonium 
[6]. Many different variants of the basic DBD concept have been proposed and, essentially, these
fall into two main categories that can be referred to as ‘high temperature’ (> \(\sim\) 700°C) and ‘low temperature (250 °C) [7].

Regarding the adsorption properties of the clay mineral [8], recent studies highlight the existence of an additional retention mechanism [9, 10]. The systematic study of the interaction of the rare earths cations (REE), such as La, Lu, Nd, Sm - as actinides chemical analogues, with natural and artificial clay minerals - revealed a reaction mechanism, based on the interaction between the lanthanide cations and the orthosilicate anions of the lamellar structure [11, 12]. At subcritical conditions (temperature and pressure), an insoluble and chemically stable phase, \(\text{REE}_2\text{Si}_2\text{O}_7\), is generated [13]. This might provide a stable immobilisation mechanism if the sorption and swelling capacities of the bentonite fail [14].

Initially, the studies focused on the structural analysis of \(\text{REE}_2\text{Si}_2\text{O}_7\) after the hydrothermal reaction between REE cations and clay minerals [9, 12, 14]. More recently, Alba et al., [11] quantified the \(\text{Eu}^{3+}\) immobilization by a standard saponite and Villa-Alfageme et al. [15] studied \(\text{Eu}^{3+}\) retention mechanisms by FEBEX and MX-80 bentonites, two of the recommended bentonites for the construction of barriers. Results proved that two mechanisms were involved in \(\text{Eu}^{3+}\) retention by the bentonites: adsorption in specific and unspecific sites and a chemical reaction consisting on the formation of europium disilicates.

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

Previous experiments were not undertaken using uranium, on the contrary REE were the major components. This work is focused on the analysis of uranium and zirconium retention by FEBEX
bentonite and the quantification of the immobilisation mechanisms through hydrothermal treatments with uranium and zirconium.

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

In previous studies we observed that during hydrothermal treatments in a steel reactor, the cations Eu³⁺, Sm³⁺ and ZrO²⁺ reacted not only with clay minerals, but also with the steel [11, 24, 25]. Furthermore, it was found that both reactions compete. Here, we expand our analysis to the retention of uranium by steel containers. Few studies to study the role of the backfill material in the kinetics and the corrosion mechanisms of steel containers have been conducted to date. An understanding of the sorption/retention of radionuclides on the materials used to construct the engineered barrier (clay and container waste) is necessary to adequately predict the long-term performance of radioactive waste disposal facilities.

Concerning the hydrothermal conditions conducted in our experiments, it should be noted that they are not completely expected in the geological repositories currently under consideration: initial storage temperatures in DGR are expected to be greater than 200 °C, with temperatures falling below 150 °C several hundred years after emplacement [26]. But most important, pressure in DGR is expected to be below the maximum subcritical pressure conditions used in the hydrothermal treatments, ~ 100 atm. Nevertheless, the studies described here have practical
interest firstly because the hydrothermal conditions of high pressure and temperature are used to
measure in reasonable times the reactions, many studies have been carried out by simulating the
deep geological disposal at temperatures up to 350 °C to increase the reaction rate [1, 14, 27].
Besides, experiments will be of particular interest for DBD repositories were higher temperatures
and pressures are expected [6, 7, 28].

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

2. Materials and methods

2.1. Bentonite.

The FEBEX bentonite was extracted from the Cortijo de Archidona deposit (Almería, Spain).
The processing at the factory consisted of disaggregation and gently grinding, drying at 60 °C and
sieving by 5mm [29, 30]. The montmorillonite content of the FEBEX bentonite was above 90%
(92±3%) [31]. The main characteristics of FEBEX bentonite are the following: (Ca0.5Na0.08K0.11)(Si7.78Al0.22)(Al2.78FeIII0.33FeII0.02Mg0.81)O20(OH)4 is the structural formula, total
charge/u.c. is 1.19 and the theoretical cation exchange capacity (CEC) value, deduced from the
molecular formula, is 158.2 meq/g [32].

2.2. U and Zr solutions

Two sets of reaction solutions were prepared. In order to make the structural characterisation
of the sample after the hydrothermal reactions, a first set was prepared containing only the
tetravalent actinide simulator ZrO2+ [33]. 1.382 g of ZrO(NO3)2·7H2O, were used to get 3.09
mmol ZrO2+, that were dissolved in 40 ml distillate water.
A second set was prepared using 0.016 mmol $^{238}$U and completed with 1.103 g of ZrO(NO$_3$)$_2$·7H$_2$O (Sigma-Aldrich). The stable analogous, ZrO$^{2+}$, was added to the uranium to obtain higher concentrations of U-ZrO$^{2+}$. 3.09 mmol (*) were dissolved in 40 ml distillate water. $^{238}$U was obtained from solid 6-hydrated uranyl nitrate, UO$_2$(NO$_3$)$_2$·6H$_2$O (Panreac). Initial activity of the prepared solution was approximately 50 Bq. Since uranium is radioactive, it is possible to directly quantify the reaction measuring the uranium activity before and after the hydrothermal treatment.

2.3. Hydrothermal treatments

Three hundred milligrams of powdered sample (FEBEX bentonite) and 40 ml of the solution with Zr or Zr-U were transferred into an 71 ml stainless steel T316SS hydrothermal reactor [34] and heated under autogenous pressure. Reaction products were collected by filtration using 0.45 µm Milipore filters and air-dried at 60ºC. In the DGR bentonite surrounds the steel and not the opposite; however, these experiments cannot be designed accordingly, given that the conditions of temperature and pressure needed for an hydrothermal treatment are actually attained when the bentonite is placed inside a sealed steel reactor that is placed in a stove.

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

2.4. Structural characterization methods.

The analysis of the hydration state of the interlayer space after the treatments and the detection of new crystalline phases were undertaken using X-ray diffraction (XRD) and a semiquantitative standard method ($\Delta2\theta$=3-70º; step=0.015º; t=0.1s; tube conditions: 40 kV y 30 mA; divergence

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* 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
slit: fixed 0.5º; sample with spin = 30 rpm; using nickel filter). A D8I powder diffractometer, located at Centro de Investigación, Tecnología e Innovación Universidad de Sevilla, CITIUS was used (θ:0, Bruker, D8 Advance A25 model, Cu anticathode, incidence slits variable or fixed, soller slits, Ni filter in the diffracted beam, linear detector).

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

2.5. Radioactive measurements

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

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

3. Results and discussion

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

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

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

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

The initial spectra of the sample showed a peak at -93.6 ppm due to Q\(^3\)(0Al) environment associated to montmorillonite [38]. After the hydrothermal treatment at 300 °C, this signal decreased abruptly and ever more significantly with the reaction time. New signals are detected at -91.2 ppm, due to kaolinite [39], at -81.0 ppm , due to ZrSiO\(_4\) [40], and at -108 ppm, due to
Q⁴(0Al) of tridimite [41]. The amount of Si associated to those environments depends on both temperature and reaction time and were in good agreement with the XRD results.

The ²⁹Si MAS NMR spectra were deconvoluted and the percentage of Si environment of FEBEX (original sample), Kaolinite (secondary phase from FEBEX breakdown) and ZrSiO₄ (phase originated by chemical reaction between ZrO²⁺ and FEBEX) were analysed as a function of temperature, Figure 4a, and time reaction, Figure 4b.

Figure 4a displays the evolution of the phases with temperature at the maximum time reaction. An increase of temperature causes a decrease on the Si signal intensity associated to a decrease in FEBEX content (phyllosilicate 2:1) and an increase of the Si signal intensity of kaolinite (phyllosilicate 1:1). However, the intensity of the Si signal of ZrSiO₄ remains almost constant, 18%. Time effect is shown in Figure 4b and follows a similar trend. A progressive decrease of FEBEX and an increase of kaolinite were observed as reaction time increases. The ZrSiO₄ phase remained also constant, ca. 18%, except for 5 days reaction time, where the phase decreased to ca. 10%. The lowest pH in the final solution (pH=1.2) was obtained at 300 ºC after five days reaction time.

The structural analysis has demonstrated that the hydrothermal treatment not only caused the adsorption of ZrO²⁺ by FEBEX, but also two other mechanisms, the crystallization of ZrO₂ and the chemical interaction with the bentonite, were involved. At the lowest temperature, 150 ºC, the kinetic of reaction allowed to detect that before the formation of ZrSiO₄, the lamellar structure was broken-down and a reconstructive mechanism was followed.

3.2. Quantification of the reactivity of bentonite with UO₂²⁺

The structural analysis showed the existence of a chemical reaction with the clay mineral that includes the formation of new stable and insoluble phases of zirconium silicates. To quantify the
immobilisation, instead of using uniquely zirconium, as the trivalent stable element analogous to uranium, uranium was added to zirconium in the hydrothermal treatment (see section 2).

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

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

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

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

Cation Exchange capacity (CEC) for FEBEX bentonite is 158.8 meq/100 g. For hydrothermal treatments of two days ($t=2$ days) and per 100 g of bentonite, only at 300 ºC the $\text{UO}_2^{2+} - \text{ZrO}_2^{2+}$
immobilised milliequivalents were over CEC, 700 ± 40. For reaction times longer than two days, the UO$_2^{2+}$ - ZrO$_2^{2+}$ immobilised milliequivalents were over CEC at 300°C, 200 °C and 100 °C. The highest amount of milliequivalents retained by 100 g of bentonite were found at 300°C for 26 days, 1200 ± 70, and at 200°C for 28 days 1150 ± 70. Milliequivalents of retained uranium were over CEC even for short hydrothermal treatments; this result emphasises that processes of formation of new phases, additional to the adsorption, did occur. In the previous section the structural study revealed that the insoluble and stable phases detected were silicates and oxides.

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

Uranium-zircon immobilization ability was compared to that of europium from previous studies [11, 15]. The immobilization ability of FEBEX was considerably higher for uranium than for europium, since in the case of FEBEX the bentonite was only able to retain europium over CEC at 300 °C and below 300 °C the amount of retained europium was of the same order of CEC. Here, regardless the reaction time, at 100 °C and higher temperatures, the mechanism of retention of uranium due to chemical reaction dominates over the immobilisation of the uranium through adsorption. This in an important conclusion in the study of the HLRW and SNF, because uranium is one of its major components and the formation of stable phases implies that the storage capacity of HLRW HLRW and SNF by the FEBEX bentonite might be higher than expected. Furthermore, our conclusions have direct impact in the study of DBD because they were obtained from hydrothermal experiments at subcritical pressure conditions (10 MPa), which are closer to the expected conditions in the DBD (200 °C- 700 °C and 40 - 150 MPa) [7].
3.3. Reaction rate of $\text{UO}_2^{2+}$-FEBEX bentonite interaction

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

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

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

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

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

$k$ value is the same order of magnitude for 300 ºC ($k = 14 \cdot 10^{-3}$ days$^{-1}$) and 200 ºC ($k = 27 \cdot 10^{-3}$ days$^{-1}$) and their values are very close according to their uncertainties. To analyse the kinetic of reaction at 100 ºC longer reaction times are needed to obtain a good precision for the reaction constant. For a hydrothermal treatment of two months, the associated uncertainty for $k$ and its regression coefficient were unsatisfactory (Table 3). Thus, at 100 ºC the reaction constant could only be obtained in order of magnitude ($k \approx 2 \cdot 10^{-3}$ days$^{-1}$).
The value of the reaction constant, \( k \), seems to be temperature dependent. Results from Table 3 provided evidences of a change in the reaction rate with temperature. Thus, for temperatures ranged between 300-200 °C, corresponding half-live times had a mean value of ca. 1 month. However, the half-life is, in order of magnitude, longer than one year for 100 °C. That means that at 200-300 °C, the uranium could be completely removed from the solution in six months, when 5 times the half-lives are completed; but six years would be needed for the total removal of uranium with FEBEX at 100 °C. It is remarkable that both periods of time are not significant in comparison to the half-life of the uranium isotope (4.47 \( 10^9 \) years).

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

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

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

### 3.4. Reaction of Uranium with the steel

The immobilisation of uranium with steel was also analysed and the results are plotted on Figure 7. This figure shows the ratio of uranium immobilised by the steel reactor to the spiked uranium. The uranium immobilised by the steel was calculated subtracting the uranium measured in filter and solution to spiked uranium. The retention by the steel depends on temperature and, as for the bentonite, uranium retention by steel presents a singularity at 200 °C. At 200 °C, a strong
linear dependence ($R^2=0.93$) with the reaction time is observed and the amount of immobilised uranium by the steel increases from 40%, at the beginning of the treatment, up to 70%. However, at 300 ºC and 100 ºC the uranium retention by steel is lower and remains constant: 30% and 15% of uranium is sorbed at 300 ºC and 100 ºC, respectively. The results are compatible with previous ones for Eu$^{3+}$, Sm$^{3+}$ and ZrO$^{2+}$ [11, 24, 25].

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

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

4. **Summary and conclusions**

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

The kinetics of reaction uranium-clay minerals is a first-order reaction and exhibit Arrhenius dependence with temperature. Removal of uranium from solution by the bentonite at temperatures...
over 200 °C would be completed in less than a year. When the temperature diminished below 200 °C, several years would be needed for a complete removal. This reaction velocity was similar for europium and uranium.

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

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

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

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

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References


[34] A.C. Perdigón, Estudio del sistema saponita/Lu(NO3)3/H2O en condiciones hidrotérmicas, University of Sevilla, Spain, 2002.


[37] M.D. Alba, A.I. Becerro, M.A. Castro, A.C. Perdigon, Hydrothermal reactivity of Lu-

[38] C.A. Weiss, S.P. Altaner, R.J. Kirkpatrick, High-Resolution Si-29 Nmr-Spectroscopy of 2-1
Layer Silicates - Correlations among Chemical-Shift, Structural Distortions, and Chemical

Si-29 Nuclear Magnetic-Resonance Spectroscopic Study of Layer Silicates, Including Clay-

[40] M. Magi, E. Lippmaa, A. Samson, G. Engelhardt, A.R. Grimmer, Solid-State High-

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

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>P$^{[a]}$ (b)</th>
<th>Time (days)</th>
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<tbody>
<tr>
<td>100</td>
<td>1.01</td>
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<tr>
<td>150</td>
<td>4.76</td>
<td></td>
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<tr>
<td>200</td>
<td>15.54</td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>85.90</td>
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</tbody>
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[a] The maximum pressure corresponds to the water vapor pressure at this temperature.

Table 2. $^{238}$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 $^{238}$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.

<table>
<thead>
<tr>
<th>Treatment time (days)</th>
<th>$^{238}$U measured in bentonite (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>300 °C</td>
</tr>
<tr>
<td>2</td>
<td>29 ± 2</td>
</tr>
<tr>
<td>5</td>
<td>42 ± 3</td>
</tr>
<tr>
<td>7</td>
<td>39 ± 6</td>
</tr>
<tr>
<td>14</td>
<td>51 ± 3</td>
</tr>
<tr>
<td>26</td>
<td>50 ± 3</td>
</tr>
<tr>
<td>28</td>
<td>49 ± 3</td>
</tr>
<tr>
<td>63</td>
<td></td>
</tr>
<tr>
<td>84</td>
<td></td>
</tr>
</tbody>
</table>
Table 3. Kinetic parameter of adsorption-reaction of uranium with FEBEX

<table>
<thead>
<tr>
<th>T (ºC)</th>
<th>k·10⁻³ (days⁻¹)</th>
<th>T_{1/2} (days)</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>14 ± 4</td>
<td>50 ± 10</td>
<td>0.693</td>
</tr>
<tr>
<td>200</td>
<td>28 ± 3</td>
<td>25 ± 2</td>
<td>0.9782</td>
</tr>
<tr>
<td>100</td>
<td>2 ± 2</td>
<td>418 ± 415</td>
<td>0.2302</td>
</tr>
</tbody>
</table>
Fig. 1. Uranium concentration versus $^{235}\text{U}$ counts per second (cps) measured through gamma spectrometry. Calibration has been performed for a) liquid solution after hydrothermal treatment b) filter containing solid phase after treatment.

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

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

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

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

Fig. 6. $^{238}\text{U}$ (%) collected in the solution after the hydrothermal treatment (unreacted uranium) 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. Results have been fitted to an exponential function.

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