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Retention of cesium and strontium by uranophane, Ca$(UO_2)_2(SiO_3OH)_2 \cdot 5H_2O$

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ABSTRACT

This work determines the capacity of uranophane, one of the long-term uranyl secondary solid phases formed on the spent nuclear fuel (SNF), to retain radionuclides (cesium and strontium) released during the dissolution of the SNF. Sorption was fast in both cases, and uranophane had a high sorption capacity for both radionuclides (maximum sorption capacities of $1.53 \cdot 10^{-5}$ mol m^{-2} for cesium and $3.45 \cdot 10^{-3}$ mol m^{-2} for strontium). The high sorption capacity of uranophane highlights the importance of the formation of uranyl silicates as secondary phases during the SNF dissolution, especially in retaining the release of radionuclides not retarded by other mechanisms such as precipitation.

1. Introduction

In order to provide the safety assessment of a deep underground repository, long-term predictions on the release of radionuclides from the spent nuclear fuel (SNF) and their likely migration through the geosphere and biosphere are necessary. After the release of some mobile radionuclides from the SNF, the main mechanism for their retention before their incorporation to the biosphere is the sorption onto mineral phases. In particular, the formation of uranium(VI) secondary solid phases due to oxidative alteration processes of UO_2(s) could have a key role in the retention of radionuclides in the near-field of the SNF.

Leaching experiments of SNF demonstrated the formation of a number of secondary solid phases depending on the chemical compositions of the leachates. In particular, in the presence of Si, ubiquitously present in most groundwaters, uranyl silicates were found to be formed after the SNF dissolution. For instance, the SNF (burnups of 27 and 30 MW d/kgU) leaching experiments carried out by Wilson with the so-called J-13 water resulted in the formation of the uranyl silicates uranophane, $Ca(UO_2)_2(SiO_3OH)_2 \cdot 5H_2O$, and soddyite, $(UO_2)_2SiO_4 \cdot 2H_2O$, at 85 °C [1–3]. With a similar water composition (EJ-13 water) and temperature (90 °C), leaching experiments with a SNF with burnups of 30 and 43 MW d/kgU carried out by Finn et al. [4] and Finch et al. [5] showed the formation of at least three uranyl silicates: soddyite, boltwoodite ($KUO_2(SiO_3OH) \cdot H_2O$) and uranophane. A mixture of these three uranyl silicates was also found in the contaminated sediments at the Hanford site [6].

One of the main effects of the formation of uranyl secondary solid phases is the possible incorporation of radionuclides released from the SNF through different mechanisms such as sorption or ionic exchange [7]. The sorption capacity of uranyl secondary solid phases was tested in different previous works and, in particular, some experiments were carried out in order to test the incorporation of some radionuclides to uranophane such as neptunium, strontium and cesium [8,9]. In such experiments, in uranophane synthesized in the presence of solutions which contained a certain amount of the radionuclide, it was actually incorporated at some extent to the uranophane lattice. These experiments could not identify the mechanism by which the radionuclides were incorporated to the solid. For this reason, the main objective of the present work is to determine the sorption capacity of uranophane through batch experiments consisting on mixing weights of the solid with solutions containing strontium or cesium.

On one hand, strontium was chosen because the ^{90}Sr isotope is considered one of the most important radioactive isotopes in the environment [10,11], being of particular concern because of its high fission yield, its penetrating ionizing radiation (β and γ) during the first several hundreds of years, and its chemical similarity to calcium which might be eventually replaced by strontium in human bones [12,13]. On the other hand, cesium was chosen because it is present in radioactive wastes as a fission product, and the ^{135}Cs (half-life: $3 \cdot 10^6$ years) and ^{137}Cs (half-life: 30 years) isotopes are considered harmful isotopes contributing to the radiation hazard of the nuclear waste [9]. In addition, due to the high solubility of most strontium and caesium solid

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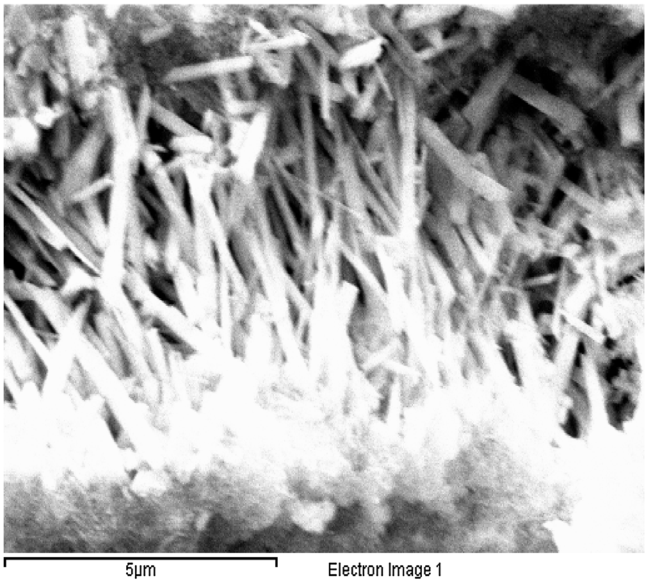

Fig. 1. Morphology of the synthesized solid determined by SEM.

phases, the most probable mechanism for their retention, once released from the nuclear waste, will be sorption on the uranyl secondary solid phases formed on the SNF surface or on mineral phases surrounding the repository.

2. Experimental

2.1. Synthesis and characterization of uranophane

Uranophane was synthesized following the procedure developed by Nguyen et al. [14]. Uranyl nitrate, calcium acetate and sodium silicate solutions were mixed together at pH = 8 and heated at 363 K for 24 h. The solid phase obtained was later cleaned with Mili-Q water and introduced into a PARR reactor in contact with ultra-pure water for four weeks at 398 K, in order to recrystallize the uranophane. Finally, the solid was filtered, rinsed with Mili-Q water and stored under dry conditions.

X-ray diffraction (XRD) and RAMAN spectroscopy showed that the solid was pure α-uranophane. In addition, the solid synthesized had the typical needle shape morphology of uranophane [15] (see Fig. 1 for a microphotograph of the solid surface made with Scanning electron microscopy, SEM).

The specific surface area of the synthesized uranophane was determined following the BET methodology. The solid obtained from the synthesis was grinded and sieved, and the surface area for particles with less than 0.05 mm size was 33.42 ± 0.06 $m^2 g^{-1}$.

The point of zero charge of the solid (pH_{pzc}) was determined by using the so-called 'immersion methodology' [16–18]. 0.05 g of uranophane were immersed in 20 cm^3 of a 0.01 mol dm^{-3} NaCl solution with a known initial pH (between 5 and 10, measured with a GLP-22 Crison 50-14 pH-meter). The equilibrium pH was measured after 24 h of contact. The variation of the equilibrium pH against initial pH (Fig. 2) showed a V-shaped curve. From the vertex of the curve, a pH_{pzc} of 7.9 ± 0.1 was calculated. The value obtained was similar to the theoretical value calculated for uranophane, pH_{pzc} = 8, [16].

2.2. Experimental methodology

Cesium and strontium solutions were prepared dissolving $CsClO_4$ (Acros Organics) and $Sr(NO_3)_2$ (Merck) in Milli-Q water. Sorption batch experiments were carried out at room temperature and following the same methodology reported in previous works (see for example reference [19]). In short, 0.05 g of uranophane were put in contact with 20 cm^3 of a strontium or cesium solution in polystyrene tubes. The tubes were continuously stirred until equilibrium was reached. At the end of the experiment, samples were taken and filtered through 0.22 μm MICROPORE pore-size filters. Strontium and cesium concentrations in solution were determined by Inductively Coupled Plasma Mass Spectrometry (ICP-MS).

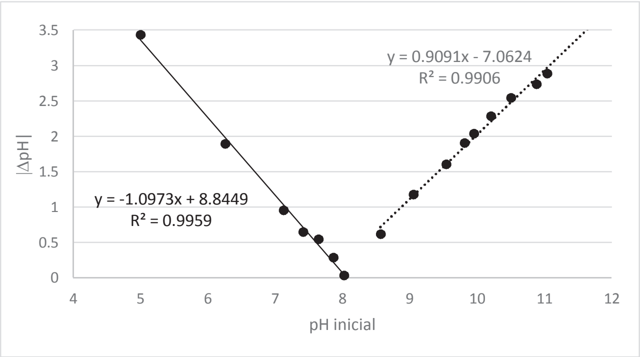

Fig. 2. Evolution of the solution pH as a function of the initial pH value.

When necessary, the pH of the solutions was varied by adding either $HClO_4$ (Merck) or NaOH (Acros Organics). Experiments were carried out at two different ionic media: 0.1 mol dm^{-3} and 0.01 mol dm^{-3} $NaClO_4$ (Merck) both under oxic conditions (in synthetic air).

Two different series of experiments were carried out for each radionuclide: sorption kinetic experiments and sorption isotherm experiments.

In the first series, the evolution of the radionuclide concentration in solution was determined as a function of time in experiments with the same radionuclide concentration, weight of solid and pH. For each radionuclide, two series of experiments, with different ionic medium (0.01 mol dm^{-3} and 0.1 mol dm^{-3} $NaClO_4$, respectively), were carried out. The initial concentration of the radionuclide was $7.5 \cdot 10^{-7}$ mol dm^{-3} in the case of cesium and $1.25 \cdot 10^{-5}$ mol dm^{-3} in the case of strontium. The solutions were put in contact with 0.05 g of uranophane. The different solutions of each series of experiments were in contact with the solid during different times. Once separated from the solid, each solution was filtered and final strontium or cesium concentrations were determined by ICP-MS.

In the second series, the evolution of the radionuclide concentration in solution was measured in different experiments with a variable initial concentration of the radionuclide and the same weight of solid and pH (sorption isotherms). Isotherms were carried out in a 0.01 mol dm^{-3} $NaClO_4$ ionic medium, although some experiments were additionally carried out at 0.1 mol dm^{-3} in order to corroborate the effect of the ionic strength observed in the kinetic experiments.

3. Results and discussion

3.1. Kinetics of sorption and effect of the ionic strength

Sorption kinetics experiments were performed in order to establish the time needed to reach the equilibrium in the sorption process (which was subsequently used in sorption isotherms experiments as the ending time). In addition, the knowledge of the rate of sorption contributes to evaluate the actual influence of the kinetics of the process on the radionuclides retention in the near-field of a high level nuclear waste repository (HLNWR), that is, whether the radionuclides retention process would be kinetically controlled.

The evolution of the amount of radionuclide sorbed on uranophane as a function of time is shown in Fig. 3. The percentage of sorption was calculated from the ratio between moles sorbed of radionuclide and moles initially present at the solution.

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