

Radiolysis effects on U–Pu co-precipitation experiments in granitic–bentonitic groundwater under oxidizing and anoxic conditions

J. Quiñones^{a,*}, E. Iglesias^a, A. Martínez Esparza^b

^a CIEMAT, Avda Complutense 22, 28040 Madrid, Spain

^b ENRESA, C/ Emilio Vargas 7, 28043 Madrid, Spain

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Abstract

The main objective of this paper is to study the role of groundwater radiolysis in the spent fuel matrix alteration process. In order to split the influence of each radiation field, the paper focuses on the α -radiation field effect. For this reason the system selected was U–Pu in a synthetic granitic–bentonitic groundwater (carbonate media) in order to simulate the environmental conditions of the Spanish repository scenario [ENRESA, Publicación Técnica ENRESA 03/99 (1999) 219]. The experimental procedure used allows both the influence of the α -radiation field on the U secondary phase formed (and its solubility) and the Pu concentration in solution under simulated environmental conditions to be studied and makes it possible to determine whether any co-precipitation process takes place under these environmental conditions.

Previous experimental evidence provided by Haschke et al. [J.M. Haschke, T.H. Allen, L.A. Morales, *Science* 287 (2000) 285] pointed to a reaction cycle between Pu^0 and water vapor (at 250 °C) generating $\text{PuO}_{2+x}(\text{s})$ for the first time. Taking this work into account, the objective is to check whether this reaction mechanism will have any influence under the environmental conditions considered.

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1. Introduction

The definition and the evolution of the source term for high level waste repositories are key issues related to performance assessment studies. They are essential to determine the most conservative; but realistic, concentration for each radionuclide under repository conditions. The stability of spent fuel and its ability to retain radionuclides is not a property inherent to the materials, but depends rather on the waste package and the properties of the container, including their corrosion in groundwaters in the event of water infiltration. Important processes controlling radionuclide release include: dissolution in voids and at grain boundaries, inventories of segregated radionuclides, caused by the radiolytic production of oxidants, oxidative dissolution of the fuel matrix, radionuclide sorption on solid phases in the near field and the formation of secondary solid alteration products by

precipitation or co-precipitation, this also providing new host phases for the retention of radionuclides [1,2].

This empirical approach is of particular importance for thermodynamic databases, but it is not sufficiently complete to unambiguously predict solubilities in multi-component systems, such as aqueous media in contact with spent fuel. Furthermore, the on-going work will support realistic geochemical modeling of spent fuel/groundwater interactions by identifying radionuclides and the thermodynamic properties of elements needed to be described in terms of solid solution, the solubility of which is better described by pure phases.

This paper describes the co-precipitation phenomena of dissolved spent fuel in different media [2–4], and focuses on the results obtained from precipitation and co-precipitation tests performed with U and Pu in a supersaturated solution of granitic–bentonitic groundwater. This scenario would take place after $\approx 10,000$ years of disposal following contact between the groundwater and the spent fuel. The α -radiation field will also have a major effect on the spent fuel alteration process, and also as regards assessment of the influence of this α -radiation field

* Corresponding author. Tel.: +34 913466290; fax: +34 913466233.
E-mail address: javier.quinones@ciemat.es (J. Quiñones).

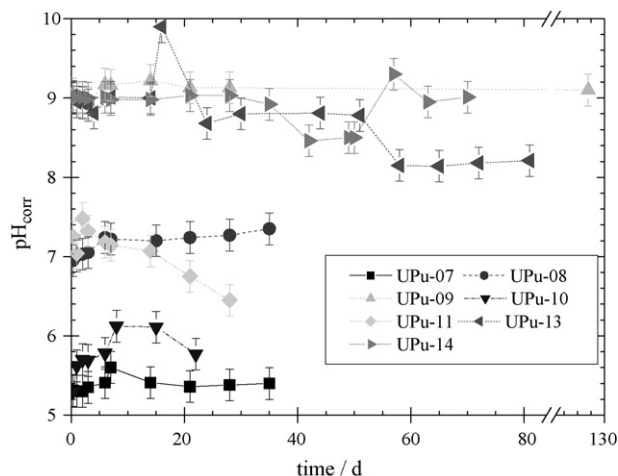


Fig. 1. Evolution of pH during co-precipitation experiments.

on the U secondary phases formed and the final concentration value obtained for U and Pu.

2. Experimental methodology

Co-precipitation experiments were carried out under oxic (air atmosphere) and anoxic (N_2 , N_2 - CO_2 atmospheres) conditions at room temperature and pressure ($P=0.1$ MPa and $T=298$ K). The tests were performed in a synthetic granite–bentonitic groundwater (carbonate media)[5].

In relation to the ^{241}Pu starting solution, a purification process was initially performed to separate the Am from its daughter, which had reached a condition of secular equilibrium during sample storage since the last such process (DOWEX 1×8 column used). A titration process was performed in accordance with the established procedure [2–4]. NaOH (0.1 N) was used to adjust the pH to three different values (5.3, 7 and 9). The system was stirred during the process at 200 rpm. The starting solutions used had a molar fraction ratio between Pu/U $\approx 2 \times 10^{-6}$, identical to that of spent fuel with a burnup of 40 MWd/kg U.

Prior to chemical analysis, aliquots were filtrated and ultrafiltrated through 220 and 8 nm, respectively. The samples were acidified and prepared for U and Pu analysis using α and β spectrometry and ICP-MS.

3. Results and discussion

The methodology used for the experimental process allows for strict control of the pH until the system achieves a steady state. The evolution of pH and Eh redox potential values for each experiment is shown in Figs. 1 and 2, respectively. Most of the tests were performed in a controlled atmosphere and in the absence of oxidizing agents. The environmental parameters of each different experiment are summarized in Table 1. The U and Pu concentrations in solution are shown in Figs. 3 and 4, for each experiment. In all the figures presented, the solid and open symbols correspond to the values obtained from filtrated and ultrafiltrated aliquots, respectively.

Fig. 5 shows the mean U and Pu concentration data obtained for each selected value (both filtrated and ultrafiltrated data). As has been mentioned above, the U or Pu average concentration value was calculated from at least the last five concentration values measured in each experiment (once the system had achieved a steady state). The U concentration is independent from the initial redox conditions (Fig. 5); however, Pu concentration values were not independent from the redox potential attained. When

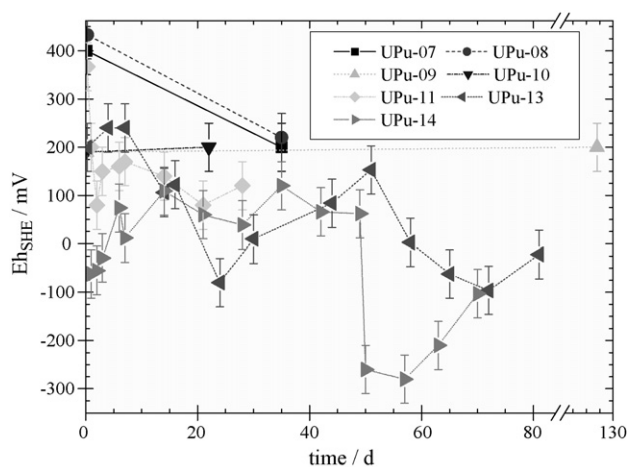


Fig. 2. Evolution of redox during U–Pu co-precipitation experiments.

Table 1
Experimental conditions

Experiment, label	Synthetic groundwater	Redox conditions (atmosphere)	pH
U–Pu, 7	AGB	Air	5.3
U–Pu, 8			7.0
U–Pu, 9			9.0
U–Pu, 10	AGB	Anoxic (CO_2 - N_2)	5.3
U–Pu, 11			7.0
U–Pu, 13	AGB	Anoxic (CO_2 - N_2)	9.0
U–Pu, 14			9.0

these results are compared to those from tests performed under similar conditions, but in the absence of an α -radiation field and under oxic conditions [4] (see Fig. 6) at $pH > 8$, similar U concentration behaviors were observed. This similar behavior (for anoxic and oxic conditions) might be explained as a consequence of the water α -radiolysis, i.e., the radiolysis generates sufficient oxidant species to produce (under anoxic conditions) an increase

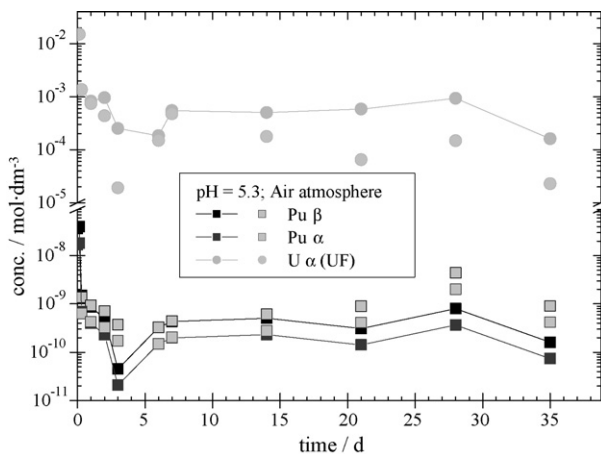


Fig. 3. Evolution of U and Pu concentration in solution in a co-precipitation experiment at fixed pH (5.3) and under oxidizing conditions.

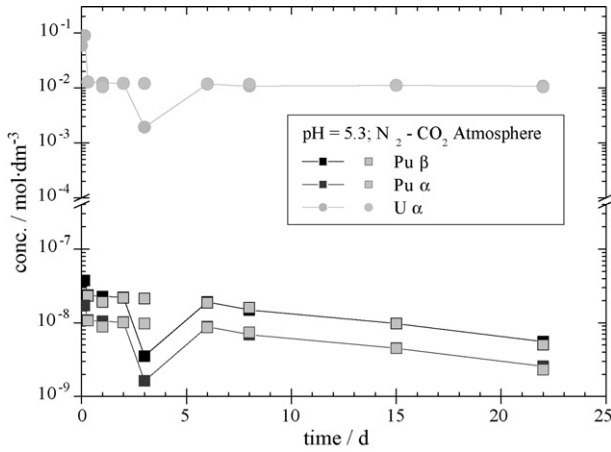


Fig. 4. Evolution of U and Pu concentration in solution in a co-precipitation experiment at fixed pH (5.3) and under initially anoxic conditions.

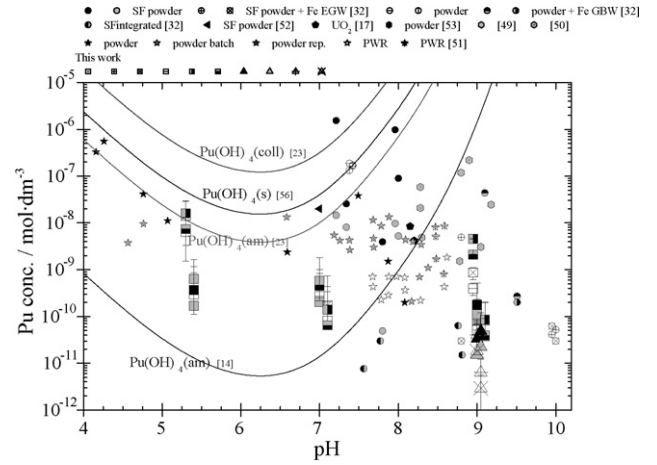


Fig. 7. Comparison of the [Pu] obtained in this experiments with those published in previous papers [6,7] and solubility values calculated for the pure phase.

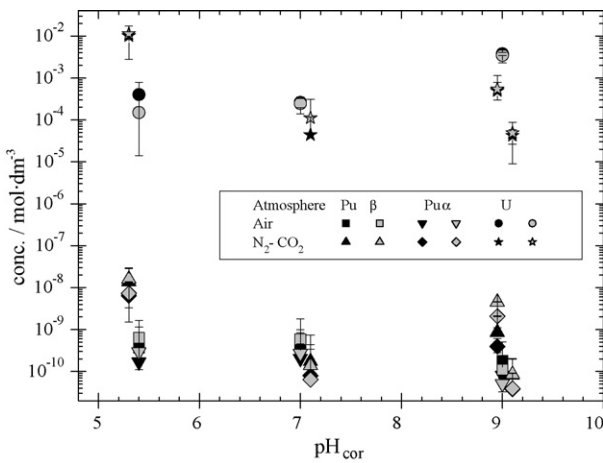


Fig. 5. Evolution of U and Pu concentration vs. pH and initial redox conditions.

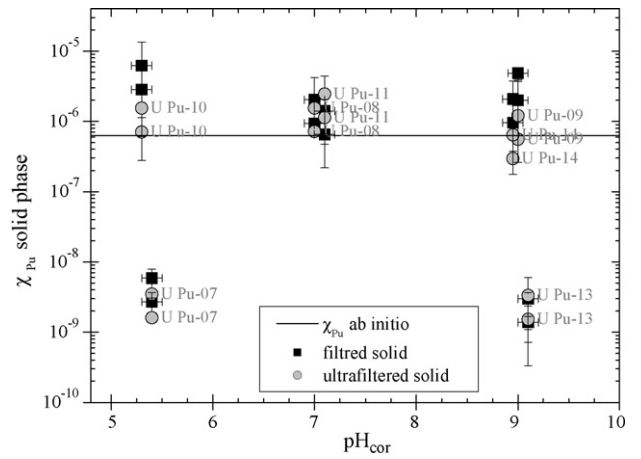


Fig. 8. Evolution of Pu molar fraction in solid phase vs. pH.

of the final U concentration in solution measured similar to that found under oxic conditions. In the case of Pu, the final solution concentration is very similar to that measured both in spent fuel [6] and/in Pu-doped pellet leaching [7] experiments (see Fig. 7). Moreover the molar fraction of Pu/U (measured by ICP-MS,

see Fig. 8) remains the same as in the starting solutions. A co-precipitation process between U and Pu was not observed under the environmental conditions simulated. The physicochemical characterization of the solid precipitated by XRD shows (unlike in the case of previous experiments performed in the absence of

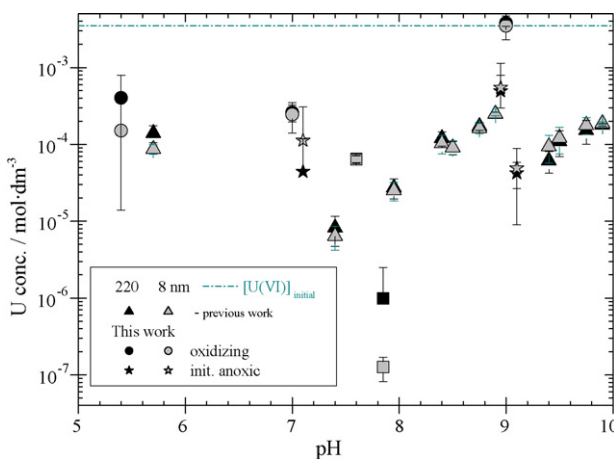


Fig. 6. Influence of redox, pH and presence of Pu on the U concentration in solution.

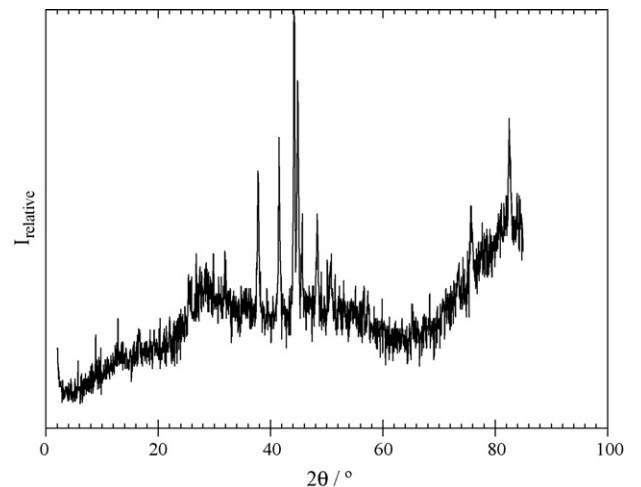


Fig. 9. Solid phase diffraction pattern.

Pu [4]) an amorphous structure (XRD-pattern) in all the solid phases observed (see Fig. 9).

4. Conclusions

U–Pu co-precipitation studies and characterization of the solid phases formed show that Pu versus U exemplifies the influence that an α -radiation field has on the U concentration in solution achieved in the carbonate media system (U solubility value). This experimental evidence shows that when the spent fuel is altered and the radionuclides are dissolved in the surrounding groundwater, the environmental conditions will change from reducing to oxidizing conditions. Performance assessment studies of the repository (at this period of time) will be necessary to consider not only the radiation field generated by the spent fuel but also those coming from dissolved or precipitated radionuclides. This scenario will have a relevant role for long periods of time (in excess of 10,000 years).

The U concentrations measured show similar values for experiments performed under oxidizing conditions and those performed under initially anoxic conditions. This experimental evidence underlines the key role of water radiolysis in the alteration rate of the spent fuel under repository conditions.

The bulk characterization of the precipitated solid phases shows that the Pu versus U molar fraction continues in both the solid and aqueous phases. This fact seems to indicate that a simultaneous precipitation process of the pure phases has taken place, and not of the mixed phase of U–Pu, although the experimental work performed provides no evidence of a co-precipitation process.

The thermodynamic model proposed is based on an assumed simultaneous $\text{Pu}(\text{OH})_4$ (am, anhyd) and sodium uranate precipitation, with no co-precipitation phenomena in the system on the environmental conditions interval proposed for the study.

The presence of Pu in solutions produces an increase of oxidants due to water radiolysis, and a modification of U solubility. This fact might have a direct effect on the definition of the source term, from the point of view of the safety analysis for a repository. This may affect the possible formation of secondary phases on the matrix, passivation effects – and consequently changes in the matrix alteration rate – and solubility of those elements sensitive to redox conditions.

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