COPRECIPITATION OF SIMFUEL IN BENTONITIC-GRANITIC GROUNDWATER UNDER OXIDIZING CONDITIONS

J. Quiñones[+], J.A. Serrano[+], P. Diaz Arocas[+], J. Cobos[+], J.L. Rodriguez[+],
A. Martinez-Esparza[*], J. Esteban[*]
[+]CIEMAT. Dept. de Fision Nuclear. Avda. Complutense 22. 28040-Madrid. SPAIN
*Enresa. C/ Emilio Vargas 7. 28043-Madrid. SPAIN

ABSTRACT

To determine the concentration controlling solid phases and coprecipitation process for elements contained in spent nuclear fuel, SIMFUEL coprecipitation trials under simulated bentonitic-granitc groundwater were performed. These experiments were carried out under oxidizing conditions at pH values ranging from 5 to 10. In this work an effort to determine whether solubility of pure phases could predict the behaviour of each element or whether it would be necessary to consider the formation of mixed solid phases was made.

Steady state for all elements was achieved after 10 days. The highest U concentrations values were achieved for pH > 8. Sr steady state concentration showed slight changes with pH. In the case of Ba, for pH > 8 the steady state concentrations underwent a high reduction. For lanthanide elements La, Ce, Nd and metals Y, Ru and Rh the tendency was to decrease with pH.

A tentative approach for modelling Sr concentration as a function of pH in bentonitic-granitic groundwater was performed. The comparison of experimental and thermodynamic data supports the idea of a possible control by the precipitation of different pure solid phases. As a function of pH values the controlling phases chosen were: pH < 7 Celestite, 7 < pH < 8 Strontianite and for pH > 8 Calcite.

This work was supported by a CIEMAT-ENRESA agreement and a EU Contract FI4WCT950004.

INTRODUCTION

During the last 30 years the concept of geological disposal of spent nuclear fuel in corrosion resistant containers has been investigated in several countries [1, 2, 3]. The objective of the disposal concept is to minimize the transport of radionuclides into the biosphere so that the effect on man and the environmental is negligible.

The repository safety assessment requires the definition and knowledge of different phenomena involved in the degradation of the waste package and the migration of radionuclides into the geosphere. One of the key topics to define is whether in modelling the dissolution process of the waste package under repository conditions if it is enough to consider only thermodynamic control or if the process could be controlled by kinetic factors.

For safety assessment of the repository the radionuclide release from spent fuel to near field is a parameter normally controlled by solubility [4, 5, 6]. The second question that appears is whether the solubility control comes from a precipitation process of a pure solid phase or from mixed solid phases. [7]

This paper presents the results obtained in coprecipitation experiments with SIMFUEL (a chemical analogue of spent fuel [8]) under simulated repository conditions. The leachant used was bentonitic granitic groundwater [9], because granite is considered in the Spanish repository concept as one candidate host rock. Coprecipitation studies were performed in the pH range of 5 – 10.

A tentative approach for modelling the Sr concentrations as a function of pH in bentonic granitic water was performed. The comparisons between experimental and thermodynamic data suggest the idea of a possible control by precipitation of different pure solid phases.

EXPERIMENTAL CONDITIONS

Coprecipitation experiments were started from uranyl supersaturated solutions. This solution was prepared by dissolving SIMFUEL (pellets supplied by AECL) fragments into strong acid media.

The titration process was used to select the chosen pH by slow addition of 0.1 N NaOH solution. Adjusted pH values were in the range between 5.7 – 10. The pH was readjusted every 12 h. After some days the pH remained constant. The reaction solution was continuously stirred at 200 rpm. At least, 10 aliquots of the aqueous suspensions were taken during the experimental time (more than 1 month).

The samples were filtered using membranes with a pore size of 0.45 μm. Some of those aliquots were additionally ultrafiltered through membranes of 1.8 nm, to obtain the upper limits for colloidal contributions to the totally dissolved quantity of the element.

During the coprecipitation trials pH and Eh were measured. The values reported in the paper were previously corrected according to the ionic strength of the leachants [6].

Aliquots of filtered and ultrafiltered solutions were analysed by ICP-MS and fluorimetric techniques. The data presented in this work are the mean value obtained from the analyses. The error plotted was calculated for each mean concentration value using the following equation $\varepsilon = 1.96 \cdot \frac{\sigma_n}{\sqrt{n}}$

The solution used in this coprecipitation test was bentonitic granitic groundwater [9]. The tests were performed at room temperature.

RESULTS AND DISCUSSION

In all the tests the starting concentration of U was 10^{-3} mol/kg H_2O. The initial supersaturated solution had the same mole fraction (related to U) as in SIMFUEL. This solution had an initial pH of 1 and it was titrated until the pH of interest was reached. Aliquots were filtered and some of them ultrafiltered before analyses. In all plots, they are labelled with 0,22 µm and 1.8 nm, respectively.

Results of U steady state concentration obtained are given in Fig. 1. During the tritation process a yellow solid phase is formed in all the experiments. This phase formed explained the depletion of U concentration in solution. As can be observed, for pHs higher than 8 the U steady state concentration is around 10^{-4} mol/kg H_2O. The trials were performed under atmospheric conditions and due to carbonate complex formation, an increase in U steady state concentration in the pH range of 7 to 9 is detected.

Results from Sr and Ba steady state concentrations are given in Fig. 2. Initial average concentration for each element is plotted as dotted lines. As can be observed, there is a low influence of colloid formation in steady state concentration for both elements. For pH > 7 depletion respect to the initial concentration is measured.

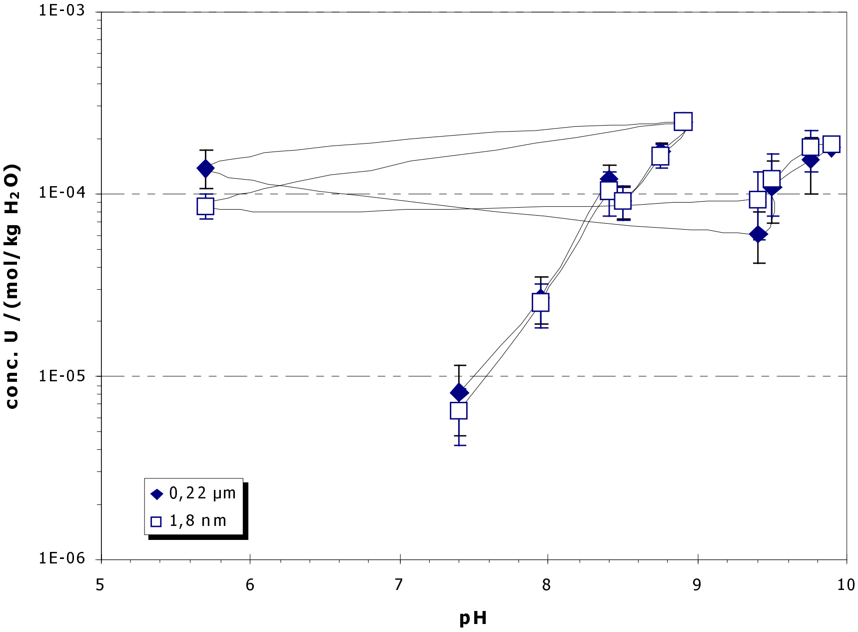

Fig. 1 U steady state concentration vs pH in bentonitic-granitic media.

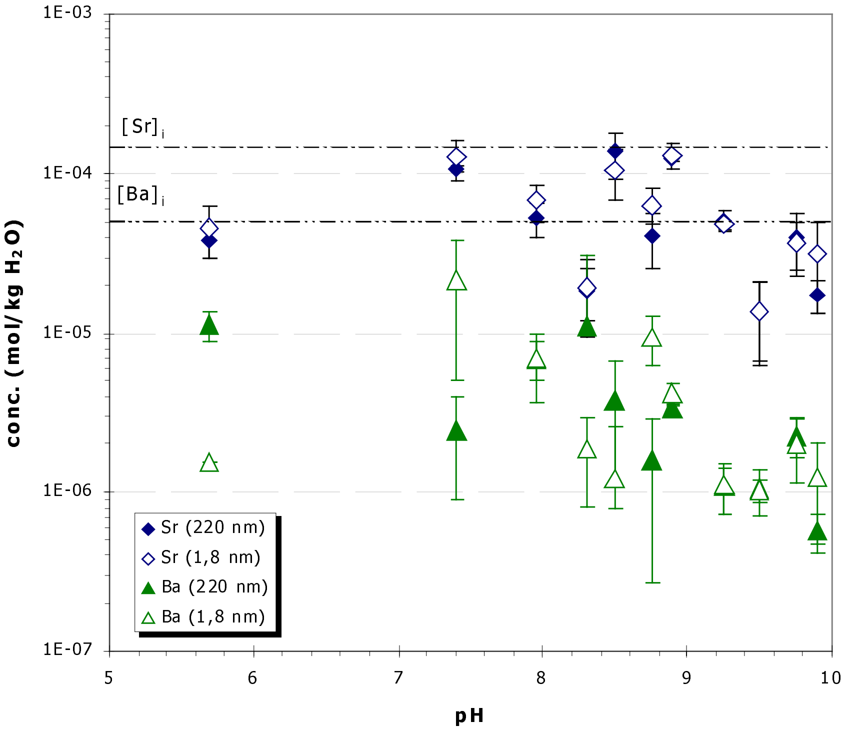

Fig. 2 Sr and Ba concentrations in bentonitic-granitic media under oxidizing conditions

In the case of Ba in all test the steady state concentrations underwent a high reduction, i.e. for pH > 8 the reduction was higher than two orders of magnitude, however Sr concentration remains almost constant in all the pH range studied.

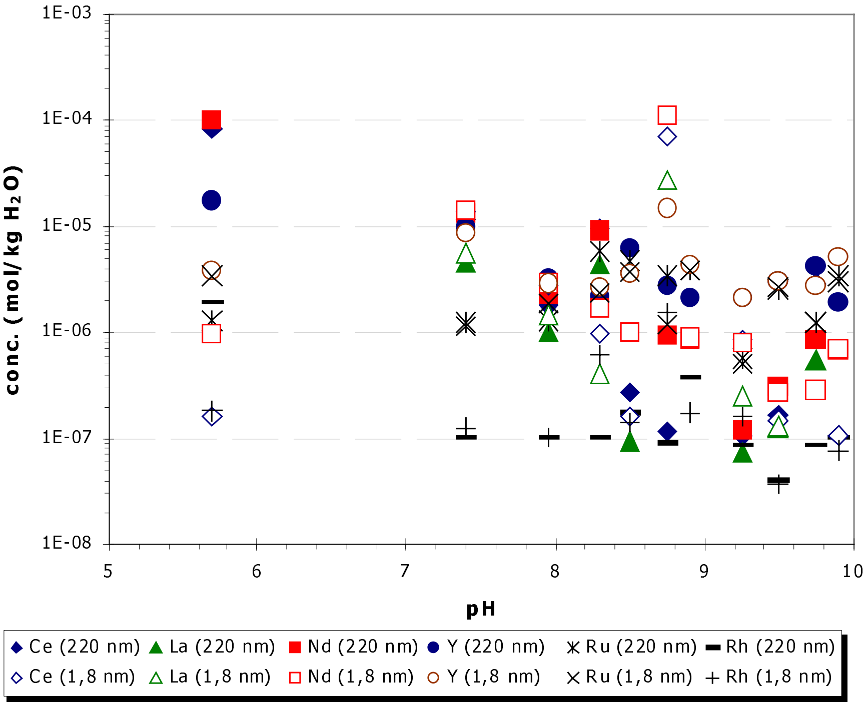

Fig. 3 Concentration of SIMFUEL minor elements in bentonitic-granitic media.

For lanthanide elements La, Ce, Nd and for metals Y, Ru and Rh the tendency is to decrease their concentration with pH. In aqueous solution the predominant oxidation state of lanthanides is +3 (Ce(IV) ions are metastable) [10]. Under experimental conditions Y(III) is stable state whilst Ru and Rh show a different oxidation state. La, Ce, Nd and Y show a close behaviour as a function of pH. For pH > 7.5 the steady state concentration of these elements remains almost constant.

A tentative approach for modelling Sr steady state concentration as a function of pH is given in Fig. 4. In triangle points SIMFUEL leaching concentration values obtained are given. The lines represent the Sr solubility calculated as function of the control solid phase considered (celestite, strontianite or calcite). A comparison between experimental [11] and thermodynamic data [12] of Sr solubility considering a solid phase formation support the following chemical control model: For pH < 7 the solid phase that controls the Sr solubility is celestite; when 7 < pH < 8 the phase is strontianite, and for pH > 8 the calcite formation controls the Sr concentration in solution.

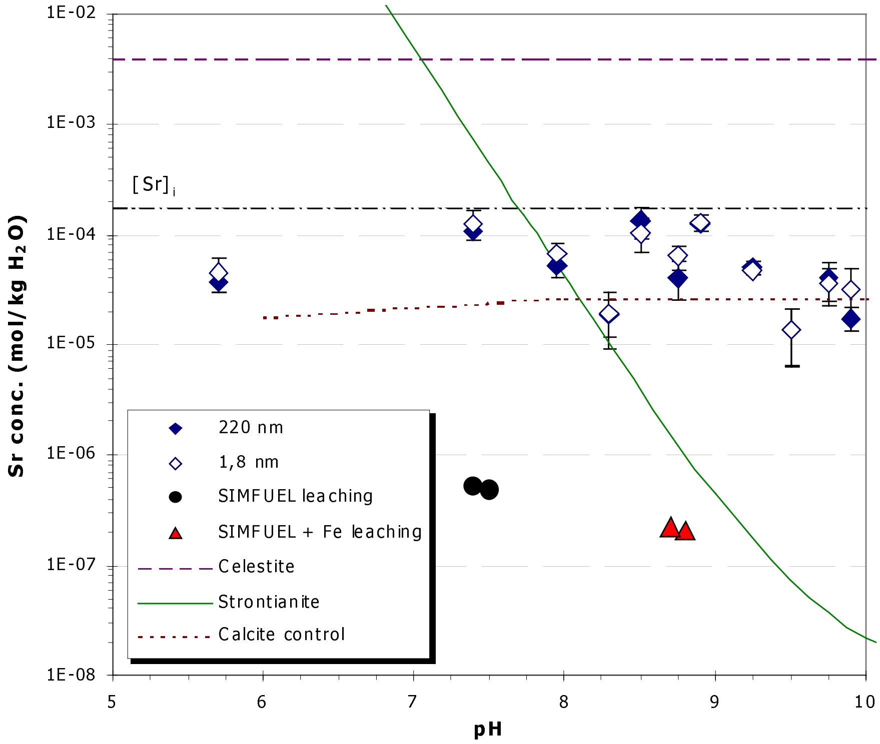

Fig. 4 Sr concentration from experimental and calculated data.

On the other hand, as can be observed in Fig. 4, the values achieved from leaching are lower than obtained in coprecipitation tests. This fact could be explained by taking into account that the amount of the solid dissolved in the case of leaching tests is very small as comparison with precipitation trials.

CONCLUSIONS

Coprecipitation studies are a very useful tool for understanding the behaviour and upper concentration of key elements under final repository conditions.

The highest U concentrations values were achieved for pH > 8. Sr steady state concentration remains almost constant. However in the case of Ba, for pH > 8 the steady state concentrations underwent a high reduction.

From experimental Sr data obtained in bentonitic-granitic groundwater and thermodynamic data, Sr concentration seems to be controlled by the precipitation of different pure solid phases. As a function of pH values the controlling phases chosen were: pH < 7 celestite, 7 < pH < 8 strontianite and for pH > 8 calcite.

References

1 Grambow B., Loida A., Dressler P., Geckeis H., Diaz P., Gago J., Casas I., de Pablo J., Gimenez J., Torrero M.E. "Reaction of high burnup spent fuel and UO2 in saline brines at room temperature" KfK Report 5377 (1994)

2 Johnson L.H. and Werme L.O. MRS Bulletin 12/1994.
3 Forsyth, R.S., Werme L.O., Spent Fuel Corrosion and Dissolution, J. Nucl. Mater. **190**, 3-19(1992)
4 Bruno J., Grenthe I. and Muñoz M. Mat. Res. Soc. Symp. Proc. **50**, 717-726 (1985).
5 Van’t Hoff J.H. Z. Physik, Chem. **5** 322 (1890).
6 Geckeis H., Grambow B., Loida A., Luckscheiter B., Smailos E., Quiñones J. Radiochim. Acta **82**, 123-128 (1998)
7 Quiñones J., Grambow B., Loida A., Geckeis H. J. Nucl. Mater. **238**, 38 (1996)
8 Lucuta P.G., Balmer B.J., Matzke Hj and Hartwig D.S., Preparation and Characterization of SIMFUEL: Simulated CANDU High-Burnup Nuclear Fuel: Atomic Energy of Canada Report AECL-1017 (1989)
9 Martinez A., Melon A., Valladares J., Rivas P. CIEMAT Specific Procedure Nº PR-X8-01 (1996)
10 Cotton S. “*Lanthanides and Actinides*” MacMillan education Ltd. (1991) ISBN 0-333-53603-7
11 Serrano J., Quiñones J., Diaz P., Rodriguez J.L., Cobos J., Caravaca C. Spent fuel Workshop. Las Vegas USA (1998)
12 *Stability Constants of Metal-Ion Complexes Part A Inorganic Ligands. IUPAC Chemical Data Series, No. 21. Pergamon Press (1982)*