ELSEVIER

Journal of Nuclear Materials 298 (2001) 63–68

journal of nuclear materials

www.elsevier.com/locate/jnucmat

The effect of coprecipitation in some key spent fuel elements

J. Quiñones *, J. Serrano, P. Diaz Arocas

Departamento de Fisión Nuclear, CIEMAT, Avda Complutense 22, 28040-Madrid, Spain

Abstract

Performance assessment (PA) of high-level waste (HLW) repositories needs to know real aqueous concentrations of key radionuclides under repository conditions for assuring the safety of the emplacement. The scarcity of these values under repository conditions leads to the use, in the PA studies, of the solubility of pure phases, which is a conservative assumption. Coprecipitation experiments are a very useful tool for giving realistic solubilities of key radionuclides. In this work, experimental data obtained from spent fuel (SF) and SIMFUEL coprecipitation tests under granite and saline conditions are presented. The experimental concentrations measured for several elements when equilibrium was achieved were much lower than expected considering only the solubility of pure phases. To explain this discrepancy, a tentative approach for modelling these experimental leaching and precipitation results of uranium, plutonium, americium, and strontium taking into account solid solution formations was made.

1. Introduction

During the last 30 years the concept of final geological disposal of spent nuclear fuel in corrosion resistant containers has been investigated in several countries [1–3]. The last objective of this disposal concept is to minimise the transport of radionuclides into the biosphere so that the effect on man and the environment 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 modelling the dissolution process of the waste package under repository conditions is enough to consider only thermodynamic control or if the process could be controlled by kinetic factors [4–6]. The second question that appears is the role of secondary phase formed on the thermodynamic and kinetic control of the processes and whether the solubility control comes from a precipitation process of a pure solid phase or from mixed solid phases [6].

It has been reported that coprecipitation processes can play a key role in controlling radionuclide concentrations during spent fuel (SF) dissolution [7]. Solution concentrations from coprecipitation experiments give empirical upper limits for radionuclide concentrations under near field conditions. However, there are still a large uncertainty associated to the interpretation of coprecipitation data, identification of solid phase formed and their use in performance assessment (PA) calculations.

This paper presents experimental results obtained in coprecipitation experiments with SIMFUEL (chemical analogue of SF) and U–Pu solutions under simulated repository conditions. Furthermore, data previously obtained by coprecipitation experiments with spent fuel are reviewed. This study allows to demonstrate the relevance of coprecipitation procedure for spent fuel performance assessment under repository condition since it provides element solubilities in solution. Also a comparison between spent fuel coprecipitation and leaching results is discussed.

2. Experimental procedure

2.1. Materials and reagents

Coprecipitation experiments with SF, SIMFUEL and U–Pu solutions in different media were performed. The SF coprecipitation experiments were carried out in a

---

* Corresponding author. Tel.: +34-91 346 62 16; fax: +34-91 346 62 33.

E-mail address: javier.quinones@ciemat.es (J. Quiñones).

0022-3115/01/$ - see front matter © 2001 Elsevier Science B.V. All rights reserved.
PII: S 0 0 2 2 - 3 1 1 5 (0 1) 0 0 6 1 1 - 0

hot cell facility under remote control and SIMFUEL and U–Pu in a conventional globe box. The SF fragments used had a burnup of 50 MWd/kg U. SIMFUEL composition specimens emulates a burnup of 50 MWd/kg U [8]. U–Pu ratio in the initial supersaturated condition was 0.01.

Aqueous starting solutions, supersaturated with respect to any uranyl oxide hydrate, were prepared by dissolving uranium oxide matrix samples in acid dilution (aqua regia). Aliquot of this former solution (1 ml) was added to the ground water solution (Table 1) ($\approx$200 ml). The result solution has a uranium concentration $\approx 5 \times 10^{-3}$ mol (kg $H_2O)^{-1}$. This solution has a pH $\approx$ 1 [7]. Titration process to selected pH value is discussed in Section 2.2.

Experiments were carried out in two different media: (1) salt brine, which consists in a dissolution of NaCl 5 mol l^{-1}, (2) synthetic groundwater, obtained from the interaction of a granitic groundwater with bentonite from Almeria (Spain) GBW [9]. In Table 1 chemical composition of this synthetic groundwater used is showed. All reagents used in coprecipitation tests were Merck p.a. Solutions were prepared with MilliRo/MilliQ water.

2.2. Precipitation method

The titration to the selected pH was performed in two steps: At first the pH value was adjusted to a value of 3 by adding a solution containing 2 mol (kg $H_2O)^{-1}$ NaOH. No precipitation was observed. Thereafter the titration solution was changed to a solution containing 0.1 mol (kg $H_2O)^{-1}$ NaOH. This procedure resulted in instantaneous formation of a yellow or orange precipitate. Due to the proceeding precipitation reaction the pH returned with time to lower values. The pH decrease was readjusted every 12 h by adding necessary quantities of the titration solution. After some days the pH remained constant, titration was terminated and the reaction vessel (borosilicate made) was sealed. The reaction solution was continuously stirred at 200 rpm. Aliquots of the aqueous suspension were taken at certain time intervals with a syringe for filtration [7,11].

Table 1
Chemical composition of synthetic groundwater [9]

Element	NaCl 5 m (g/l)	GBW (mg/l)
Ca^{2+}		135
K^{+}		20
Mg^{2+}		600
Na^{+}	130	3750
Br^{-}		15
Cl^{-}	200	6550
F^{-}		
HCO_3^{-}		27
NO_3^{-}		110
SiO_2		8.3
SO_4^{2-}		1500
pH_{meas}	7	7.5
pH_{theo}		7.3

The samples were filtered using two different types of membrane filters having a pore size of 0.45 μm (SF) or 0.22 μm (SIMFUEL and U–Pu) and 1.8 nm, respectively. In this paper those aliquots that were filtered through membranes of 1.8 nm are labelled as ‘UF’.

2.3. Analytical methods

The pH_{meas} of the solution was measured using Ross electrode. Corrections for liquid junction potential were performed by calibration with solutions of known HCl activity with reference to the pH convention of Pitzer [10]. The corrected value ‘$pH_{correct}$’ is obtained as follows:

$$pH_{correct} = pH_{meas} + K, \tag{1}$$

where ‘K’ is a constant value for each type of solution, 0.25 for NaCl 5 mol (kg $H_2O)^{-1}$ solution and 0.1 for GBW. The experiments were performed in a range of pH from 5.7 to 12.

The Eh measurements were realised by using combined Pt electrode (Metrom). The values measured were taken after more than 2 h stabilisation, i.e., when the measured drift was at 0.0 mV/min. The liquid junction potential of the Eh-electrode was determined by measuring the potential of the electrode in H_2-saturated (1 atm) NaCl solutions at a known activity ‘a_{H^+}’. Reported Eh values are consistent with Pitzer’s ionic splitting convention.

The redox potential was continuously monitored by means of a platinum wire, using an Ag/AgCl electrode as reference. The Eh measurements in the SIMFUEL experiments gave values in the range of $Eh_{SHE} = -200$ ($\pm$20) mV in both salt brine and GBW and those in the SF experiments were $Eh_{SHE} = 400$ ($\pm$25) mV. Although, the initial redox conditions were the same (anoxic), the presence in spent fuel coprecipitation experiments of high radiation fields (α, β and γ) produce the water radiolysis (oxidant species) which justify the strong difference between the data Eh measured.

Uranium concentrations in the solution were analysed by laser fluorescence and ICP-MS. The minor elements concentrations from SIMFUEL were determined by ICP-MS. Pu and U concentration from coprecipitation studies were measured by liquid scintillation counting.

3. Results and discussion

From SF coprecipitation experiments in saline solutions (5 mol (kg H_2O)$^{-1}$ NaCl) and in GBW the concentrations of Sr, Am, Cm, Eu, Pu and U during coprecipitation process in the pH range 5–12 were studied.

Fig. 1 shows U concentration in solution obtained from SF leaching tests [1,13] in comparison with that from SF, U–Pu and SIMFUEL coprecipitation experiments.

The U(VI) concentrations determined in SF leaching experiments were in most cases lower than in coprecipitation experiments. Equilibrium concentrations of U(VI) obtained in SF coprecipitation tests are similar to those found in U–Pu and SIMFUEL. These concentrations are in the range of those obtained with Na-polyuranate [11]. This indicates that Na-polyuranates could be the phase that controls the uranium solubility under these experimental conditions.

The U concentration at pseudo-equilibrium conditions in SIMFUEL coprecipitation experiments performed in GBW are shown in Fig. 2 for the samples filtered through 0.22 μm and for the samples filtered through membranes of nominal pore size of 1.8 nm (UF). During the titration process a yellow solid phase was precipitated in all the experiments. XRD analyses showed a Na-polyuranate type phase as formed as the main solid. Since these experiments were performed under atmospheric conditions an increase in U steady state concentration in the pH range 7–9 is detected due to carbonate complex formation. As can be observed, at pH higher than 8 the U steady state concentration is around 10^{-4} mol (kg H_2O)$^{-1}$.

This scatter in the U concentration observed in both media (saline Fig. 1 and GBW Fig. 2) is typical for uranyl oxide hydrate formation at ambient temperature, which may be due to difference in crystallisation degree and particle size of the solid phase formed [11,12].

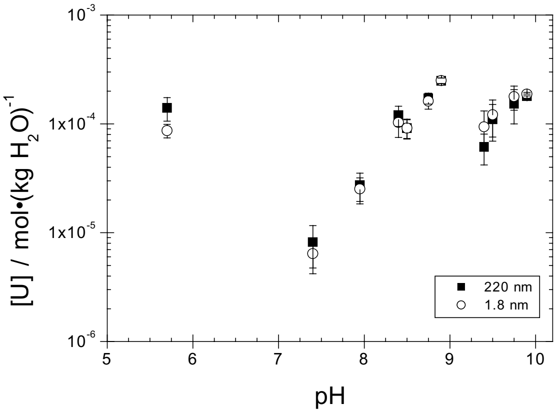

Fig. 2. Steady state U concentration from SIMFUEL coprecipitation experiments in GBW (bold points correspond with filtrated aliquots and hollow points to ultrafiltrated aliquots).

The concentrations of Am, Cm, Eu and Pu were measured, their pH dependence was evaluated. In Am, Cm and Eu a significant decrease of their concentrations with pH were observed (Figs. 3 and 4). The apparent equilibrium concentrations for these elements were achieved within less than 10 days and remained constant until test termination. Fig. 3 shows that apparent equilibrium concentrations of Am decrease with pH, with a pattern resembling typical solubility curve of pure hydroxide phase in the absence of carbonate [15].

All trivalent actinides (Am, Cm) and rare earth elements (Eu, Nd, La, Ce) have been found to behave alike during SF dissolution [1,13] and SF coprecipitation experiments, due to their similar chemical properties.

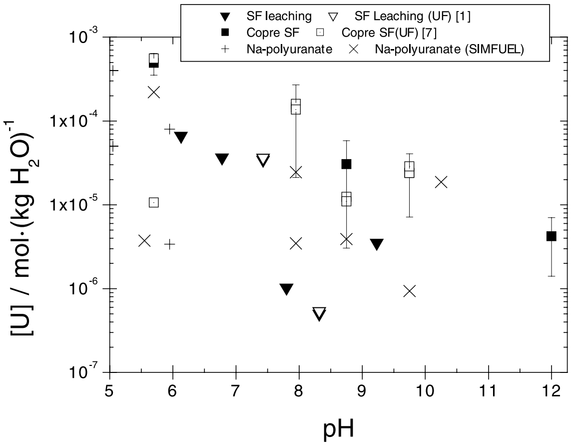

Fig. 1. U concentrations from SF, SIMFUEL, UO_2, U–Pu experiments in saline solutions.

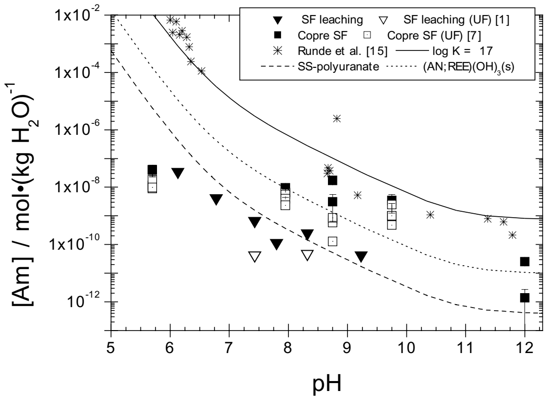

Fig. 3. Am concentration from leaching and coprecipitation SF tests in saline solutions.

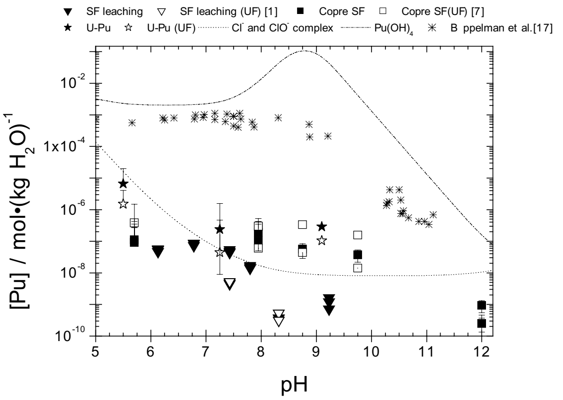

Fig. 4. Pu concentration from SF, SIMFUEL and U–Pu experiments in saline solutions.

In Fig. 3, a comparison of the coprecipitation data of the present work with other obtained by Grambow et al. (leaching experiments) [14] shows that radionuclide concentrations are always the highest in the coprecipitation experiments. The apparent equilibrium concentrations from coprecipitation tests were lower than the solubilities of pure $Am(OH)_3(s)$, $Cm(OH)_3(s)$ or $Eu(OH)_3(s)$ [15]. The discrepancies of more than two orders of magnitude could be related with a different solid phase formation.

From the data on trivalent actinide (Fig. 3) one can propound the formation of a solid solution phase '(AN, REE) $(OH)_3(s)$'. The calculated Am solubility curve considering a control by (AN, REE) $(OH)_3(s)$ formation (dotted line in Fig. 3) agrees with data obtained from SF leaching and coprecipitation tests [16]. The mechanism propounded is that during coprecipitation process the solutions became supersaturated with respect to rare earth hydroxide phases and subsequently a trivalent hydroxide solid solution will be formed. This phase plays a role as a host for incorporation of Am, Cm and REE.

Fig. 4 shows the Pu concentrations from SF and U–Pu coprecipitation and leaching tests. No attempt has been made to determinate the valence state of dissolved Pu under these conditions and, therefore, solubility constraints are not well defined. By comparing our Eh/pH measurements with the Eh/pH stability diagram for various aqueous Pu-species [17] we may assume that $Pu(OH)_4$ would be the dominant solution species.

The results obtained in SF and U–Pu coprecipitation tests were compared with those obtained by Büppelmann and Kim [18] in 5 mol $(kg\ H_2O)^{-1}$ NaCl under oxidising conditions ($Eh > 1$ V). As can be observed in the Fig. 4 the Pu concentrations obtained by Büppelmann are the highest. The difference in the Pu concentrations must be associated with ClO^- formation and subsequent interaction with Pu. This effect is only valid if the α-radiation field is low and ClO^- complexation can be ignored. Not only the redox state of solution species is uncertain but also the solid phases may contain either Pu(IV) or Pu(VI).

The Pu concentrations from the SF coprecipitation experiments were compared with solubility of $Pu(OH)_4(am)$ (dotted line in Fig. 4) [18]. A relatively good agreement can be observed between them, which suggests that the Pu concentrations are controlled by formation of $Pu(OH)_4(am)$.

An effort was performed in order to elucidate the role of strontium as indicator of the SF matrix alteration [19]. According to Kleykamp [20] strontium is homogeneously distributed into the SF [20]. Grambow et al. [14] and Loida et al. [21] in saline solutions and Bruno et al. [26] in granite solutions have observed a congruent dissolution behaviour of Sr with U with independence of the media.

The coprecipitation tests performed in saline solutions (Fig. 5) and GBW (Fig. 6) will allow verifying whether Sr concentrations in solutions remain or not stable under repository conditions.

In case of saline solutions and anoxic conditions (Fig. 5) the concentrations obtained from coprecipitation tests are always higher than those from leaching experiments of SF. Furthermore, the Sr concentration under this condition does not show any solubility control due to solid phase formation.

The Sr concentrations in GBW measured when tests achieved the equilibrium are given in Fig. 6. As can be observed, there is a small influence of colloid formation in steady state concentration. For $pH > 7$ a decrease respect to the initial concentration are measured.

Geochemical reaction path models were applied to the interpretation of Sr behaviour in SIMFUEL coprecipitation tests in GBW under oxidising conditions has.

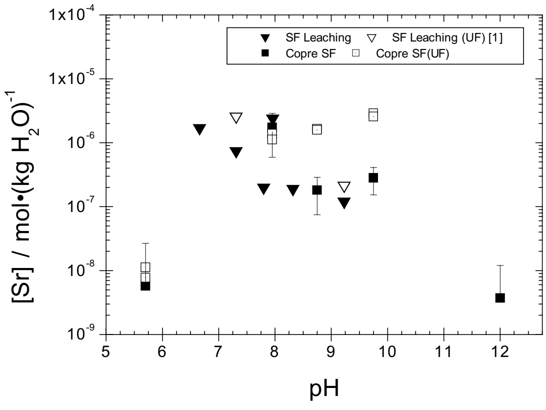

Fig. 5. Comparison of apparent ^{90}Sr equilibrium concentration vs. pH in 5 m NaCl solutions obtained from SF leaching tests [1] with the present SF solubility/precipitation tests [7].

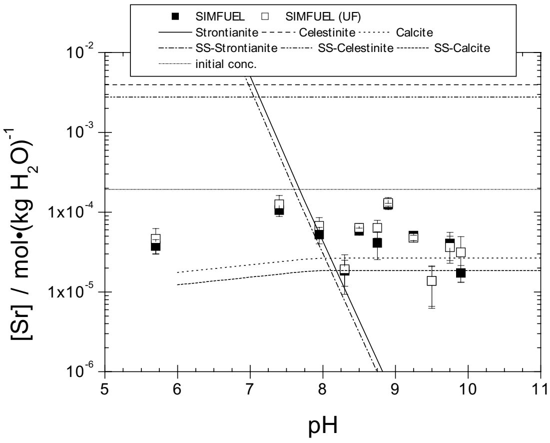

Fig. 6. Sr concentrations from experimental and calculated data in GBW and oxidising conditions.

The data bases used for modelling were ‘data1.com’ and ‘phreeqc.dat’ for EQ3 [22] and PHREEQC [23], respectively. A tentative approach for modelling Sr steady state concentration as a function of pH is given in Fig. 6. The lines represent the Sr solubility calculated taking into account a control due to solid phase formation (celestite, strontianite or calcite). The comparison between measured [25] and modelled Sr concentration [24] 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.

4. Conclusions

Coprecipitation tests are a powerful tool for the assessment of the expected higher radionuclide concentrations expected release from spent fuel under repository conditions. In SF coprecipitation experiments the presence of high radiation fields (α, β and γ) modify the redox conditions from initially anoxic to oxic.

The uranium concentration measured in saline solutions shows that the main solid phase formed is Na-polyuranate. This phase is independent of the starting solution (SF, SIMFUEL or U–Pu).

In the coprecipitation experiments with SF and U–Pu, the Pu concentration in saline solution appears to be controlled by solubility of pure phase $Pu(OH)_4(am)$.

The results of the present work give strong indications for coprecipitation phenomena controlling maximum solution concentrations of trivalent actinides and lanthanides by (AN;REE) $(OH)_3(s)$ formation. Apparent equilibrium concentrations in saline solutions are considerably lower for these elements than that expected from the solubility of pure hydroxide phases. The scatter in the experimental data is too high to allow distinction between ideal and real solid solution behaviour.

In case of Sr, this element does not show solubility control in all conditions tested in this paper (saline and GBW) which would hold to the reliability of this element as indicator of the SF matrix alteration.

Acknowledgements

This work has been carried out in the Department of Nuclear Fission of the CIEMAT inside the agreement of the Association CIEMAT ENRESA (Annex XIV) in the area of the definitive storage of spent fuel. The SF coprecipitation work has been performed at Forschungszentrum Karlsruhe under the agreement for cooperation in the Area of Direct Disposal of Spent Fuel between ENRESAand Forschungszentrum Karlsruhe, under the agreement between CIEMAT and ENRESA and under the contract FI4W-CT95-0004 with the Commission of the European Union. The authors would like to thank A. Martinez Esparza, J.A. Esteban for continuing encouragement and M.J. Tomas, J.M. Cobo, A. Fariñas and J.M. Altelarrea for their valuable help for performing this work.

References

[1] B. Grambow, A. Loida, P. Dressler, H. Geckeis, P. Diaz, J. Gago, I. Casas, J. de Pablo, J. Gimenez, M.E. Torrero, Reaction of high burnup spent fuel and UO2 in saline brines at room temperature, KfK Report, 5377, 1994.
[2] L.H. Johnson, L.O. Werme, MRS Bull. 12/1994.
[3] R.S. Forsyth, L.O. Werme, J. Nucl. Mater. 190 (1992) 3.
[4] J. Bruno, I. Grenthe, M. Muñoz, Mater. Res. Soc. Symp. Proc. 50 (1985) 717.
[5] J.H. Van't Hoff, Z. Phys., Chem. 5 (1890) 322.
[6] H. Geckeis, B. Grambow, A. Loida, B. Luckscheiter, E. Smailos, J. Quiñones, Radiochim. Acta 82 (1998) 123.
[7] J. Quiñones, B. Grambow, A. Loida, H. Geckeis, J. Nucl. Mater. 238 (1996) 38.
[8] P.G. Lucuta, B.J. Balmer, Hj. Matzke, D.S. Hartwig, Preparation and Characterization of SIMFUEL: Simulated CANDU High-Burnup Nuclear Fuel: Atomic Energy of Canada Report AECL-1017, 1989.
[9] B. Martinez, A. Melon, Valladares, Prepatation of a Synthetic Bentonitic-Granitic Water, Specific Procedure No. PR-X8-01, Internal report CIEMAT, 1996.
[10] B. Grambow, R. Müller, Mater. Res. Soc. Symp. Proc. 176 (1990) 229.
[11] P. Diaz-Arocas, B. Grambow, Geochim. Cosmochim. Acta 62 (1998) 245.
[12] M. Torrero, I. Casas, J. de Pablo, M.C.A. Sandino, B. Grambow, Radiochim. Acta 66&67 (1994) 29.
[13] A. Loida, B. Grambow, H. Geckeis, P. Dressler, Mater. Res. Soc. Symp. Proc. 353 (1995).

[14] B. Grambow, A. Loida, P. Dressler, H. Geckeis, N. Müller, J. Gago, I. Casas, J. de Pablo, J. Giménez, M.E. Torrero, Chemistry of the reaction of fabricated and high burnup UO2 fuel with saline brines, Final Report EUR 17111 FI2W-CT90-0055, European Commission, 1997.

[15] W. Runde, PhD Universität München, 1993.

[16] J. Quiñones, B. Grambow, A. Loida, H. Geckeis, Coprecipitation Phenomena in Spent Nuclear Fuel Alteration, Part I: Experimental procedure and initial results on radionuclide behaviour in 5 m NaCl solutions, Technical Report Ciemat ITN/RR-32/II-96, 1996.

[17] H. Capdevilla, P. Vitorge, E. Giffaut, Radiochim. Acta 58&59 (1992) 45.

[18] K. Büppelmann, J.I. Kim, RCM 01088, June 1988.

[19] B. Grambow, SKB Technical Report 89–13, Stockholm, 1989.

[20] H. Kleykamp, J. Nucl. Mater. 131 (1985) 221.

[21] A. Loida, B. Grambow, G. Karsten, P. Dressler, Mater. Res. Soc. Symp. Proc., vol. 506, Materials Research Society, 1998.

[22] T.J. Wolery, EQ3NR A computer program for geochemical aqueous speciation-solubility calculations: Theoretical manual, user's guide and related documentation (version 7.0) 1992.

[23] S.C. Charlaton, C.L. Macklin, D.L. Parkhurst, PHREEQCIA Graphical user Interface for Geochemical Computer Program PHREEQC. US Geological Survey. Water-Resources Investigation Reports 97-4222, 1997.

[24] D.L. Parkhurst, D.C. Thorstenson, L.N. Plummer, 1980, Phreeqe – A computer program for geochemical calculations: US Geological. Survey Water-Resources Investigations Report 80–96, p. 195. Revised and reprinted August, 1990.

[25] J. Serrano, J. Quiñones, P. Diaz, J.L. Rodriguez, J. Cobos, C. Caravaca, Spent Fuel Workshop, Las Vegas, USA, 1998.

[26] J. Bruno, E. Cera, M. Grive, U.B. Eklund, T. Eriksen, Experimental determination and chemical modelling of radiolytic processes at the spent fuel/water interface, SKB Technical Report TR-99-26, 1999.