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Direct disposal of spent nuclear fuel: comparison between experimental and modelled actinide solubiluties in natural waters

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Abstract

Experimental results from two independent sets of fuel corrosion experiments are compared and are found to be in good agreement. The experimental steady state concentrations for actinides from mildly oxidising and anaerobic corrosion tests are compared with calculated solubilities. It was found that the calculations failed to reproduce the values obtained in the experiments. The discrepancies were, in some cases, of several orders of magnitude. Possible ways to investigate the reasons for these discrepancies are indicated. © 1998 Elsevier Science S.A.

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1. Introduction

Direct disposal of used nuclear fuel has been given serious consideration since the late 1970s [1,2]. Spent fuel disposal is now the main alternative for high-level waste management in Canada, Finland, Spain, Sweden and USA, and is also considered in Germany and in France, at least for special fuels. The majority of light-water reactor fuels are made from uranium, enriched in ^{235}U, although fuels with fissile plutonium are also in use. The ^{235}U enrichment is typically in the range 3–4%. In the reactor, the ^{235}U is consumed (‘burned’) by nuclear fission caused by thermal neutrons and at the same time higher actinides are produced by capture of neutrons. At present, the majority of the fuel has a burn-up of 35–45 MWd kg^{-1} U. Older fuels have, in general, lower burn-up, but the current trend is towards higher burn-up, 55–60 MWd kg^{-1} U. At moderate to high burn-up, fission of transuranium isotopes, especially ^{239}Pu becomes important. After removal from the reactor, a BWR fuel with a burn-up of about 55 MWd kg^{-1} U contains about 93% U, 0.08% Np, 0.9% Pu, 0.06% Am and 3×10^{-4}% Cm. The contents of Np, Am and Cm are burn-up dependent, while Pu is relatively constant due to fission. The remainder are fission products.

The activity of the fuel will, after a few hundred years, be dominated by the actinides. The radioactivity itself is not the only decisive factor for the health risks associated with the radionuclides. The form of intake, inhalation or ingestion, has significance. The most important factor, however, is the accessibility of the radionuclides through their ability to dissolve and spread by ground-water flow to the biosphere, i.e., the chemical behaviour of the elements.

2. Background

The chemical form of the U in light-water reactor fuel is nearly stoichiometric uranium dioxide both before and after irradiation. The actinides are generally viewed as forming solid solutions with UO_2 (see Ref. [3] and references therein). The release of these elements when the fuel is in contact with water will, therefore, depend on the UO_2 dissolution and corrosion processes. At low pe, UO_2 has a very low solubility, while at higher redox potentials U(VI) species are stabilised and the solubility increases with orders of magnitude. Most natural deep groundwaters are oxygen free and reducing. However, the radiation field from the fuel will decompose the surrounding water through radiolysis. The extent of the radiolysis will depend on the radiation dose rate, which in turn depends on the time after removal from the reactor when the ground-water will come into contact with the fuel. Radiolysis does not in itself change the redox state of the system, since equivalent amounts of oxidising and reducing species are produced. Hydrogen is the final reducing radiolysis product and can be regarded as being relatively inert at low temperatures as well as being more mobile. The oxidising species are far more reactive and can,

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therefore, in practice, create a local oxidising environment close to the fuel surface. Under these conditions the fuel can oxidise and the fuel matrix dissolves mainly as UO_2^{2+} species, which subsequently may precipitate. The extent of dissolution will be controlled by the ligands present in the ground-water, which will also control the precipitation of the solid phase.

3. Experimental studies

Experimental studies of spent fuel corrosion have been going on since the late 1970s (see Refs. [4,5] and references therein). In this paper we shall limit ourselves to experimental studies performed in low salinity ground-waters, although there are studies performed and in progress directed towards disposal of spent fuel in salt formations [6]. We shall also discuss, primarily, dissolution data for U, Np and Pu. Am is also expected to be of concern for nuclear waste management, but will be discussed in less detail for reasons explained below. The experimental data discussed in this paper originated mainly from the Swedish Nuclear Fuel and Waste Management Co. (SKB) programme carried out at Studsvik, but also from the work of Wilson at Pacific Northwest Laboratory [7,8]. The majority of the studies in low salinity ground-water have been performed under oxidising conditions, but there are also some data available from anaerobic conditions.

The experiments in SKB's programme were performed with fuel-clad segments, containing about 16 g UO_2, immersed in 200 ml of water in a 250 ml Pyrex flask at 20–25°C. The atmosphere in the test vessels was air or Ar $+5\%$ H_2. Water samples (10 ml) were centrifuged through membrane filters (Amicon Corporation, USA) with nominal pore apertures of 1.5–2.0 nm [9,10] or ultracentrifuged. After each exposure the fuel specimens were transferred to new flasks with fresh solutions. The analysis for actinides was performed by alpha spectrometry and mass spectrometry (ICP-MS). In this paper we shall mainly restrict our discussion to what is referred to as Series 11: a series performed using fuel from a segment of a stringer rod with burnup varying between 21 and 49 MWd kg^{-1} U along the fuel column [10]. Two water types were used: deionised water and a synthetic granitic ground-water with a bicarbonate concentration of 2 mM.

Wilson's experiments in Series 2 [7] were performed at 25°C in fused silica with bare fuel with separated cladding present. The fuel specimens, one set with a burnup of 30.2 MWd kg^{-1} U and the other with a burnup of 27.5 MWd kg^{-1} U, had weights of about 82 g and 26 g, respectively. The water used was a ground-water from the Nevada test site and was similar to the synthetic ground-water used in the Swedish programme. Most importantly, the bicarbonate concentration was about 2 mM and pH 7.7–8.5. The water volume was 250 ml and 50 ml samples were drawn periodically for analysis and the same volume of fresh solution was added to maintain a constant volume in the test vessel. The atmosphere in the test vessels was air. The water samples were filtered through 0.4 μm and 1.8 nm filters. The second filtration had little effect on the solution concentrations, with the exception of Am and Cm. Series 3 [8] was performed in stainless-steel vessels in the same way with specimen weights of about 80–85 g for both fuels.

4. Results

The results for the steady state concentrations from the discussed experiments are summarised in Table 1.

The results from SKB's Series 11 from mildly oxidising conditions are shown in Fig. 1 for bicarbonate ground-water. The initial pH of the solutions was 8.2 and after exposure, the pH was 8.3–8.5. Each data point represents the average of ten parallel experiments. The standard deviations between these experiments are ±30% for U and ±40% for Np and Pu, but there are occasional 'flyers'. The data were obtained using laser fluorescence for U, alpha spectrometry for Pu and ICP-MS for Np. If one disregards the data for the first 200 days cumulative contact, when the contact periods were shorter than 100 days and steady state may not yet have been established, the average concentrations reach virtually constant levels, which are nearly the same for each contact period. It cannot be seen in the figure, but these steady state concentrations are indepen-

Table 1
Summary of solution concentrations measured by SKB and Wilson

Actinide	GW SKB	Wilson series 2	Wilson series 3	Wilson series 1	DIW SKB	Anaerobic SKB
U	−5.0	−5.2	−5.9	−8.3	−8.0	−6.4
Np	−9.0	−8.6	−8.9		−8.6	−10.6
Pu	−8.7	−8.4(HBR) −9.1(TP)	−8.4	−6.9	−7.7	−10
Am	≤−11	−9.8[a]	−9.8	−8.6[b]		

[a] 0.4 μm filtered solutions; 1.8 nm filtered solutions gave log[Am(M)]=−11.3.

[b] 0.4 μm filtered solutions; 1.8 nm filtered solutions gave log[Am(M)]=−10.2.

GW, ground water; DIW, deionised water.

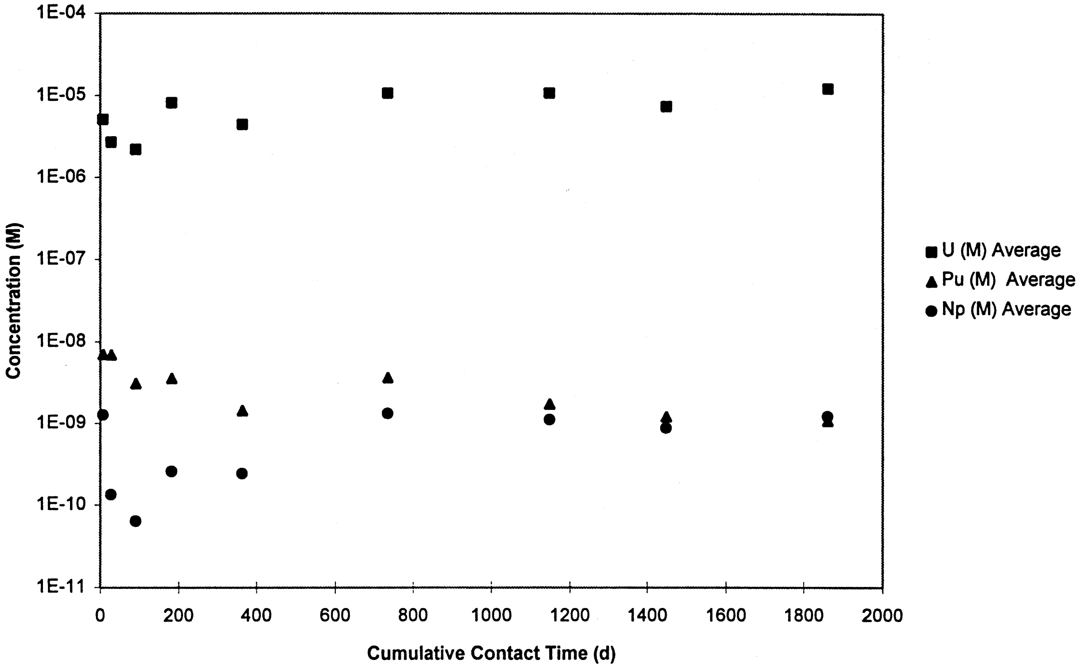

Fig. 1. Concentrations of U, Np and Pu in synthetic granitic ground-water, pH=8.2, as a function of cumulative contact time.

dent of fuel burnup. The U concentrations show, however, a slow increase in final concentrations throughout the whole experiment. As in the earlier experiment, the Pu concentration was somewhat higher in the earlier contacts. The initially lower Np concentrations are probably caused, to some extent, by ICP-MS analysis of archive rather than freshly sampled solutions.

For comparison, a similar plot is shown of the corresponding data obtained by Wilson [7]. Wilson's data have been re-plotted to the same form as SKB's data Fig. 2. Wilson took samples during each of the five cycles in his experiment. In the early cycles, Wilson allowed the fuel specimen to dry between the cycles and, thereby, be exposed to oxidation, which resulted in early high concentrations, dropping with time to steady state. When the fuel specimens were kept wet during the cycle change, the opposite was the case. With the longer exposure times in SKB's programme, such effects could not be observed.

A limited set of experiments in Series 11 was also performed in deionised water. The obtained results are

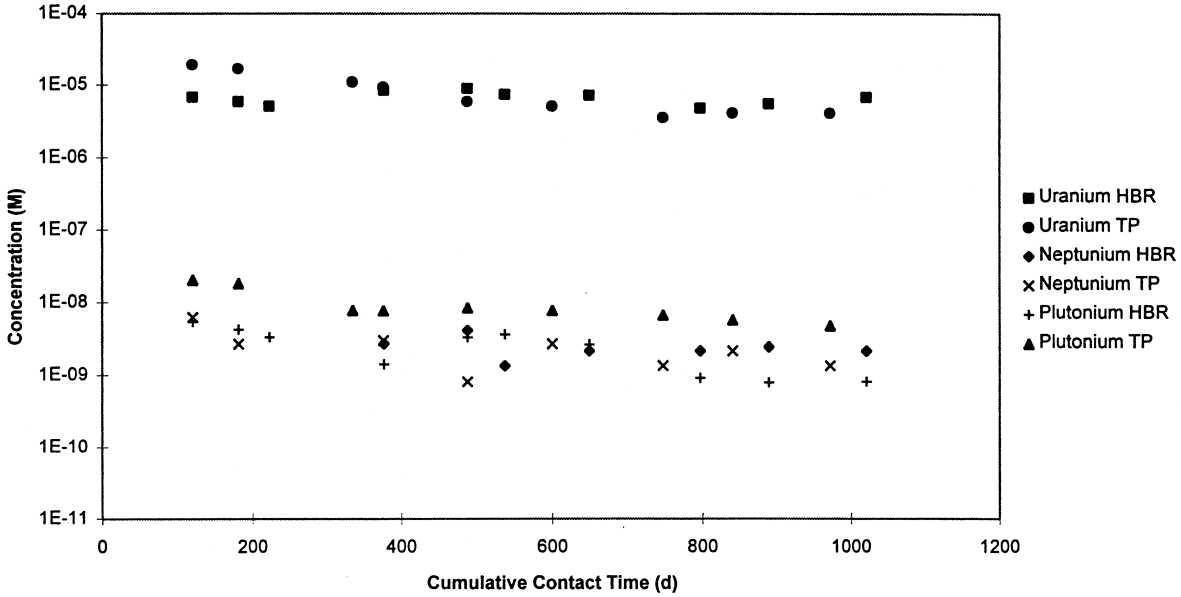

Fig. 2. Concentrations of U, Np and Pu from Wilson's Series 2 experiments as a function of cumulative contact time.

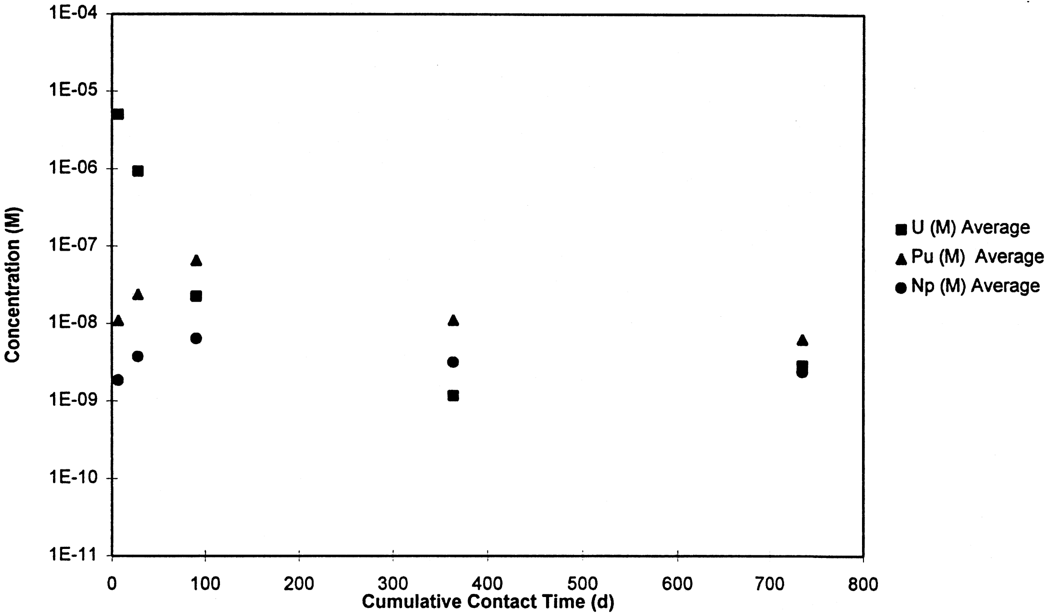

Fig. 3. Concentrations of U, Np and Pu in deionised water, pH=6–7, as a function of cumulative contact time.

presented in Fig. 3. The absence of complexing ligands results in considerably lower uranium concentrations in these experiments. Initially, uranium is found at concentrations comparable to those in bicarbonate water; however, longer exposures give values in the same range as for Pu and Np. The pH ranged from 6 to 7, resulting in a larger spread of data than was observed in ground-water. The data do confirm, however, that in the absence of ligands, the uranium concentrations in solution are very low. Wilson's Series 1 experiments were performed essentially as those in Series 2, but in distilled water and with Turkey Point fuel only [11]. A pH of about 6 was measured in Series 1. There is a good agreement between the Wilson's and SKB's U concentrations, but Wilson's Pu concentrations are higher than those measured by SKB.

Reliable results for americium have not been obtained in SKB's experiments. The reason for this is that the analyses with both alpha spectrometry and ICP-MS have been performed without chemical separation of the actinides and overlap with other isotopes prohibits direct analysis of americium [12]. Wilson [7,8] analysed for Am after chemical separation and the analytical results are, therefore, clearly more reliable. These data show very low solution concentrations and also an apparent effect of filtration. This was interpreted as the presence of colloids or suspended particles as the main carriers of the Am activity; Wilson does not rule out the possibility of adsorption of Am during the filtration procedures.

It should be pointed out that Wilson found the amounts of actinides corresponding to release congruent with uranium, if the amounts recovered from rinsing and acid stripping of vessels were added to the amounts in solution. This was not the case in SKB's experiments. It is believed that the reason for this is to be found in the differences in specimen preparation, i.e., bare fuel versus cut segments of fuel with cladding. In the latter case, the precipitation of actinides can have taken place inside the fuel specimen and not be accessible to recovery. An acid rinse of the specimens themselves would obscure the release of any precipitated material through massive dissolution of fresh fuel during an acid rinse.

One set of experiments in Series 11 was performed under anaerobic conditions. The intention was to achieve these conditions by de-aerating the synthetic ground-water and performing the tests under an atmosphere of flowing Ar + 5% H_2. It appears that these conditions were not stable, and that carbon dioxide was lost to the atmosphere in the test vessels with a resulting increase in pH and also a precipitation of calcite. About half of the carbonate content was lost from solution and the final pH was found to be about 9.6. Simulations with EQ3/EQ6 confirmed that this change is compatible with a loss of 0.2 mM of carbonate, 60% of which is lost to the atmosphere and 40% by forming $CaCO_3$. The formation of $CaCO_3$(s) was also confirmed experimentally, by high Ca releases in experiments performed in low ionic strength NaCl solutions. Co-precipitation of actinides with this calcite cannot be excluded, but have not yet been confirmed.

The results from the anaerobic tests are presented in Fig. 4. Also in these tests, steady state conditions appear to be reached, after which there are relatively stable concentrations in solution. There is a slow trend upwards in uranium concentrations at the longer exposure times. This could have been caused by leakage of air into the test vessels, but may also reflect a slow increase in redox potential due to accumulation of radiolysis products. The

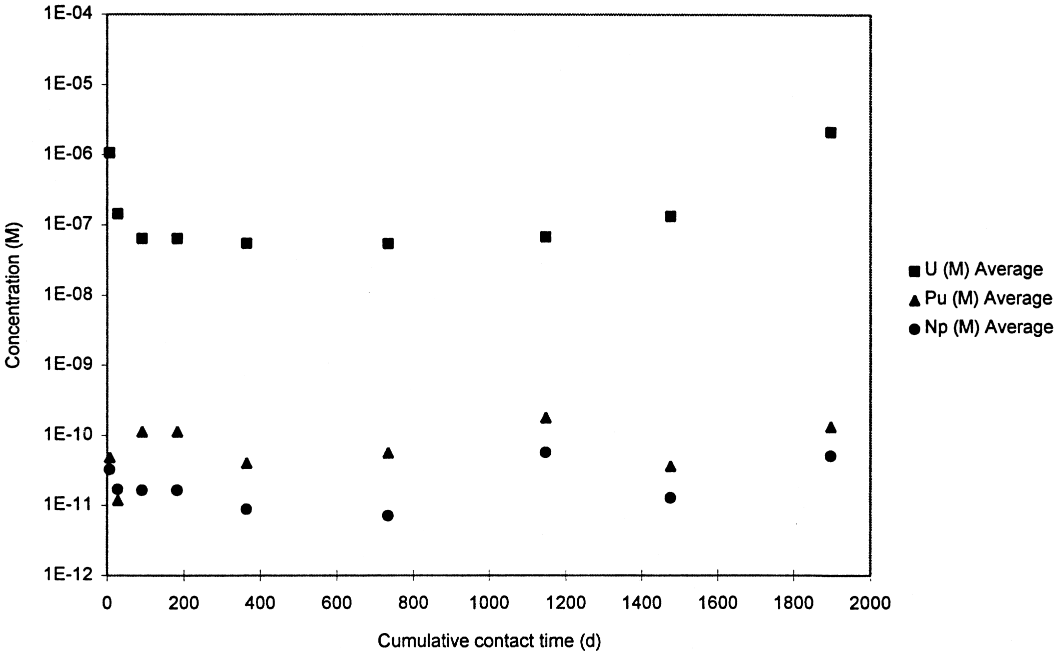

Fig. 4. Concentrations of U, Np and Pu in synthetic granitic ground-water, anaerobic conditions, pH=9.6, as a function of cumulative contact time.

ninth contact shows an unexpectedly high uranium concentration. The reason for this is still unknown but the experiments are continuing and future contacts may show if there is a trend towards higher uranium concentrations.

5. Discussion

The measured U concentrations are difficult to correlate with solubility control as calculated assuming chemical equilibrium. The differences between ground-water and deionised water clearly indicate precipitation of a secondary phase. There is no obvious reason to assume less oxidation of the UO_2 matrix in deionised water compared with bicarbonate water. This is also confirmed by the Np and Pu concentrations measured in deionised water, which are, if anything, slightly higher than in ground-water. The measured Pu and Np concentrations clearly show that 100–1000 times more U than found in solution must have been dissolved and subsequently re-precipitated in order to allow for these values. On specimens corroded in deionised water, a yellow deposit of dehydrated schoepite has been observed [19]. In tests on the synthetic bicarbonate ground-water, under anaerobic conditions, with fuel previously exposed to deionised water, the existence of solid U(VI) phases in the system was manifested in an increased uranium release, with solution concentrations in the range 10^{-5} M. There was no corresponding increase in Pu and Np concentrations.

The lower solution concentration of U in deionised water is compatible with the much lower carbonate content in those tests, but the only reasonable solid phase to precipitate would be a uranyl hydroxide. A comparison between calculated solubilities of predicted phases and the measured data has been performed with the EQ3NR code [13] using SKB's database, which is based on Nagra's database [14], but supplemented with actinide data from Refs. [15,16] for U, Ref. [17] for Pu and Ref. [18] for Am. At $E_h=300$ mV (pH 7), where schoepite is stable, the calculations showed an equilibrium uranium concentration of 10^{-4} M with $(UO_2)_3(OH)_5^+$ as dominating aqueous species. This is three orders of magnitude higher than what was measured. It has previously been shown that assuming a redox potential controlled by the U_3O_7/ U_3O_8 equilibrium, rather good agreement can be obtained between calculated U solubilities and measured data [10]. The choice of U_3O_7 can be justified, since an oxidation of the fuel to a stoichiometry of $UO_{2.33}$ is generally considered to be required for the onset of dissolution of (VI) [4]. If U_3O_7 is assumed to be the solubility limiting phase, the following uranium concentrations were calculated: deionised water $\log[U(M)]=-7.2$, synthetic bicarbonate ground-water $\log[U(M)]=-4.5$ and synthetic bicarbonate ground-water under anaerobic conditions $\log[U(M)]=-7.1$, assuming potentials of 200 mV, 100 mV and −100 mV, respectively. The results of these calculations give a fair agreement with the measured data, but it is difficult to reconcile the assumptions with precipitation of a secondary phase as obviously has been the case at least for the experiments in deionised water.

With a U concentration of 10^{-5} M, at least 2×10^{-6} moles U have been dissolved, since precipitation of a secondary U phase cannot be excluded. The congruent amount of Pu, based on an inventory of 0.9%, is 1.8×10^{-8}

moles, corresponding to 9×10^{-8} M if all of the Pu was in solution. This is about a factor of 50 higher than actually detected. For Np, the congruent amount for an inventory of 0.08% is 1.6×10^{-9} moles, or a concentration of 8×10^{-9} M. This is again more than detected in solution, although only somewhat less than a factor of ten.

It is clear that, at least for Pu and probably also for Np, a precipitation of an actinide-rich phase must have occurred. If that is the case, the amount of Pu in this phase can be estimated to be less than about 2×10^{-8} moles or 5 μg. Obviously, this small amount cannot readily be identified and characterised on the radioactive fuel or elsewhere in the system.

The calculations give a concentration of Pu of about 10^{-10} M, virtually independent of the redox conditions and water chemistry used in the experiments. This is at least a factor of ten lower than was experimentally measured, but may be considered as in fair agreement. The solid phase is predicted to be $Pu(OH)_4$(am) with $Pu(OH)_4$ as the dominating aqueous species.However, the calculations fail to reflect the differences measured in ground-water, deionised water and in ground-water under anaerobic conditions.

For Np, the situation was even more discouraging. At $E_h=300$ mV, a Np concentration of 5×10^{-5} was predicted, with NpO_2^+ as the dominating solution species. With U_3O_7 as the solubility limiting phase for U, the following Np concentrations were calculated: deionised water $\log[Np(M)]=-6$, synthetic bicarbonate ground-water $\log[Np(M)]=-7.2$ and synthetic bicarbonate ground-water under anaerobic conditions $\log[Np(M)]=-7.9$. The predicted solubility limiting phase was $Np(OH)_4$(am). All overestimate the actual concentrations by at least a factor of 100.

For Am, the calculations had to be considered as grossly inadequate, with a predicted concentration in deionised water at pH 6 in equilibrium with $Am(OH)_3$(am) of 6 mM, as compared with measured value of 10^{-9}–10^{-10} M. Saturation with respect to $Am(OH)_3$(am) is, of course, unlikely and the expected concentration if the solid phase had not yet precipitated, would have been in the order of what is found experimentally. In synthetic ground-water in equilibrium with $AmOHCO_3$ the calculations predicted an Am concentration of about 5×10^{-8} M. This is at least a factor of 50 higher than measured in the experiments. Based on the inventory of Am in the fuel, a concentration comparable to that of Np is to be expected if saturation has not occurred. The discrepancies are, of course, much larger if the solution data after 1.8 nm filtration are considered.

It is our opinion that these discrepancies between the calculations and the observations of spent fuel behaviour under laboratory conditions must be clarified since predicted radionuclide solubilities are used in performance assessments, and the selection of solubilities and speciation has a large effect on the outcome of a performance assessment.

6. Conclusions

Comparison between experiments performed independently under very similar conditions, such as those by SKB and Wilson, give very similar and reproducible results for the actinides regardless of variations in parameters such as burnup and irradiation history. There is a large body of data on the solubilities of pure actinide phases; however, it appears that the information available is insufficient to explain the experimental results. This may be due to insufficient pertinent thermodynamic data. The problems with the thermodynamics of the actinides in relation to nuclear waste management have already been pointed out [20]. It does not seem that collecting and refining thermodynamic data for pure, single phase actinides will alone improve our understanding of the fuel–water system.

More fuel corrosion experiments of the type performed by SKB and Wilson are not likely to increase our understanding of the corrosion process and the mechanisms for actinide release from the fuel. Specific, well-controlled experiments aimed at measuring the solubilities of actinide phases, especially those with mixed composition, are needed. In view of the very low actinide concentrations in the solutions, the experiments also pose considerable analytical difficulties. No doubt such experiments will be time consuming, but they appear to be necessary if our understanding of the corrosion of spent nuclear fuel is to improve.

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References

[1] Handling and Final Storage of Unreprocessed Spent Nuclear Fuel, Kärnbränslesäkerhet (KBS), Stockholm, Sweden, 1978.

[2] J. Boulton (Ed.), Management of Radioactive Fuel Wastes: The Canadian Disposal Program, Atomic Energy of Canada Limited, Report AECL-6314, 1978.

[3] Evaluation of Spent Fuel as a Final Waste Form, IAEA Technical Reports, Series No. 320, International Atomic Energy Agency, Vienna, 1991.

[4] L.H. Johnson, D.W. Shoesmith, Spent fuel, in: W. Lutze, R.C. Ewing (Eds.), Radioactive Waste Forms for the Future, North-Holland Physics Publishing, The Netherlands, 1988.

[5] V.M. Oversby, Nuclear waste materials., in: R.W. Cahn, P.Haasen, E.J. Kramer (Eds.), Materials Science and Technology, vol. 10B,

Nuclear Materials, part 2, B.R.T. Frost (Ed.), VCH Verlagsgesellschaft mbH, Federal Republic of Germany, 1994.
[6] A. Loida, B. Grambow, H. Geckeis, J. Nucl. Mater. 238 (1996) 11–22.
[7] C.N. Wilson, Results from NNWSI series 2 bare fuel dissolution tests, Pacific Northwest Laboratory, Report PNL-7169, UC-802, 1990.
[8] C.N. Wilson, Results from NNWSI series 3 spent fuel dissolution tests, Pacific Northwest Laboratory, Report PNL-7170, UC-802, 1990.
[9] R.S. Forsyth, L.O. Werme, J. Bruno, J. Nucl. Mater. 138 (1986) 1–15.
[10] R.S. Forsyth, L.O. Werme, J. Nucl. Mater. 190 (1992) 3–19.
[11] C.N. Wilson, Results from NNWSI Series 1 Spent Fuel Leach Tests, Westinghouse Hanford Company Report HEDL-TME 84-30, UC-70, 1985.
[12] R.S. Forsyth, U-B. Eklund, Spent nuclear fuel corrosion: The application of ICP-MS to direct actinide analysis, SKB Technical Report 95-04, 1995.
[13] T.J. Wolery, EQ3NR, A computer program for geochemical aqueous speciation-solubility calculations: Theoretical manual, user's guide, and related documentation (Version 7.0), Lawrence Livermore National Laboratory.
[14] F.J. Pearson Jr., U. Berner, Nagra Thermochemical Data Base, I Core Data, Nagra Technical Report 91-17, 1991.
[15] I. Grenthe, J. Fuger, R.J.M. Konings, R. Lemire, A.B. Muller, C. Nguen-Trung, H. Wanner, Chemical Thermodynamics of Uranium, Elsevier, Amsterdam, 1992.
[16] I. Puigdomenech, J. Bruno, Modelling uranium solubilities in aqueous solutions: validation of a thermodynamic database for the EQ 3/6 geochemical codes, SKB Technical Report 88-21, 1988.
[17] I. Puigdomenech, J. Bruno, Plutonium solubilities, SKB Technical Report 91-04, 1991.
[18] R. Silva, G. Bidoglio, M. Rand, P. Robouch, H. Wanner, I. Puigdomenech, Chemical Thermodynamics of Americium, Elsevier, Amsterdam, 1995.
[19] R.S. Forsyth, U-B. Eklund, O. Mattsson, D. Schrire, Examination of the surface deposit on an irradiated PWR fuel specimen subjected to corrosion in deionized water, SKB Technical Report 90-04, 1990.
[20] J. Fuger, J. Nucl. Mater. 201 (1993) 3–14.