

**The effect of hydrogen on
dissolution of spent fuel in
0.01 mol×dm⁻³ NaHCO₃ solution**

Trygve Eriksen, Mats Jonsson
School of Chemical Science and Engineering,
Nuclear Chemistry, KTH

August 2007

Svensk Kärnbränslehantering AB

Swedish Nuclear Fuel
and Waste Management Co
Box 5864

SE-102 40 Stockholm Sweden

Tel 08-459 84 00
+46 8 459 84 00

Fax 08-661 57 19
+46 8 661 57 19



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This report concerns a study which was conducted for SKB. The conclusions and viewpoints presented in the report are those of the authors and do not necessarily coincide with those of the client.

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Abstract

The effect of H₂ on oxidative dissolution of fragments of irradiated PWR fuel has been studied in 0.01 mol×dm⁻³ NaHCO₃ (pH 8.2) equilibrated with either Ar, 7% H₂/93% Ar or 30% H₂/70% Ar at a pressure of 0.1 MPa.

Whereas H₂ was found to reduce the rate of O₂ formation, the concentration of H₂O₂ was, within experimental uncertainties, the same in all experiments. The release of the fission products Sr and Cs was the same in all experiments indicating constant oxidation of the fuel matrix.

The concentration of the redox sensitive elements U, Np, Tc and Mo in solution after 20 days leaching was lower in the presence of H₂ than in Ar saturated solution, the effect being more pronounced for U and Tc.

Based on the assumption of congruent dissolution of Sr and Cs the experimental data indicate that H₂ did not suppress the fuel dissolution. The lower concentrations of the redox sensitive elements in the presence of H₂ point at a marked change in redox conditions and reduction by radiolytically formed reductants and/or catalytic surface reactions.

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1 Introduction

High partial pressures of H_2 may build up in a deep repository for spent nuclear fuel as a result of corrosion of steel container components. The effect of H_2 on oxidative dissolution of $UO_2(s)$ and spent nuclear fuels has therefore been studied at different chemical conditions and radiation fields and are reported in a number of publications /King et al. 1999, Röllin et al. 2001, Broczkowski et al. 2005, Wren et al. 2005, Cera et al. 2006/.

/King et al. 1999/ studied the effect of γ -radiation on the corrosion potential E_{corr} of UO_2 in $0.1 \text{ mol} \times \text{dm}^{-3}$ NaCl solution at 5 MPa overpressure of either H_2 or Ar. The corrosion potential, being a measure of the degree of oxidation of UO_2 , is established by the balance between the electrochemical reduction and oxidation processes. The rate of dissolution is related to the surface potential /Shoesmith et al. 1994, 2003/ and can be estimated from E_{corr} measurements.

In the absence of radiation no significant difference was observed in the steady state E_{corr} of UO_2 measured at Ar or H_2 overpressure. However, in the presence of radiation ($11.3\text{--}15.9 \text{ Gy} \times \text{h}^{-1}$) H_2 was found to have two effects on the oxidation of $UO_2(s)$. Not only did H_2 suppress the oxidation of $UO_2(s)$ by radiolytic oxidants but it also produced more reducing conditions than observed with H_2 and Ar in the absence of radiation.

Sunder and Miller (unpublished data as given in /King et al. 1999/) observed no differences in E_{corr} measured in $0.1 \text{ mol} \times \text{dm}^{-3}$ NaClO_4 solution in contact with H_2 at a pressure of 0.1 MPa and irradiated with γ -radiation (dose rates 5 to $200 \text{ Gy} \times \text{h}^{-1}$).

/Broczkowski et al. 2005/ studied electrochemically the effect of H_2 on the corrosion potential in $0.1 \text{ mol} \times \text{dm}^{-3}$ KCl of two 1.5at% SIMFUEL electrodes, one with and one without incorporated ϵ -particles. Using a 5% H_2 /95% Ar mixture E_{corr} was found to be pressure dependent over the total pressure range 0–0.21 MPa. In the absence of ϵ -particles no substantial change in corrosion potential was observed in solutions saturated with the H_2 containing gas mixture or Ar. In contrast, the corrosion potential of the electrode with ϵ -particles was clearly lowered in solution saturated with the H_2 containing gas mixture.

/Röllin et al. 2001/ studied the dissolution of spent UO_2 fuel in $10 \text{ mmol} \times \text{dm}^{-3}$ NaCl solution under reducing (H_2), anoxic (Ar) and oxidizing (20% O_2 , 80%Ar) conditions. Whereas the rates of dissolution in Ar and (20% O_2 , 80% Ar) saturated solutions were not found to differ significantly the rate of dissolution in H_2 saturated solution was found to decrease by up to four orders of magnitude.

/Cera et al. 2006/ studied the dissolution of PWR-fuel with 40 MWd/kgU burn up in a series of long contact time (400–900 days) experiments using sealed ampoules. Each ampoule contained 1g fuel fragments in 30 cm^3 Ar flushed NaCl- and NaHCO_3 containing solution and 30 cm^3 gas phase. At the end of the experiment the gas phase was analyzed for O_2 and H_2 by mass spectrometry, H_2O_2 in solution was measured by a luminescence method /Eriksen et al. 1995/, actinides and fission products in solution were analyzed with ICP-MS and the uranium concentration was also measured using laser fluorimetry.

The data from gas phase and H_2O_2 analyses clearly indicate steady state conditions for radiolytically formed molecular oxidants and reductants in the time interval 400–900 days.

The concentrations of H_2 and O_2 in the gas phase were approximately 5% and 2.5% respectively and the H_2O_2 concentration in the range $10^{-8}\text{--}10^{-7} \text{ mol} \times \text{dm}^{-3}$.

Also the concentrations of actinides and fission products were constant within the time period 400–900 days. The experimental data indicate that the oxidative dissolution of the fuel fragments, although the concentration of oxidative radiolysis products in the solution remained constant, was suppressed.

Here we report the results of a limited study of the effect of initial saturation of the leach solution with 7% H_2 /93% Ar and 30% H_2 /70% Ar gas mixtures.

2 Experimental

2.1 Material

Fragments from a PWR fuel rod, Ringhals DO-7-S14 with a calculated burn up of 40 MWd/kgU were used in the experiments. The weight of the fragments used in the experiments was approximately 2 g. Test solutions were prepared from Millie-Q purified water purged with AGA 5.7 quality argon, containing less than 0.5 ppm oxygen. AGA gas mixtures 7% H₂/93% Ar and 30% H₂/70% Ar were used in the constant hydrogen concentration experiments.

2.2 Experimental arrangement

The experimental set up is depicted in Figure 2-1. Fuel fragments were transferred to a quartz vessel with approximately 60 cm³ total volume. The vessel, containing the fuel fragments, was placed in a lead shield in a glove box with argon atmosphere and connected to gas and solution sampling and analysing systems.

The test dissolution vessel and sensor chambers were flushed with argon or the gas mixture used in the experiment through a thin plastic tube inserted into the vessel via the sensor chamber. A volume of 30 cm³ solution containing 10 mM bicarbonate and saturated with argon or the gas mixture used in the experiment was transferred to the vessel by applying gas overpressure to the stock solution reservoir. The tube was thereafter removed and the valve connecting the reaction vessel and sensor chamber closed.

2.2.1 Gas analysis

The oxygen and hydrogen gas detector system (Orbisphere O₂ and H₂ detectors) was calibrated by flushing the sensor chamber with standardised H₂/O₂/Ar gas mixtures. After the calibration the sensor chamber was flushed with argon or the gas mixtures used in the experiment and the inlet and outlet valves closed. The reaction vessel/sensor chamber valve was thereafter opened to allow radiolytically formed oxygen and hydrogen to diffuse into the sensor chamber. Detector readings were taken at time intervals.

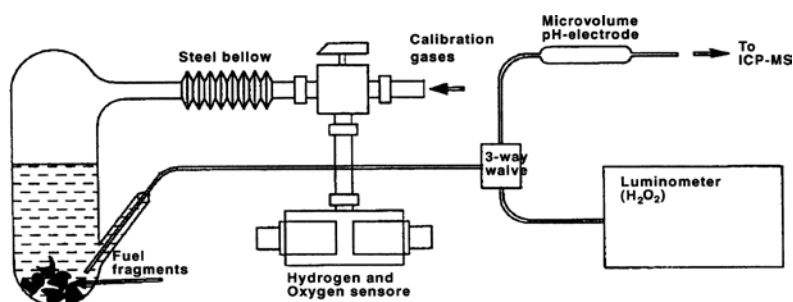


Figure 2-1. Schematic drawing of experimental arrangement.

2.2.2 Solution analysis

Small volumes (1–2 cm³) of the test solution were at time intervals removed through a capillary tube for analysis.

Hydrogen peroxide was measured by a luminescence method earlier described in detail by /Eriksen et al. 1995/. Fission products and actinides were analysed with ICP-MS (Plasma Quad 2 Plus, VG Elemental UK). Mass peak counts over the the range 54 to 254 were related to the In-115 signal from a 1 ppb internal standard. Sensitivity factors relative to In-115 were determined using a range of natural multi element standards and radionuclide standards for Tc-99 and Pu.

The uranium concentration was also measured using laser fluorimetry (Scintrex UA-3).

3 Results

3.1 Radiolytic oxidants

Figure 3-1 shows moles of oxygen plotted as a function of time. The initial equilibration of the solution with 7% H₂/93% Ar and 30% H₂/70% Ar clearly suppressed the radiolytic oxygen formation.

The hydrogen peroxide concentration in solution as a function of time is shown in Figure 3-2. The experimental data clearly indicate steady state concentrations, effectively constant in all solutions.

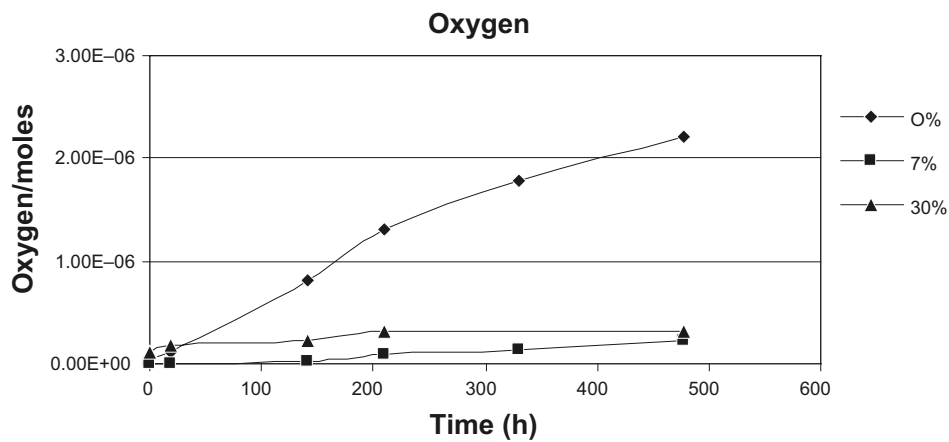


Figure 3-1. Moles of oxygen in solution and gas phase as a function of time.

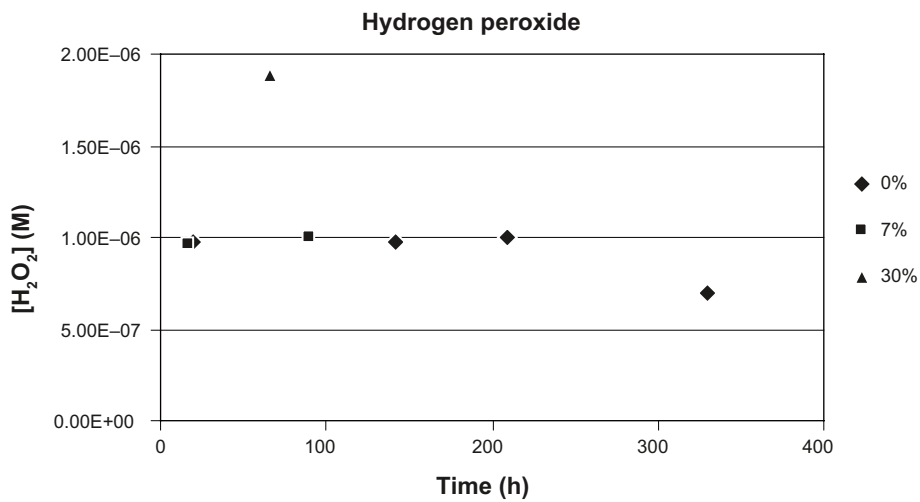


Figure 3-2. Hydrogen peroxide concentration in solution as a function of time.

3.2 Actinides

Moles uranium in solution are plotted as a function of time in Figure 3-3. In the solution initially equilibrated with argon the concentration was found to increase with time. On pre-equilibration with 7% H₂/93% Ar an initial fast increase to approx 6×10^{-8} moles was followed by a decrease to $< 10^{-8}$ moles within 200 hours. The concentration in the solution saturated with 30% H₂/70% Ar was found to be < 0.05 ppm corresponding to $< 6 \times 10^{-9}$ moles.

Moles of the actinides uranium, plutonium and neptunium in solution after 20 days leaching are plotted against hydrogen concentration in the equilibrating gas mixtures in Figure 3-4. The uranium and neptunium concentrations were found to decrease with increasing hydrogen concentration in the gas phase. In solution equilibrated with 30% H₂/70% Ar the concentrations were found to be 30–50 and 10 times lower than in the Ar equilibrated reference solution for uranium and neptunium, respectively. The plutonium concentration was found to be the same in all experiments.

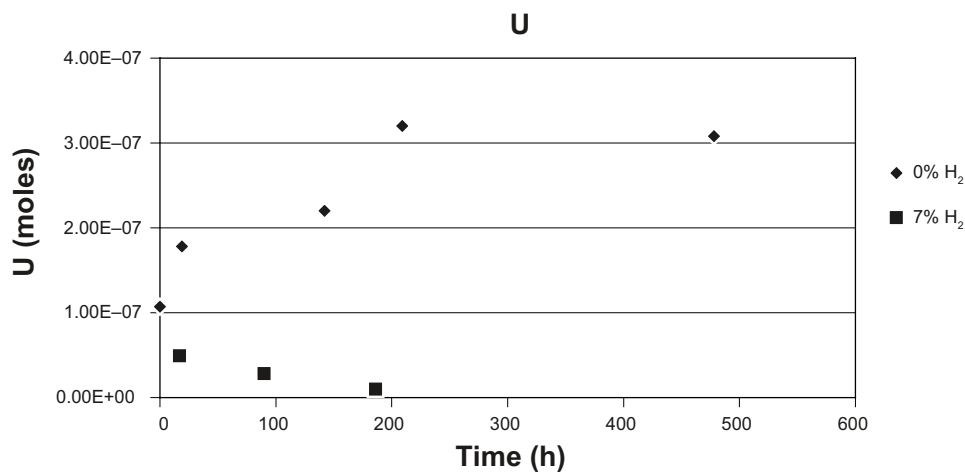


Figure 3-3. Moles of uranium in solution as function of time.

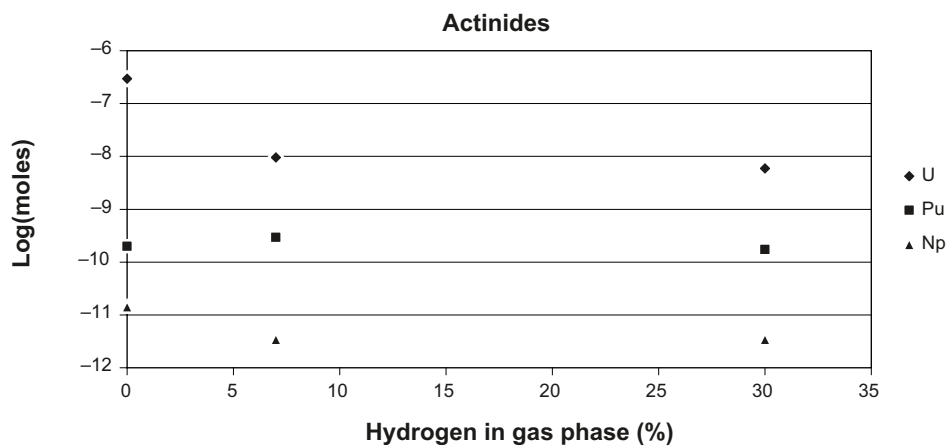


Figure 3-4. Moles uranium, plutonium and neptunium in solution after 20 days leaching.

3.3 Sr and Cs

The strontium and cesium concentrations after 20 days leaching in solutions initially equilibrated with Ar, 7% H₂/93% Ar and 30% H₂/70% Ar are shown in Figure 3-5. There is some scatter in the cesium data but taken together the experimental data indicates no hydrogen effect.

3.4 Nd and Y

Moles neodymium and yttrium in solutions equilibrated with Ar, 7% H₂/93% Ar and 30% H₂/70% Ar are shown in Figure 3-6. The experimental data indicate a very slight if any decrease in the concentrations with increasing initial hydrogen concentration.

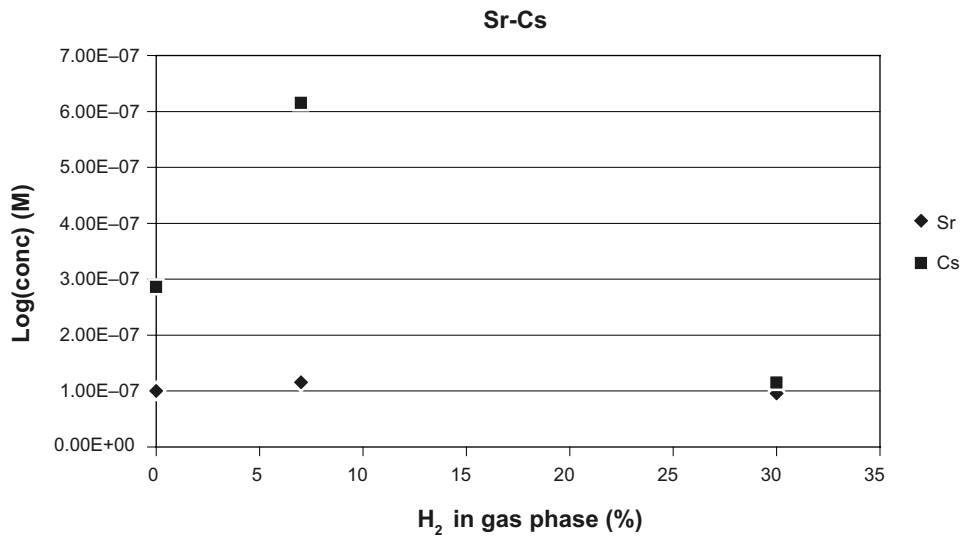


Figure 3-5. Concentration of strontium and cesium in solution after 20 days leaching.

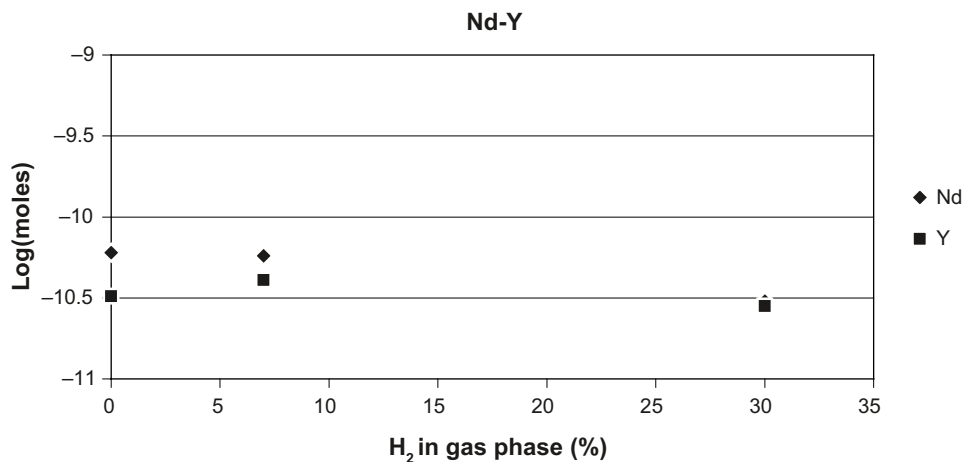


Figure 3-6. Neodymium and yttrium content in solution after 20 days leaching.

3.5 Tc and Mo

In Figure 3-7 moles of technetium and molybdenum in solution after 20 days leaching are shown as a function of hydrogen concentration in the gas phase. Whereas the Tc concentration was found to decrease by two orders of magnitude on equilibrating the solution with 30% H₂/70% Ar the effect on the molybdenum concentration decreased but slightly.

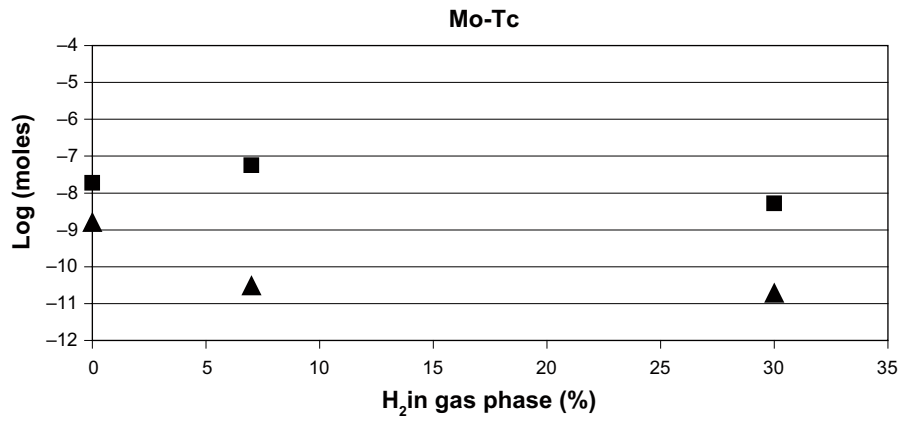


Figure 3-7. Moles molybdenum (■) and technetium (▲) in solution after 20 days leaching.

4 Discussion

The strontium and cesium concentrations in solutions pre-equilibrated with Ar and the H₂/Ar mixtures used in the leaching experiments indicate the same release in all solutions.

The strontium and cesium point, if congruent dissolution with uranium is assumed, at constant rate of oxidative fuel dissolution.

Whereas the oxygen formation was found to decrease with increasing H₂ concentration in the gas phase the hydrogen peroxide concentration in solution was found to be effectively constant in all experiments. Hydrogen peroxide is very probably the dominant oxidant /Ekeroth et al. 2006/ in the leach solutions and a constant concentration in solution ties in well with the assumption of constant rate of dissolution.

We have carried out some MACKSIMA calculations on homogeneous radiolysis in 10 mM NaHCO₃ at pH 8 irradiated with the α/β field and doserates used in modelling of earlier time resolved and long contact time experiments. A detailed description of the system and assumptions used in previous modelling are given in /Cera et al. 2006/.

In the present calculations we have taken into account the diffusive transport for long lived species (H₂O₂, O₂ and H₂) from the irradiated volume to bulk solution and distribution of O₂ and H₂ between solution and gas phase. No surface mediated reactions (H₂O₂ + UO₂(s); H₂O₂ → ½ O₂ + H₂O) are included in the calculations. Calculated homogeneous concentrations in solution after 20 days irradiation are given in Table 4-1.

As can be seen from Table 4-1, the concentration of H⁺ increases and the concentration of O₂ decreases with increasing H₂ concentration while the H₂O₂ concentration remains nearly constant. The calculated concentrations of the molecular radiolysis products are in good agreement with the measured concentrations. Furthermore, the calculated concentrations as well as the effects of H₂ on the concentrations of the molecular products are well in line with recent data on the relative impact of different radiolysis products /Ekeroth et al. 2006/. The nearly H₂ independent H₂O₂ concentration also indicates that the rate of UO₂ oxidation should be nearly constant (as indicated in Figures 3-2 and 3-5).

In earlier experiments with the same fuel /Bruno et al. 1999/ yttrium and molybdenum did not show congruent dissolution behaviour, but within a few hours reached steady state concentrations in solution. The concentrations may possibly be sorption and/or solubility controlled (NdOHCO₃, YOCO₃), /Cera et al. 2006/.

Table 4-1. Calculated concentrations in solution after 20 days radiolysis.

Species	0% H ₂ (M)	7% H ₂ (M)	30% H ₂ (M)	5MPa H ₂ (M)
OH	2.96E-14	2.93E-14	2.57E-14	1.10E-15
H	2.60E-14	3.35E-14	2.36E-13	2.86E-12
CO ₃ ⁻	3.60E-10	3.17E-10	1.85E-10	6.57E-10
H ₂ O ₂	7.17E-7	7.47E-7	8.89E-7	6.40E-7
O ₂	1.13E-6	9.77E-7	1.96E-7	1.09E-8

The decrease in the redox sensitive elements uranium, neptunium, technetium and molybdenum concentrations with increasing initial hydrogen concentration indicates a marked change of redox conditions in the solution. As the reactions of H_2 with UO_2^{2+} and TcO_4^- in solution without a catalyst at room temperature are extremely slow /Ekeröth et al. 2004, Cui and Eriksen 1996/ reduction by radiolytically formed reductants and/or by catalytic surface reactions are more probable. /Wren et al. 2005/, to explain the corrosion potential of $UO_2(s)$ in α -radiolytically decomposed water invoked two surface catalyzed processes; decomposition of hydrogen peroxide to oxygen and the recombination of hydrogen peroxide and hydrogen to form water by the formation of radical surface species. /Broczkowski et al. 2005/ have demonstrated that ϵ -particles strongly lower the corrosion potential of $UO_2(s)$. Assuming surface catalyzed reduction of UO_2^{2+} by H_2 is diffusion controlled ($k = 10^{-3} \text{ m min}^{-1}$ /Ekeröth and Jonsson 2003/, the pseudo first order rate constant for surface catalyzed UO_2^{2+} reduction in the present system would be $4.2 \times 10^{-6} \text{ s}^{-1}$. This corresponds to a half-life of approximately 2 days for UO_2^{2+} in solution. Hence, the surface catalyzed process could indeed be an important factor. However, it is not very likely that this process alone is responsible for the reduction in UO_2^{2+} concentration.

/Röllin et al. 2001/ in flow through experiments with fragments from the same fuel rod as used in the present study observe a reduction in fuel dissolution by more than four orders of magnitude on equilibrating the solution with 0.1 MPa hydrogen. The time needed to reach low steady state dissolution was, however, long (70–80 days) i.e. pointing at a very sluggish kinetic surface process which may possibly partly explain the difference in data between Röllin's studies and the present work.

5 Conclusions

Dissolution of spent fuel have been studied in 10 mM NaHCO₃ solution equilibrated with Ar, 7% H₂/93% Ar and 30% H₂. Whereas the concentrations of Sr and Cs remained the same in all experiments the concentrations of the redox sensitive elements U, Np, Tc and Mo were found to decrease with increasing hydrogen concentration.

The experimental data point at constant rate of fuel dissolution and reduction of the redox sensitive elements by radiolytically formed reductants, probably in surface catalyzed reactions.

6 References

- Broczkowski M E, Noel J J, Shoemith D W, 2005.** The inhibiting effect of hydrogen on the corrosion of uranium dioxide under nuclear waste disposal conditions. *J. Nucl. Mater.* 346 (2005) 16–23.
- Bruno J, Cera E, Grivé M, Eklund U B, Eriksen T E, 1999.** Experimental determination and chemical modelling of radiolytic processes at the spent fuel/water interface. SKB TR 99-26, Svensk Kärnbränslehantering AB.
- Cera E, Bruno, Duro L, Eriksen T E, 2006.** Experimental determination and chemical modelling of radiolytic processes at the spent fuel/water interface. SKB TR 06-07, Svensk Kärnbränslehantering AB.
- Cui D, Eriksen T E, 1996.** On the reduction of Pertechnetate by Ferrous Iron in Solution. Influence of Sorbed and Precipitated Fe(II). *Environ. Sci. Technol.* 30, 2259 (1996).
- Ekeroth E, Jonsson M, 2003.** Oxidation of UO_2 by radiolytic oxidants, *J. Nucl. Mater.* 322 (2003) 242–248.
- Ekeroth E, Jonsson M, Eriksen T E, Ljungquist, Kovacs S, Puigdomenech I, 2004.** Reduction of UO_2^{2+} by H_2 . *J. Nucl. Mater.* 334 (2004) 35–39.
- Ekeroth E, Roth O, Jonsson M, 2006.** The relative impact of radiolysis products in radiation induced oxidative dissolution of UO_2 . *J. Nucl. Mater.* 355 (2006) 38–46.
- Eriksen T E, Eklund U B, Werme L, Bruno J, 1995.** Dissolution of irradiated fuel; a radiolytic mass balance study. *J. Nucl. Mater.* 227 (1995) 76–82.
- King F, Quinn M J, Miller N H, 1999.** The effect of hydrogen and gamma radiation on the oxidation of UO_2 in $0.1 \text{ mol} \times \text{dm}^{-3}$ NaCl solution. SKB TR 99-27, Svensk Kärnbränslehantering AB.
- Röllin S, Spahiu K, Eklund U B, 2001.** Determination of dissolution rates of spent fuel in carbonate solutions under different redox conditions with a flow-through experiment. *J. Nucl. Mater.* 297 (2001) 231–243.
- Wren J C, Shoemith D W, Sunder S, 2005.** Corrosion Behavior of Uranium Dioxide I Alpha Radiolytically Decomposed Water. *J. Electrochem. Soc.* 152(11) 2005 470–481.

ISSN 1404-0344

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