Radiolysis and corrosion of ^{238}Pu-doped UO$_2$ pellets in chloride brine

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Abstract. Deaerated 5 M NaCl solution is irradiated in the presence of UO$_2$ pellets with a-radiation from ^{238}Pu. Experiments are conducted with ^{238}Pu doped pellets and others with ^{238}Pu dissolved in the brine. The radiolysis products and yields of mobilized U and Pu from the oxidative dissolution of UO$_2$ are determined. Results found for radiolysis products and for the oxidation/dissolution of pellets immersed in Pu containing brine are similar to results for Pu doped pellets, where the radiation chemical processes occur only in the liquid layer of some 10 μm thickness adjacent to the pellet. The yield of radiolysis products is comparable to earlier results, that of mobilized U from the pellets is < 1% of the total amount of oxidized species. Thus, the radiation chemical yield (*G*-value) for mobilized hexavalent U is < 0·01 ions/ 100 eV. In spite of the low radiation yield for the corrosion, the rate of UO$_2$ dissolution is higher than expected for the concentrations of long-lived oxidizing radiolysis compounds found in the solutions.

Keywords. a-Radiolysis; UO$_2$; leaching; chloride brine; radiolysis products.

1. Introduction

In the past, the a- and g-radiolysis of concentrated chloride brines was investigated with respect to the final disposal of spent nuclear fuel in a rock salt formation.[1–4] The radiation chemical processes in the solution could be simulated with a reaction kinetic model.[2,4,5]

The first step in the mobilization of radionuclides from spent fuel is oxidative dissolution of the fuel matrix.[6–8] As the only source of oxidizing species in a final disposal in the deep underground is radiolysis, it is important to know the radiation chemical yield of fuel oxidation. In a repository, the spent fuel is protected from contact with water by a thick-walled or corrosion resistant container for at least 500 years. Thereafter, the a-dose rate from the actinides dominates over g-radiation. Therefore, UO$_2$ pellets doped with a short-lived a-emitter are suitable to be used in experiments to simulate the corrosion processes of aged spent fuel. ^{238}Pu doped UO$_2$ pellets were frequently used in the past[9–11] for experiments in dilute or aerated solutions. This work describes corrosion experiments with ^{238}Pu doped UO$_2$ pellets in deaerated 5 M NaCl solution and compares them with experiments using undoped UO$_2$ pellets in deaerated 5 M NaCl solution containing dissolved ^{238}Pu. The amounts of ^{238}Pu in the pellets is varied to obtain a-dose rates 2·5 and 250 times higher than that of 500 years aged fuel.

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2. Experimental

All experiments are conducted in glove boxes in an argon atmosphere. The pellets have a diameter or edge length of about 6 mm and a mass of 0·3 to 0·8 g. After cutting, polishing and cleaning the pellets are annealed for several hours at 1400°C and then cooled down in an Ar/H_2 stream to re-establish a stoichiometric composition at the UO_2 surface. The annealing procedure is tested by XPS analysis of an undoped pellet. The U 5f peak in the valence band spectrum (figure 1) indicates that 92% of the pellet surface has a composition according to UO_2, equivalent to a mean surface composition of $UO_{2.08}$.

The nominal pellet composition and the activity concentration in the brine is given in table 1. The isotopic compositions of plutonium used for doping the three pellets (no 1–3, table 1) and which is dissolved in the brine (no 4–6, table 1) are slightly different. In both cases the main components are about 65% ^{238}Pu, 16% ^{239}Pu and 15% ^{234}U.

After the annealing process, the cold pellets are placed on a glass support in a glass vessel and 20 ml of deaerated solution (table 1) is added. An evacuated gas-sampling flask is mounted to the glass vessel and its stop-cock opened to establish a reduced pressure in the whole apparatus. The solution with the pellet is kept at room temperature
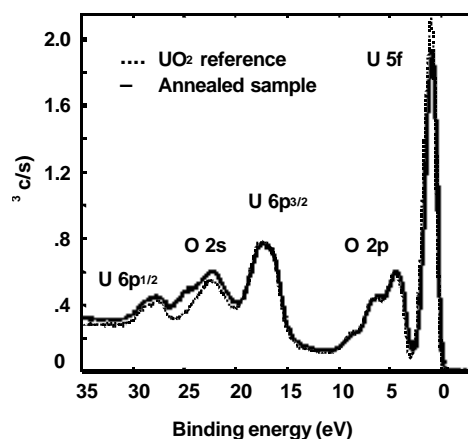

Figure 1. XPS spectrum of a UO_2 sample annealed at 1400°C in Ar/H_2 compared to a reference sample which was freshly broken in the ultra high vacuum.

Table 1. Composition of the pellets and activity concentration of the solutions.

No.	UO_2-pellet: $^{238}PuO_2$ (nom. wt.%)	5 M NaCl sol.: act. conc. (GBq/L)	pH at start
1	10	0	12
2	10	0	8
3	0·1	0	8
4	0	8·41	12
5	0	8·41	8
6	0	841	8
7	0	0	8

and stirred occasionally. The reduced pressure persists in spite of the radiolysis gas evolution as both, the gas and solution are sampled and analysed at defined time intervals. For gas sampling the gas-sampling flask is removed from the apparatus after closing its stop-cock. The gas composition is determined by mass spectroscopy, the total amount from its pressure. An aliquot of the solution is used to determine the radiolysis products HClO, ClO$_2^-$ and ClO$_3^-$ as well as pH and the redox potential.[1] The gas space above the remaining solution is then flushed with Ar, a new evacuated gas-sampling flask is attached to the vessel and the experiment continues. In the first part of the experiment in which three samples are taken within about nine months, an aliquot of each liquid sample is filtered through 450 and 1·8 nm filters. The U and Pu content of the filtrates is determined by ICP-MS in the mass range 234 to 242. Additionally, Pu is determined from the α-activity. This procedure allows the determination of truly dissolved U and Pu and give information about the particle size of material mobilized from the pellets. In the second part of the experiment, the aliquot of each sample is not filtered but acidified with nitric acid to determine the total amount of mobilized U and Pu.

3. Results

Most of the results are presented as concentrations versus the applied α-dose. The radiolysis gases are also given per kg solvent. To calculate the applied dose on the solution, it is assumed that 18·8% of the radiation energy released within a pellet surface layer of 11·8 μm thickness (which is the path length of 5·5 MeV α-particles in UO$_2$) is homogeneously dissipated in the solution, even though the maximum range of the α-radiation in the brine is only about 45 μm. The percentage M (1) considers only the geometric aspects of α-radiation emerging from the surface and assumes a linear energy loss along the α tracks. Thus, M equals the ratio of sphere segments integrated over the radius (mean segment volume) and the sphere volume.

$$M = \left[\int_0^r \frac{1}{3} \cdot p \cdot (r-x)^2 \cdot (2 \cdot r + x) \cdot \mathrm{d}x / r \left/ \left(\frac{4}{3} \cdot p \cdot r^3 \right) \right. \right] = 0 \cdot 188, \tag{1}$$

where r = range of α-radiation in the solid and x = segment height.

A derivation for CANDU fuel[12] gives even a smaller percentage of radiation energy, which is effective in the adjacent solution.

For pellets 1 and 2 (table 1), the calculated mean dose rates increase from 10 to 35 Gy/h because sampling reduces the amount of solution. For pellet 3 the dose rate increases from 0·1 to 0·17 Gy/h. The local dose rate in the solution layer actually irradiated is more than 3 orders of magnitude higher. For the experiments with pellets 4, 5 and 6 (table 1), it is assumed that the total decay energy is homogeneously dissipated in the solution, which equals a dose rate of 22·5 Gy/h and 2250 Gy/h (pellet 6). The experiment with pellet 7 serves as a reference, as the radiation level is negligible.

Figure 2 shows the generation of radiolysis gases over the applied dose. The amount of hydrogen and oxygen formed is proportional to the dose. The gas formation does not depend on pH and upon the distribution of the α-emitter in the solution. The solutions with doped pellets, where the primary products are formed in a volume of only 4 mm^3 give the same results as the solutions with Pu homogeneously distributed in 20 ml having the same mean dose. In addition to the gases, hypochlorite (figure 3), chlorite and chlorate (figure 4) are formed. While the chlorite concentration remains near 10^{-5} mol/kg, the

yield of hypochlorite increases with increasing *p*H and approaches a limiting concentration. The chlorate concentration increases with the dose, but its yield is somewhat smaller than found in earlier experiments.[4]

Figures 5 and 6 depict results for U and Pu mobilized from the pellets. In the first part of the experiments, when solution samples were filtered through 450 and 1·8 nm filters prior to analysis, the mobilization of both U and Pu from pellets doped with 10% Pu is higher at neutral *p*H compared to that at *p*H 12. With increasing time, the differences in mobilized U and Pu between the two filtrates become negligible. This indicates that both elements form precipitates, which are large enough to be removed from both filters. In the alkaline solution, the U concentration is three and the Pu concentration two orders of magnitude smaller than in neutral solution. The difference in U concentration as a func-
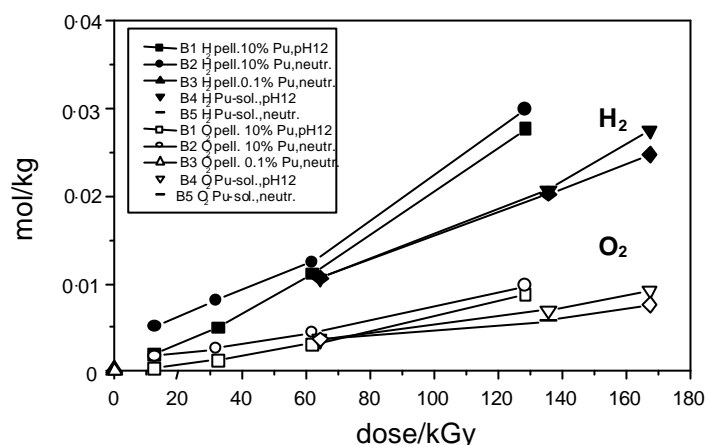

Figure 2. H_2 (filled symbols) and O_2 (open symbols) formation in 5 M NaCl solution in contact with Pu-doped pellets (B1, B2, B3) in comparison with solutions containing UO_2 pellets and dissolved Pu (B4, B5).
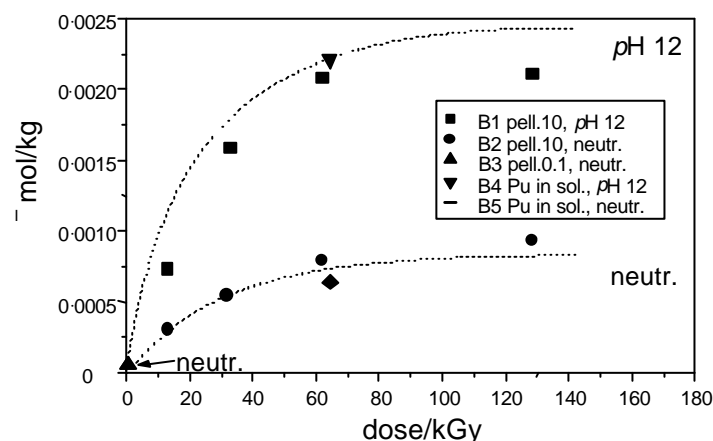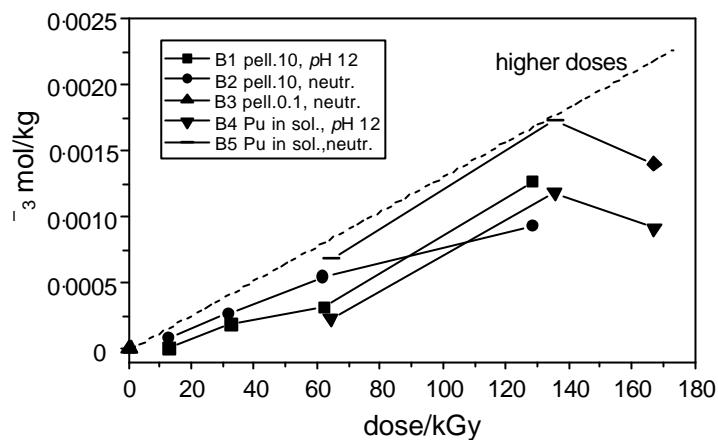

Figure 3.   Formation of hypochlorite in 5 M NaCl solution in contact with Pu-doped pellets (B1, B2, B3) in comparison with solutions containing UO_2 pellets and dissolved Pu (B4, B5).

Figure 4. Formation of chlorate in 5 M NaCl solution in contact with Pu-doped pellets (B1, B2, B3) in comparison with solutions containing UO$_2$ pellets and dissolved Pu (B4, B5). The dashed line corresponds to earlier results[4].
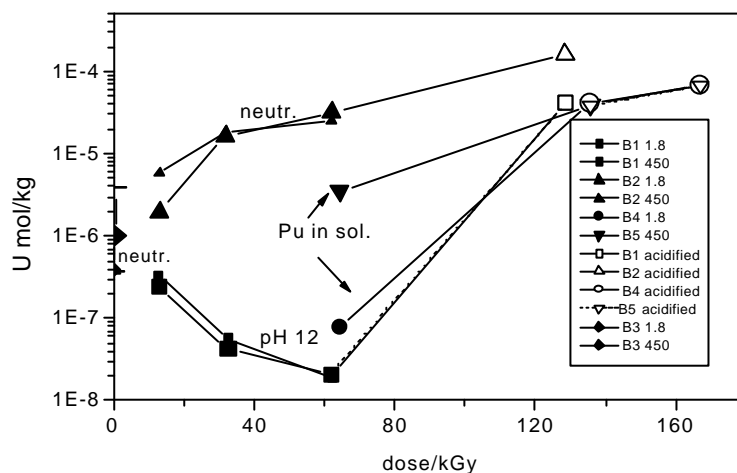

Figure 5. Mobilized uranium from UO$_2$ pellets in 5 M NaCl solution. (Pu-doped pellets: B1, B2, B3; UO$_2$ pellets and Pu in solution: B4, B5.) Closed symbols: Concentration in filtered (1·8 or 450 nm) samples. Open symbols: Concentrations in acidified samples.

tion of *p*H is less pronounced in the experiments with undoped pellets (samples 4 and 5, table 1). After the application of about 150 kGy the solutions, which are acidified immediately following sampling show U concentrations near 10^{-5} mol/kg and a Pu concentration of a few 10^{-6} mol/kg independent of *p*H and of the distribution of the *a*-source (doped pellet and Pu containing brine).

Practically no radiolysis products are found in the solutions with pellets 3 and 7 because of the low radiation level. But there is a difference in the amount of dissolved U between doped and undoped pellets. Within the first 9 months of the experiments, the U concentration in the solution with pellet 7 ranges between 10^{-8} and 10^{-9} mol/kg, that in the solution with pellet 3 is near 10^{-6} mol/kg. The Pu concentration in the latter solution is about 10^{-8} mol/kg.

The *p*H of the solutions with the pellets 1, 2, 4, 5 and 6 (table 1) does not vary with the dose. The redox potential in the alkaline solutions (pellet 1 and 4, table 1) is about +650 mV, that in the neutral solutions with pellet 2 and 5 above +950 mV. The solution with pellet 6 show a redox potential of more than +1000 mV. Such highly oxidative conditions result most probably from the generation of hypochlorite, as the redox potential drops sharply to a few 100 mV upon addition of H_2O_2, which efficiently reduces hypochlorite to chloride. The *p*H of the solutions with pellets 3 and 7 (table 1), which were neutral at the start of the experiment, shifts to *p*H 5·5 and 6·5 after some months. The redox potential of solution 3 reaches about +650 mV, that of solution 7 about 530 mV.

The experiment with pellet 6 (table 1) was finished after 4800 h which is equivalent to the application of 10·8 MGy. The pellet is rinsed with water, dried and is then investigated by scanning electron microscopy. Figure 7 compares the surface of pellets after the test to an uncorroded surface. The surface roughness increases during the experiment. It is unclear if this is a result of corrosion and/or of secondary phase precipitation.

4. Discussion

The results for radiolysis gas formation correspond well to earlier experiments.[4] The presence of UO_2 pellets and the irradiation solely from doped pellets has no impact on the radiolytic decomposition of the brine. The yields of HClO, ClO_2^- and ClO_3^- can be qualitatively described by the reaction model previously published.[2,4] According to this model, chlorate is formed in three ways: very fast by short-lived radiolysis species, by the slower reaction between chlorite and an excess of hypochlorite and very slowly by the decomposition of hypochlorite. This mechanism explains the permanent low concentration of chlorite and the limitation of the hypochlorite concentration to a plateau value, which depends on the dose rate. In the lower dose range chlorate formation does not reach the level measured for high doses[1] because of the build-up of hypochlorite. Only at
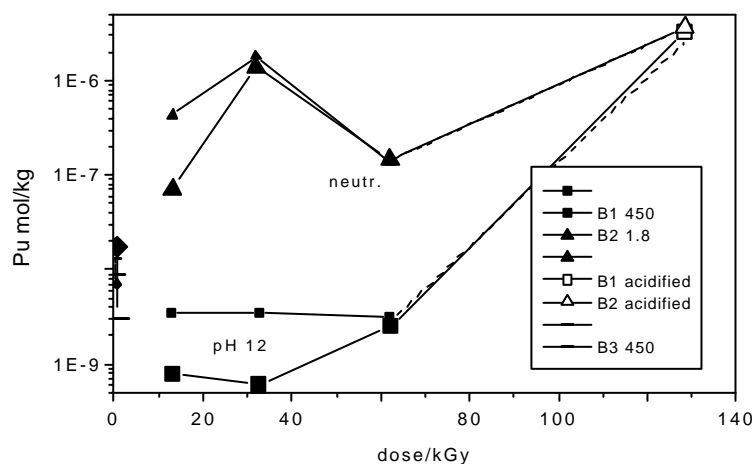
Figure 6. Mobilized plutonium from doped UO_2 pellets in 5 M NaCl solution. Closed symbols: Concentration in filtered (1·8 or 450 nm) samples. Open symbols: Concentrations in acidified samples.
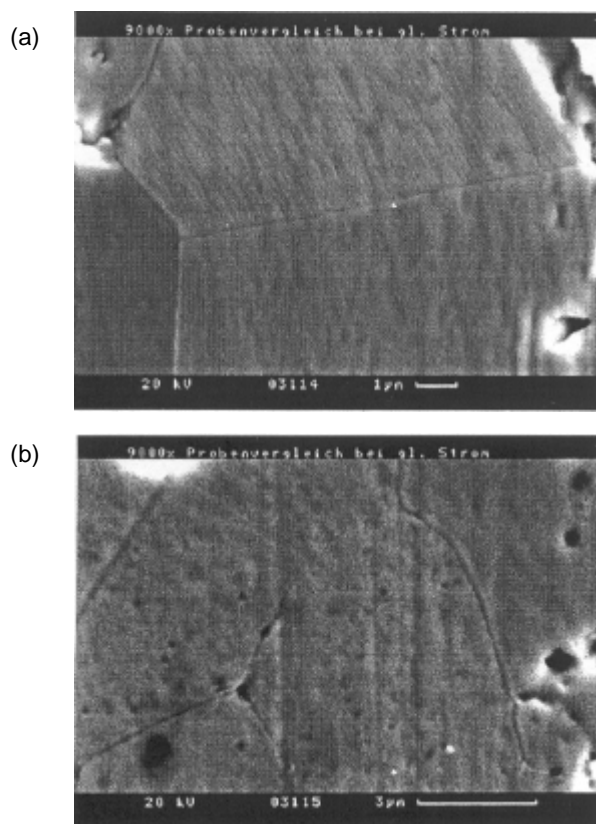
(a)

(b)

Figure 7. SEM picture of a UO$_2$ pellet before (**a**) and after (**b**) corrosion in a Pu-containing 5 M NaCl solution (4800 h, 10·8 MGy).

high doses and/or long irradiation times does the amount of hypochlorite, which has not yet been converted to chlorate become negligible. The yield of water-soluble products does not depend on the distribution of the α-source in the solution (doped pellets or Pu containing brine). Pu and/or U are mobilized from the pellets by oxidative corrosion. The U concentrations in the filtrate of the alkaline solution near 10^{-8} mol/kg and 10^{-5} mol/kg in the neutral solutions of pellets 1, 2, 4 and 5 (figure 5) correspond to published solubility data of orange coloured sodium uranate.[13] The U concentration in the solution with pellet 3 of about 10^{-6} Mol/kg is not apparently solubility controlled. The mobilized Pu from the doped pellets behaves similarly to that of U (figure 6). The Pu concentration in solution 1 is probably controlled by the hydrolysis of Pu(VI), while that in solution 2 is about 2 orders of magnitude higher due to complexation by Cl$^-$ and ClO$^-$.[14] The Pu concentration in solution 3 is not apparently solubility controlled.

From the concentrations of U and Pu in the solutions with pellets 1, 2 and 3, one can estimate that the pellets are dissolved congruently and proportional to the α-dose, provided that the analysed concentrations in the acidified solutions represent the total amounts of mobilized material from the pellets (i.e. no precipitation of secondary phases on the vessel walls and on the pellets themselves). The U concentration in solution with pellet 7

of 10^{-8}–10^{-9} mol/kg is within the order of magnitude observed for the solubility of tetravalent U.[15]

The radiation chemical yield (the *G*-value) for the oxidation of U and Pu, based on the concentrations found in the acidified solutions is less than 1% of the total yield of oxidizing species. Thus, the *G*-value for U is only < 0.01 molecules U^{6+}/100 eV. Even a somewhat lower yield for corrosion is found in experiments in 0·1 M perchlorate solution with an external α source.[17]

The mean corrosion rate for pellets 1, 2, 4 and 5 after 7400 h, equivalent to a dose of 150 kGy is calculated to be 1·7 mg/(cm^2 d). This UO_2 corrosion rate is high compared to rates observed for oxidizing agents.[6,16] After 7400 h the solutions contain roughly 10^{-3} mol/kg ClO^-, 10^{-3} mol/kg ClO_3^- (figures 3 and 4) and 3×10^{-6} mol/kg dissolved O_2 as potential oxidizing agents. According to published data for chemical corrosion, a UO_2 dissolution rate of 1·7 mg/(cm^{2}d) would require a concentration of about 0·1 mol/kg of H_2O_2, O_2 [6] or ClO^-.[16] We conclude that for the time/dose range under investigation, irradiation conditions are much more effective for UO_2 corrosion than oxidation by long-lived radiolysis species.

The mean corrosion rate for solution 7 (table 1) after 7500 h was 2.7×10^{-4} mg/(cm^2 d), which is comparable to the published rate (2×10^{-4} mg/(cm^{2}d)) for dilute aqueous solutions.[6]

Acknowledgements

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