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Journal of Nuclear Materials 297 (2001) 231–243

journal of nuclear materials

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Determination of dissolution rates of spent fuel in carbonate solutions under different redox conditions with a flow-through experiment

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Received 27 February 2001; accepted 15 June 2001

Abstract

Dissolution rates of spent UO_2 fuel have been investigated using flow-through experiments under oxidizing, anoxic and reducing conditions. For oxidizing conditions, approximately congruent dissolution rates were obtained in the pH range 3–9.3 for U, Np, Ba, Tc, Cs, Sr and Rb. For these elements, steady-state conditions were obtained in the flow rate range 0.02–0.3 ml min^{-1}. The dissolution rates were about 3 mg d^{-1} m^{-2} for pH > 6. For pH < 6, dissolution rates were strongly increasing for decreasing pH. Incongruent dissolution was found for Zr, Mo, Ru, Rh, Pd, Am and the lanthanides. The dissolution rates with $H_2(g)$ saturated solutions dropped by up to four orders of magnitude as compared to oxidizing conditions. Because of the very low concentrations, only U, Pu, Am, Mo, Tc and Cs could be measured. For anoxic conditions, both the redox potential and dissolution rates increased approaching the same values as under oxidizing conditions. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Direct disposal of spent nuclear fuel in deep geological formations is being considered by several countries [1]. The disposal of spent fuel is planned to be made in the presence of a series of barriers, which should isolate or delay the contact of spent fuel with water as well as the transport of the dissolved radionuclides in the biosphere. Transport by groundwater is the only credible mechanism for the migration of the radionuclides contained in the spent fuel in the repository to the biosphere. Spent fuel is largely $UO_2(s)$ with only a small fraction of other actinides and fission products. A great majority (>95%) of these radionuclides are dispersed or in solid solution in the $UO_2(s)$ matrix [2]. Hence it is important to evaluate the rate of dissolution of the spent fuel and the rate of release of the various radionuclides, i.e., the so-called source term. The rates of dissolution of spent fuel depend on a variety of factors as the composition of the spent fuel itself, the composition of the groundwater as well as the redox conditions under which the dissolution takes place.

Experimental studies on spent fuel leaching have been going on since the late 1970s (see [3,4] and references therein) for a variety of conditions and solution compositions. The majority of studies in low salinity bicarbonated groundwaters have been performed under oxidizing conditions. Initially, it is possible to determine the dissolution rate of the spent fuel matrix from the increase in the uranium concentration in solution. However, after an initial rapid increase in the concentration, the rate of increase levels out and in some 100–200 days, the average concentrations of the actinides in solution have reached virtually constant levels: $[U] \cong 10^{-5}$ M, $[Np] \cong 10^{-9}$ M and $[Pu] \cong 10^{-8.7}$ M [5,6]. This is mainly due to the saturation of the solution with these elements. Even though there is no increase in the concentration of the actinides with time, the

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PII: S0022-3115(01)00645-6

concentrations of some fission products, such as ^{90}Sr, continue to increase, although at a lower rate. This rate of increase may then be used to estimate the long-term spent fuel dissolution rate.

In order to avoid the problem of a potential uranium precipitation during the leaching tests, flow-through experiments are used. In such an experiment the solid phase is contained in a cell and the test solution is pumped continuously through the cell. The flow rate is usually set to a rate sufficient enough to maintain the uranium concentration far below saturation. Under such conditions dissolution rates are not solubility controlled and hereby independent of the flow rate. Flow-through experiments have been widely used to study the dissolution kinetics of uranium oxide [7–13] and spent fuel [14–17]. In the case of spent fuel, fission products and other actinides can be used besides U as monitors to calculate dissolution rates of spent fuel. These monitors exist in a variety of different chemical species. Precipitation and adsorption of some chemical species can take place even for very low concentrations. Therefore, to check the applicability of different dissolution rate monitors, we have performed leaching tests for different pH and different flow rates. Another advantage of a flow-through experiment was found for leaching tests under an inert atmosphere. The individual samples can be taken continuously without exposing the test solution to air. Under the course of dissolution tests with a 1 bar hydrogen atmosphere and room temperature, dissolution rates dropped up to four orders of magnitude as compared to oxidizing conditions in the pH range 3–9. These results confirm the results from previous experiments where high hydrogen pressures were found to have quite an impact on spent fuel leaching [18].

2. Experimental

2.1. Chemicals and apparatus

Radioactive solutions require an easy and safe handling of the flow-through system. Furthermore, the material of the flow-through cell must resist irradiation damage. Gray and co-workers [11] used empty stainless steel chromatography columns as flow-through cells. In a first series of experiments we found decreasing dissolution rates when stainless steel columns were used. Probably the stainless steel frits were corroded by the test solutions used. For the experiments described here, poly ether ether ketone (PEEK)-lined stainless steel chromatography columns (30 mm × 4.6 mm) have been used. The columns have been fitted on both ends with PEEK and teflon (PAT) frits with 2 μm openings. Spent fuel with an average burn-up of about 43 MWd kg^{-1} was crushed in a mill and sieved. A fraction in the size range 0.25–0.5 mm was rinsed with ethanol to get rid of the fines. The specific surface was determined by BET to be approximately 300 cm^2 g^{-1}. About 0.5 g of the rinsed and dried fuel fraction was loaded in the column. The test solutions were stored in a 5 l glass bottle and pumped by a single piston pump through the fuel cell. The pH and E_h (redox potential with respect to a standard hydrogen electrode) have been measured in potentiometric cells before and after the fuel cell. Samples were collected after the second potentiometric cell in polyethylene bottles containing appropriate amounts of nitric acid (Merck, suprapure) to obtain a final concentration of about 1% HNO_3. 10 ml of each sample have been measured with γ-spectrometry and inductively coupled plasma-mass spectrometry (ICP-MS).

Distilled, de-ionized water from a Milli-Q system was used to prepare all test solutions. In order to avoid absorption of dissolved species on the experimental devices all the test solutions contained 10 mM NaCl (Merck: NaCl suprapure). Different pH were established by adding $NaHCO_3$ (Merck: $NaHCO_3$ suprapure) or HCl (Merck: 30% HCl suprapure). For leaching tests under oxidizing conditions (ox) the test solutions have been in contact with the atmosphere, sparged with pressurized air or with a gas mixture containing 20% O_2/0.03% CO_2/80% Ar. The reducing conditions (red) were achieved by bubbling H_2 containing 0.03% CO_2 over a Pt foil in the test solution tank (see further for a discussion of the redox conditions). A schematic view of the flow-through experiment is shown in Fig. 1.

2.2. Electrode measurements

Metrohm glass electrodes with internal Ag/AgCl reference electrodes were used for pH measurements. The test solutions in the flow-through experiment contained always 0.01 M NaCl to get a minimal ionic strength and to avoid absorption of dissolved species. At the same time the chloride concentration prevented the precipitation of AgCl on the diaphragm, even for contact periods of more than one year. Test solutions in a pH range 3–9.3 have been used. The dead volume of the potentiometric cells and the connecting tubes was about 8 ml. Thus, after changing test solutions, stable electrode potentials were first obtained after about one day. The pH of all test solutions was in good agreement (±0.1) with the theoretical pH calculated with graphical methods as described in [19]. The redox potentials have been measured with an Au-foil and a Pt-spring with respect to the inner reference electrode (see [20] for details).

In order to express the redox potentials referred to SHE (standard hydrogen electrode) and to calibrate the glass electrode in concentration units, a preliminary Gran titration [21,22] was performed in the presence of a hydrogen electrode. For an Ag/AgCl internal reference

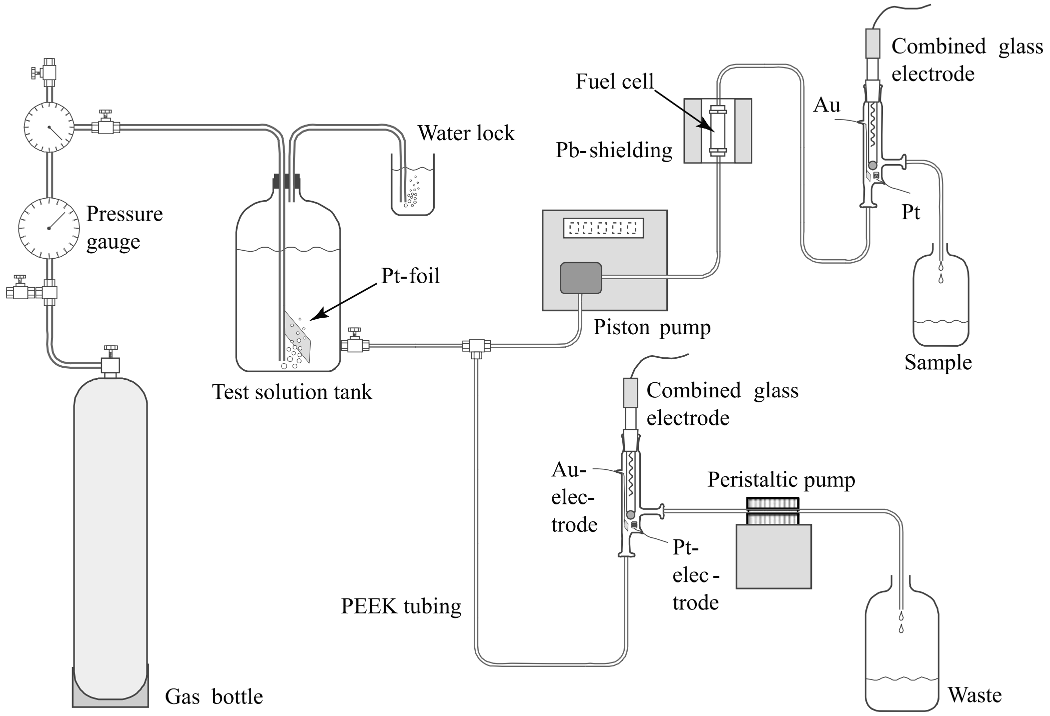

Fig. 1. Schematic overview of the flow-through experimental setup.

electrode in 3 M KCl a potential of 217 mV with respect to a SHE has been obtained.

2.3. Analysis of leach solutions

Fission products and actinides have been measured with ICP-MS. All the samples contained 1% HNO_3 and 1 ppb In-115 as internal standard. It has been measured in the mass range 80–254 amu. The acquisition time was 4 min and the wash time 2 min. Sensitivity factors for the different elements relative to In-115 have been calibrated by a one-point calibration with multielement standards. Nuclide concentrations have been calculated by relating the signals to the In-115 signal. For the determination of Sr-90 and Mo-100 isobaric interferences with Zr-90 and Ru-100 have been corrected. It was assumed that all Zr and Ru originated from fission products. The isotopic abundances were taken from ORIGEN calculations as: 19.8% Zr-93, 3.24% Zr-90 and 34.86% Ru-102, 6.79% Ru-100. Furthermore, it was assumed that the mass peaks 93 and 102 only contained Zr and Ru.

The element specific sensitivity of the ICP-MS was calibrated with two multielement standard solutions. One standard solution included 10 ppb of the elements Rb, Sr, Y, Zr, Mo, Ru, Rh, Pd, Cs, Ba, La, Ce, Nd, U and 1 ppb of Bi and In as internal standard. The other standard solution included 10 ppb Rb, Sr, Cs, 6 ppb Tc, 500 ppb U, 2.2 ppb Pu, Np and 1 ppb of Bi and In as internal standard. 1000 ppm single element standard solution from Merck were used to make the multielement standard solutions. Furthermore, our own actinide standard solutions were used. The Np standard solution contained the isotope Np-237. The Pu standard solution contained the isotopes: Pu-238 (0.13 mol%), Pu-239 (84.03 mol%), Pu-240 (14.45 mol%), Pu-241 (0.73 mol%) and Pu-242 (0.34 mol%).

Prior to ICP-MS analysis the Cs-137 concentration has been measured with γ-spectrometry. A one-point calibration was made with a 1.8 MBq (about 31 ppb Cs-137) solution. All samples were measured 30 min. The background was about 170 Bq. The detection limit (3σ) was estimated to 3 ppt Cs-137. For leaching solutions under reducing conditions the Cs-137 concentration was very close to the detection limit. Moreover, for some samples the Am-241 concentration was measured.

3. Results and discussion

3.1. Redox conditions and E_h measurements

Spent fuel leaching and other studies concerning redox sensitive elements are reported as performed under oxidizing, anoxic or reducing experimental conditions.

With oxidizing conditions usually it is meant that the experiments are performed in the presence of the laboratory atmosphere, with an oxygen partial pressure of about 0.2 atm. In this case the concentration of the dissolved atmospheric oxygen in the solution is of the order of $[O_2]_{diss} = k \cdot P_{O_2} \approx 2.5 \times 10^{-4}$ M. In the case of strongly radioactive materials, like e.g., spent fuel, one has to take into account also the oxygen produced through the radiolysis of water. In a series of experiments performed by Eriksen and coworkers [23,24] it has been shown that after some days the concentration of radiolytic oxygen reaches more or less stationary levels around $\approx 10^{-7}$ mol l^{-1}. This means that under oxidizing conditions the influence of radiolytic oxygen can be neglected, its concentration being about three orders of magnitude lower than the concentration of atmospheric oxygen.

The term anoxic (or anaerobic) groundwater in geochemical meaning usually refers to the complete absence of oxygen. However, in laboratory studies the term 'anoxic conditions' often refers to the conditions realized in a glove box or vessel, flushed with an inert gas like Ar or N_2. Under such conditions the concentration of oxygen in the gaseous atmosphere is of the order of parts per million (at best ~0.01 ppm). This corresponds to dissolved oxygen concentrations of the order of $[O_2]_{diss} = k \cdot P_{O_2} \approx 10^{-9}$–$10^{-11}$ mol l^{-1}. Taking into account the enormous difference of the oxygen concentration in the system and in the laboratory atmosphere, our experience has shown that it is difficult to lower further, or even to maintain the oxygen concentration at such levels by flushing with an inert gas. An equilibrium calculation [20] shows that for such relatively low oxygen concentrations, the redox conditions are not, as believed, mildly oxidizing or even reducing. They are in fact strongly oxidizing (the redox potential is higher than $\sim +600$ mV at pH = 8). This is in agreement with the redox potentials measured during a few measurements we carried out under Ar + 0.03% CO_2 atmosphere.

The term reducing conditions is applied for leaching tests under a hydrogen atmosphere. The redox potentials for a solution in contact with hydrogen result in very negative values, apparently confirming reducing conditions. In fact, such conditions exist only in the surface of the Pt-electrode, a known H_2 catalyst, but not in the bulk solution. In this case the Pt-electrode is simply functioning as a hydrogen electrode and responding to the concentration of the protons in solution. When the leach solution, saturated with dissolved hydrogen, contacts the spent fuel at room temperature, hydrogen should be quite inert in the absence of a catalyst [3, p. 685]. The redox conditions in the reactor containing the spent fuel should be determined mainly by the small amounts of oxygen diffusing in the system, as well as the radiolytic oxygen. However, as it will be shown in the next paragraph, dissolved hydrogen has quite an impact on the leaching of the spent fuel. The rates of dissolution of redox active species decrease by several orders of magnitude, indicating that in some way hydrogen is activated.

Fig. 2 shows the E_h vs. pH for the Au- and Pt-electrode measured after the fuel cell under oxidizing and reducing conditions. The measured redox potentials are often not Nernstian and can only be interpreted qualitatively [25–27]. Probably the major redox active species for oxidizing conditions is dissolved oxygen, and the measured potentials are quite oxidizing, but still a few hundreds of mV lower than the value calculated assuming equilibrium with dissolved atmospheric oxygen. The same type of behavior is reported in the literature [27]. The redox potentials measured with a Pt-electrode decrease with increasing pH. It seems that the sum of pH + pe is approximately constant under such conditions, indicating one electron to one proton relation in the redox potential determining process (as, e.g., in the case of oxidation by oxygen: $O_2 + 4H^+ + 4e^- = 2H_2O$). For reducing conditions the major redox active species is hydrogen in the case of the Pt-electrode. The theoretical slope of 58 mV is only obtained when hydrogen is bubbled directly over a Pt-foil. However, the measurements are quite close to the theoretical values. The redox potentials measured with an Au-electrode, which is not sensitive to hydrogen, but to the trace amounts of the redox species in the system, are higher and show large variations.

Since only small amounts of fission products and actinides dissolve during fuel-leach solution interaction, the E_h and pH values measured before the reactor changed very little after contact.

3.2. Spent fuel dissolution rates

In order to estimate the rate of dissolution of the $UO_2(s)$ spent fuel matrix, uranium may be used as a monitor, provided that the flow rate is such that uranium concentrations in the leaching solution are well

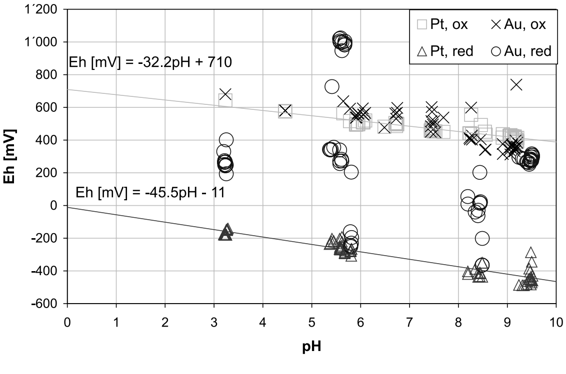

Fig. 2. The redox potentials of the test solutions after passing the fuel column, plotted vs. the measured pH.

under saturation. Besides uranium, fission products and other actinides can be used as monitors to calculate dissolution rates of spent fuel. The dissolution rate of spent fuel based on the data for component i is defined as

$$R = \frac{c_i f}{m_s A_{\mathrm{spec}} x_i}, \tag{1}$$

where

R is the dissolution rate of the spent fuel matrix based on the data for component i [mg m^{-2} d^{-1}]

c_i is the concentration of component i in the leaching solution [mg ml^{-1}]

f is the flow rate of test solution through the fuel cell [ml d^{-1}]

m_s is the mass of the spent fuel sample [mg]

A_{spec} is the specific surface area of the fuel sample [m^2 mg^{-1}]

x_i is the content of component i in the spent fuel [mg mg^{-1}].

An inventory analysis of the fuel after irradiation was made by dissolving fuel specimens. The ratio of the concentration of each nuclide to the total uranium concentration has been determined by ICP-MS. However, the inventories of fuel specimens to calculate dissolution rates must be based on the measured weights of the fuel sample. The fission product and actinide ratios have, therefore been corrected to the initial uranium weight by means of factors derived from ORIGEN calculations. The inventory analysis in g/g initial U for nuclides was used for spent fuel dissolution calculation [28]. Furthermore, the content of component i in the spent fuel, x_i, is calculated by multiplying the values from the inventory analysis with 0.88 ($= U/UO_2$).

Light water reactor fuel is a heterogeneous material, consisting of a matrix of nearly stoichiometric uranium dioxide in which the higher actinides are generally viewed as forming solid solutions with UO_2(s). The same holds for the majority of the fission and activation products (e.g., Sr and the lanthanide oxides). A small percentage of some elements (e.g., Cs, I) migrate to various degrees to the fuel-clad gap or to grain boundaries; others (e.g., Mo, Tc, Pd, Tc) form separate metallic alloy phases [2]. The majority of the radionuclide inventory is uniformly distributed throughout the UO_2(s) matrix and is released at the rate at which the fuel matrix dissolves. The release of these elements when the fuel is in contact with water will, therefore, depend on the UO_2 matrix alteration/dissolution process.

For congruent dissolution the fission products and actinides in the solution would show the same composition as in the solid phase. As a consequence, the same dissolution rate would be obtained for all the different radionuclides. For steady-state conditions the concentrations of the dissolution monitors are not solubility limited and the dissolution rate is hereby independent of the flow rate. Steady-state conditions for the dissolution of UO_2 and spent fuel based on U have been reported for flow rates 0.05–0.5 ml min^{-1} [7,8,14]. However, the various radionuclides exist in a variety of different chemical species with different solubility and adsorption characteristics. Precipitation and adsorption of some chemical species can occur even at very low concentrations. As a consequence, too low dissolution rates are obtained for some of the nuclides. The solubility of a certain radionuclide depends on its redox state and is often strongly pH dependent. Steady-state conditions have to be checked for different chemical conditions and different dissolution monitors. The dissolution rates depend strongly on the redox conditions under which the leaching tests are performed. For this reason the results obtained under oxidizing conditions (test solutions in contact with oxygen) and reducing conditions (test solutions in contact with hydrogen) will be discussed separately.

3.3. Oxidizing conditions

The applicability of dissolution rate monitors can be checked easily by comparing the mass spectra of leaching solutions with mass spectra from the fuel inventory analysis. Fig. 3 shows a mass spectrum of a fuel fraction completely dissolved in nitric acid. Fig. 4 shows the mass spectrum of a leaching solution of the same spent fuel. The fuel was leached with a 1 mM $NaHCO_3$ test solution (pH 7.3) in contact with Ar containing 20% O_2/0.3% CO_2. In the leaching solutions elements such as Zr, Ru, Rh, and Pd, which also form insoluble residues during fuel dissolution in nitric acid, have almost disappeared [29,30]. Furthermore, trivalent species like Y and the lanthanides have also very low concentrations. The solubility of the trivalent species was found to depend strongly on the pH and carbonate concentration. Congruent dissolution based on trivalent cations has been

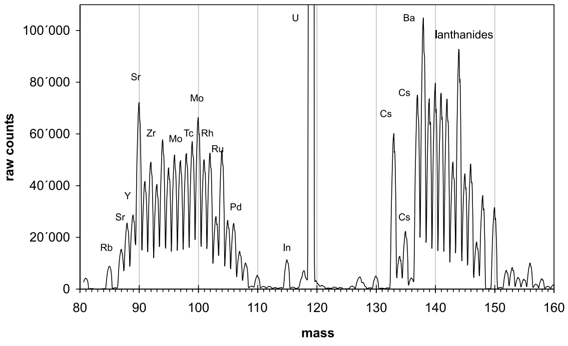

Fig. 3. Mass spectrum of completely dissolved spent fuel. A fraction of spent fuel was dissolved in concentrated nitric acid and diluted to about 10 ppm U.

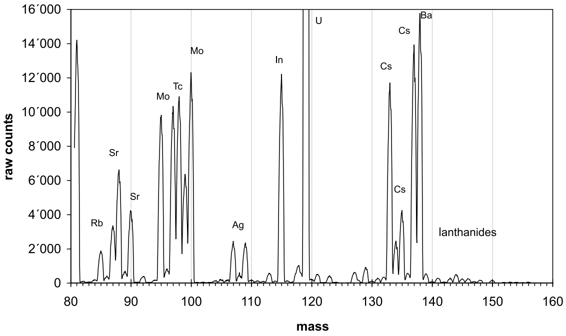

Fig. 4. Mass spectrum of a leaching solution, obtained by contacting fuel with a 1 mM $NaHCO_3$ test solution (pH 7.3), saturated with an Ar + 20% O_2 + 0.03% CO_2 gas mixture.

found for pH 5.7, whereas the trivalent species have almost disappeared for pH 6.9. The formation of solid solutions of different trivalent elements of the general form $(M^{3+}(OH)_3)$ was assumed to be the reason for these apparently very low solubilities [31]. Lanthanide concentrations much lower than those corresponding to a congruent matrix dissolution are reported also during static or flow-through leaching of spent fuel or SIMFUEL [5,32,33]. However, for total carbonate concentration above 10 mM, an almost congruent dissolution of lanthanides is observed from natural (Oklo) $UO_2(s)$ samples [32]. It is possible that non-sorbing negatively charged carbonate complexes of the trivalent ions are the reason of their recovery.

In flow experiments, it is important to ensure that constant dissolution rates are achieved. The dissolution rates are usually much higher at the beginning of a leaching experiment due to more reactive phases (partially oxidized $UO_2(s)$) on the surface of the fuel particles and more soluble fines. Constant dissolution rates have been obtained after 8–30 days. Figs. 5 and 6 show the concentrations of different components of the spent fuel for leaching tests with a 1 mM HCl and a 10 mM $NaHCO_3$ solution, respectively. The flow rate was for both tests 0.1 ml min^{-1}.

The various components of spent fuel exist in a variety of chemical species with different solubilities. Fig. 7 shows the dissolution rates based on different components for the leaching test with 10 mM $NaHCO_3$. The dissolution rates for each nuclide were calculated using (Eq. (1)). The diagram shows a typical characteristic of spent fuel leaching solutions: nuclides of the elements U, Np, Ba, Cs, Tc, Sr, and Rb show approximately congruent dissolution whereas nuclides of the elements Rh, Ru, Pd and Pu show much too low dissolution rates. For high pH molybdenum nuclides showed congruent dissolution rates, whereas neodymium nuclides showed much too low dissolution rates. For low pH, neodymium nuclides showed congruent dissolution whereas molybdenum nuclides showed much too low dissolution rates.

A closer look at the dissolution rates for different pH leads to the following result: Rb, Cs and Sr, Ba belong to the alkali and earth alkali elements and are very soluble. U, Np and Tc are expected to exist as U(VI), Np(V) and Tc(VII) species, [UO_2^{2+}, NpO_2^+ and TcO_4^-] and hereby expected to be soluble, too. Indeed, approximately congruent dissolution rates with U-238 have been obtained in the whole pH range 3–9.3 for these nuclides (Np-237, Sr-90, Ba-138, Cs-137, Tc-99, Rb-85). For low pH slightly lower dissolution rates for Tc-99 were obtained. For leaching solutions with low concentrations of the fission products Rb-85 and Ba-138 natural contamination can disturb the measurements, while natural contamination by Zr-90 disturbs Sr-90 measurements. The corresponding dissolution rates turn out too high. The dissolution rates for other chemical elements

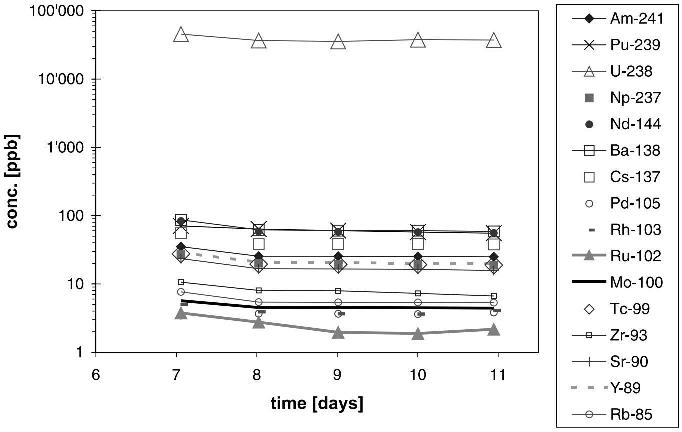

Fig. 5. Concentration of different components of the spent fuel for a leaching test with 1 mM HCl under oxidizing conditions, with a flow rate of 0.1 ml min^{-1}.

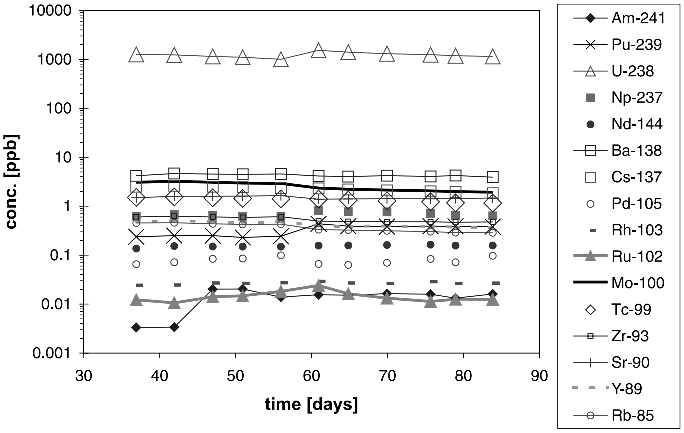

Fig. 6. Concentration of different components of the spent fuel for a leaching test with 10 mM $NaHCO_3$ under oxidizing conditions, with a flow rate of 0.1 ml min^{-1}.

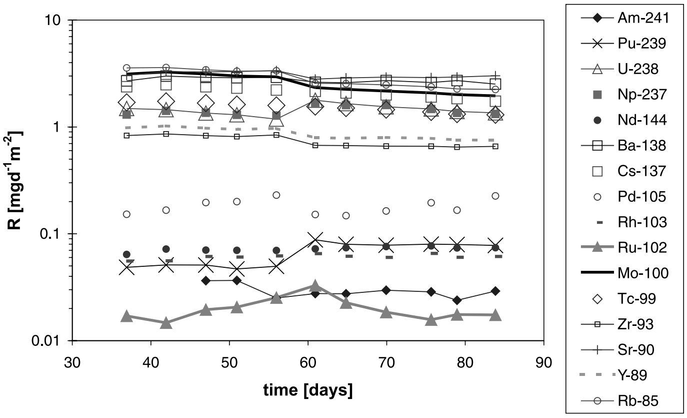

Fig. 7. Dissolution rates based on different monitors. The spent fuel was leached with 10 mM $NaHCO_3$ under oxidising conditions.

showed strongly pH dependent dissolution rates. Elements such as Ru, Rh, Pd and Pu were only partly soluble. The dissolution rates of Ru-102, Rh-103, Pd-105 and Pu-239 were about 10–30% for pH 3 and for pH > 3 about 1–10% of the dissolution rates based on soluble species. For high and low pH, Zr (Zr-93) and Y (Y-89) showed approximately congruent dissolution rates, whereas too low dissolution rates based on these nuclides were found for pH around 7. The dissolution rates for Mo-100 were about 10% for pH < 5 and for pH > 6 about 150% of the dissolution rates based on soluble species. This may be due to the preferential dissolution of Mo from the 5-d metal particles [34].

The concentrations of Pu-240 on the other hand did not show steady-state dissolution rates. An upper limit of about 0.7 ppb Pu was found. In static leaching experiments similar upper limits were found [6,33]. This upper limit can be correlated to thermodynamic solubility data, since Pu concentrations in such conditions are mainly determined by the slightly soluble Pu(IV) oxide.

For trivalent cations like the lanthanides, Y and Am, approximately congruent dissolution rates have been obtained for pH < 6. For pH > 6, the dissolution rates of Y-89 were about 30% and the dissolution rates of the lanthanides about 1–10% of the matrix dissolution rates based on soluble species. Similar results were found in a qualitative analysis for Am-241. As Am-241 interferes with Pu-241, Am and Pu had to be separated first. The analysis has been done with HPLC-ICP-MS and is reported elsewhere [35].

For steady-state conditions, the dissolution rate is independent of the flow rate. The concentration of a dissolution product is thus proportional to the inverse flow rate. Fig. 8 shows the Np-237, U-238 and Cs-137 concentrations versus the inverse flow rate for the leaching with a 10 mM $NaHCO_3$ solution. All three nuclide concentrations are approximately proportional

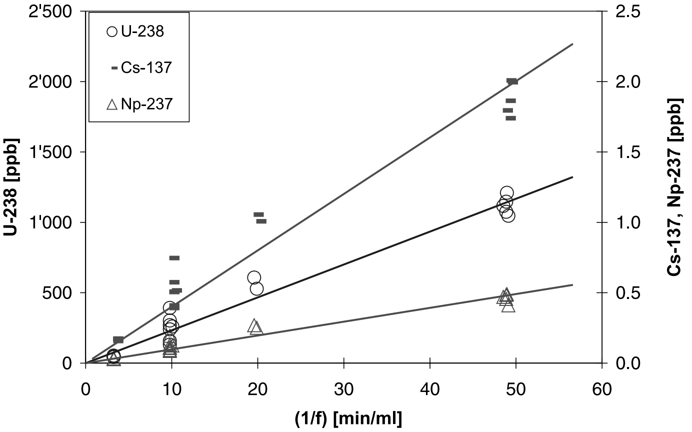

Fig. 8. Steady-state conditions are checked by plotting concentrations of dissolved fuel components vs. the inverse flow rate. Dissolution tests were performed with a 10 mM $NaHCO_3$ (pH 9.3) solution under oxidising conditions.

to the inverse flow rate in the flow rate range 0.02–0.3 ml min^{-1}. U-238 concentrations of about 2 ppm can be expected for flow rates of 0.02 ml min^{-1}. From the diagram, the linear relationship with the inverse flow rate seems to be valid even at such levels; thus it can not be concluded that this concentration is an upper limit (or saturation) U concentration. In flow-through experiments with UO_2, Wilson et al. [11] found an upper U concentration of 700 ppb U and Casas et al. [8] an upper concentration of 10 ppb. The results from a flow-through experiment can easily be compared with the results from static leaching tests considering the time the test solution spends in the fuel cell. This contact time is proportional to the inverse flow rate and is for a column volume of 0.5 ml and a flow rate range of 0.02–0.1 ml min^{-1} in the range 25–5 min. For static leaching tests with spent fuel the volume to surface ratio was about 10 000 times higher. Therefore, upper limit U concentrations of about 2 ppm were found first after contact periods of about 200 days. However, these concentration limits could not be correlated to the thermodynamic solubility of U in the oxidation state VI [6,33].

The rate of dissolution of spent fuel based on different nuclides was studied extensively by Forsyth [36]. Static dissolution tests with ground water under oxidizing and anoxic conditions have been made for different spent fuel specimens. Nuclide concentrations in the leaching solutions were correlated to the different production pathways in the spent fuel and to different corrosion processes. In the flow-through study we wanted to investigate the effect of the chemistry of the test solution on the dissolution of fission product and actinide species. The results give a very good overview of the order of magnitude of the dissolution rates and the solubility of different chemical species. Minor differences for dissolution rates based on different nuclides were not tried to correlate to any corrosion mechanism, as the results are not accurate enough. For example for leaching solutions with low concentrations of the fission products Rb-85, Sr-90 and Ba-138 often contamination with natural Rb, Zr-90 and Ba disturbed the measurements. Furthermore, the test solutions have often been changed, dissolution rates based on different nuclides still showed minor variations with time which could easily lead to wrong interpretations. However, some of the results shall be compared with the results from static leaching tests. In the present flow-through experiment Cs, Tc and Np show approximately congruent dissolution with U in the whole pH range, whereas for static leaching experiments, the release fractions for Tc and Cs were found to be up to 10 and 100 times higher and for Np up to 5 times lower than U release fractions [36]. The dissolution rates of Pu were less than 10% of the dissolution rates based on nuclides that show congruent dissolution. Similar results for Pu concentrations were also found for static leaching tests. The authors assumed that precipitation of actinide-rich phases must have occurred [6]. In other flow-through studies Gray also obtained approximately congruent dissolution rates based on U, Cs-137, Tc-99 and Sr-90 [15].

In Fig. 9 and the upper curve of Fig. 14 (which is exactly the same as Fig. 9, but allows one to display the dissolution rates of a few more nuclides separately) the dissolution rates based on U-238, Np-237, Ba-138, Cs-137, Tc-99, Sr-90 and Rb-85 have been plotted versus pH. All these nuclides show approximately congruent dissolution. The dissolution rates were found to be independent of pH in the pH range 7–9.3 and strongly dependent for $pH < 6$. Grandstaff suggested for the dissolution rate of $UO_2(s)$ a classical kinetic rate law with a first order dependence on the hydrogen ion and the total carbonate concentration [37]. In our work, the dissolution rates could be fitted by a classical kinetic rate law of the form

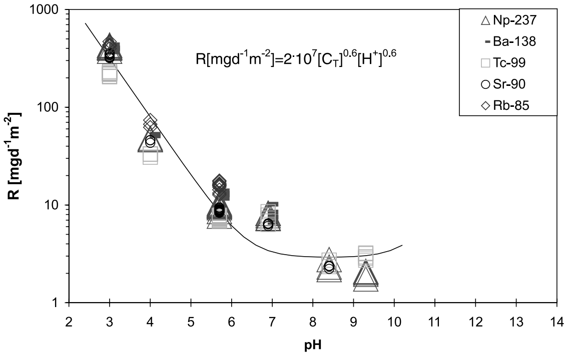

Fig. 9. Dissolution rates based on several spent fuel components, for leaching under oxidizing conditions and in carbonate solutions of different pH.

$$R_{\mathrm{ox}}\ [\mathrm{mg\ m^{-2}d^{-1}}] = k \cdot (\mathrm{C_T})^{0.6}(\mathrm{H^+})^{0.6},$$

where $(\mathrm{C_T})$ and $(\mathrm{H^+})$ is the total carbonate concentration and the proton concentration, respectively, and $k = 2 \times 10^7$ [mg m^{-2} d^{-1} l^2 mol^{-2}].

Many different kinetic rate laws are suggested in the literature. Values of the reaction order with respect to the hydrogen ion concentration vary between −0.3 and 1, while with respect to the carbonate concentration values between 0.1 and 1 were found. The experiments were often performed in a very narrow pH range around 8, where probably the two effects of a pH and carbonate change compensate each other.

In our work the aim was to get an overview of the dependence of the dissolution rates on pH, carbonate concentrations and flow rate. Therefore, test solutions have often been changed. More accurate dissolution rates could probably be obtained with longer waiting times, hence more constant rates. However, our results compare well with some literature data. A comprehensive review of published data on dissolution rates of UO_2, SIMFUEL and spent fuel under different leaching conditions has recently been reported by Oversby [38]. Similar dissolution rates have been found for spent fuel. In flow-through experiments Gray [14,15] obtained dissolution rates of about 4 mg d^{-1} m^{-2} for a 2 mM $NaHCO_3$ test solution of pH 8. In static dissolution tests Grambow et al. [31] obtained dissolution rates of 5–7 mg d^{-1} m^{-2} for 95% saturated NaCl of slightly alkaline pH. Werme and Forsyth reported dissolution rates as 'fraction of inventory in aqueous phase' (FIAP). Considering the fact that for these dissolution tests the specific surface was only about 4 cm^2 g^{-1}, dissolution rates based on Sr of about 7 mg d^{-1} m^{-2} have been found for tests with carbonate solutions around pH 8 [33,36].

For UO_2(s) less uniform dissolution rates have been found. Casas et al. [8] found in static leaching experiments dissolution rates of 0.3–4 μg d^{-1} m^{-2} for 0.01 M $NaClO_4$ solutions of pH 8 and a partial pressure of oxygen of 0.05 bar. With a flow-through experiment the same authors found at the same conditions a dissolution rate of 80 μg d^{-1} m^{-2} [8]. In flow-through experiments with 10 mM $NaClO_4$ solutions, dePablo et al. [13] found for pH 8 a dissolution rate of 0.2 mg d^{-1} m^{-2}, while for pH 8.5, when the solution additionally contained 10 mM $NaHCO_3$, a dissolution rate of 3.3 mg d^{-1} m^{-2} was obtained. In NaCl brines and static leaching, Grambow et al. [31] obtained dissolution rates of 6 μg d^{-1} m^{-2}. Gray et al. [12] found in an inter-laboratory comparison dissolution rates of about 2 mg d^{-1} m^{-2} for flow-through tests with 2 mM $NaHCO_3$ solutions (pH 9).

3.4. Reducing conditions

The dissolution rates of spent fuel in flow-through tests with H_2(g) saturated solutions dropped by up to four orders of magnitude as compared to oxidizing conditions dissolution rates (compare upper and lower curve in Fig. 14). The concentrations of U and Pu were high enough for reliable mass spectrometric determinations. The concentrations of fission products and other actinides were in the low ppt range and hereby near the detection limits. Cs could be analyzed by γ-spectrometry, although the concentrations were also near the detection limit. Fig. 10 shows the concentrations of spent fuel components obtained in leaching test with 1 mM HCl. Similar dissolution rates were found for U-238 and Cs-137. The rates decreased continuously during the first four days. After six days stable dissolution rates were obtained for flow rates of 0.1 and 0.02 ml min^{-1}.

When decreasing further the flow rate to 0.01 ml min^{-1}, much higher dissolution rates were obtained. For this low flow rate it seems that the low hydrogen input does not succeed to neutralize both the radiolytic oxidants produced and the oxygen diffusing into the system, which both increase due to the increased resi-

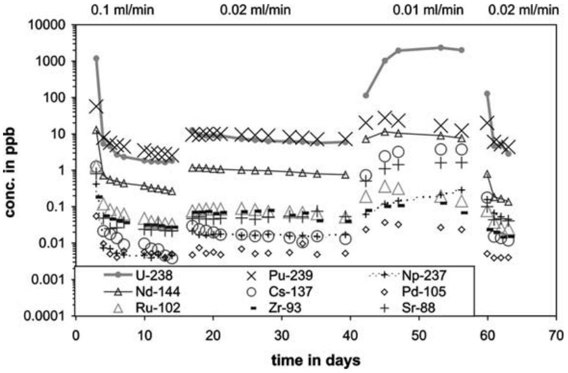

Fig. 10. Concentrations of spent fuel components for a leaching test with 1 mM HCl test solution for different flow rates under reducing conditions.

dence time of the solution in the reactor. A similar effect was observed for the dissolution rates of Np-237, Nd-144, Ba-137, Ru-102, Pd-105 and Sr-88. For oxidizing conditions, much lower dissolution rates for Pd-105, Ru-102 and Pu-239 as compared to the U-238 and the other soluble elements were observed. In contrast to this, the dissolution rates of these nuclides under reducing conditions were higher than the dissolution rates of the soluble elements at such acidic solutions.The dissolution rates of Pu-240, even though much lower than in the case of oxidizing conditions, were up to 100 times higher than the dissolution rates based on Cs-137. Furthermore, the dissolution rates of the insoluble species did not increase for a flow rate of 0.01 ml min^{-1}, where a possible oxygen contamination was noticed.

One reason for the abrupt increase of the Cs and U concentrations for a flow rate of 0.01 ml min^{-1} could be oxygen diffusing into the system. Another oxygen source would be the radiolysis of water. However, for a flow rate of 0.01 ml min^{-1}, the contact times of the test solutions with the spent fuel are still less than one hour. For such short contact times the concentrations of oxygen and hydrogen built through radiolysis are expected to be around 4×10^{-9} mol l^{-1} O_2 and 3×10^{-9} mol l^{-1} H_2 [24]. The hydrogen concentration for a test solution in contact with 100% H_2 is expected to be around 8×10^{-4} mol l^{-1} H_2. Fig. 11 shows the redox potentials measured with an Au- or Pt-electrode after the fuel cell for the same time period. For flow rates of 0.1 ml min^{-1}, the redox potentials decreased strongly when sparging the test solution with an $H_2 + 0.03\%$ CO_2 gas mixture. After three days, stable redox potentials were obtained. When the flow rate was lowered to 0.02 ml min^{-1}, the redox potentials started to increase slowly. A further decrease of the flow rate to 0.01 ml min^{-1} caused a strong increase of the potential measured with the Pt-electrode to about the same values as measured under oxidizing conditions. The redox potential measured with a Pt-electrode before the fuel cell showed about the same trend, although the redox potential increase for lower flow rates was less pronounced. This would indicate that oxygen diffusion is the main cause of the increase of the redox potentials, while the larger increase in the readings of the redox electrodes after the reactor may be due to a larger pathway and/or the contribution of radiolytic oxidants.

Fig. 12 shows the results of a leaching test with a 10 mM $NaHCO_3$ solutions under reducing conditions. The dissolution rates were decreasing so that first after 50 days approximately constant dissolution rates have been achieved. Approximately congruent dissolution was found for U-238, Am-241, Pu-239 and Cs-137. Furthermore, Np-237 and Nd-144 also showed congruent dissolution at the beginning. But after about 20 days of leaching, their concentrations, like those of most of the spent fuel components, were dropping under the detection limit of about 1 ppt. An exception were Mo and Tc, which were released at measurable concentrations during all the leaching period.

The test of the steady state conditions under reducing conditions is shown in Fig. 13. Due to the very low concentrations of most of the radionuclides, only the U-238, Am-241 and Cs-137 concentrations are accurate enough to be plotted versus the inverse flow rate. As seen from the Fig. 13, the concentrations of these nuclides are approximately proportional to the inverse flow rate in the flow rate range 0.02–0.3 ml min^{-1}.

In Fig. 14 the dissolution rates based on Cs-137 and U-238 for oxidizing and reducing conditions are plotted versus pH. The dissolution rates of Cs-137 and U-238 under reducing conditions decreased by up to four orders of magnitude as compared to the corresponding rates under oxidizing conditions. As mentioned before, at room temperature hydrogen is quite inert in the absence of a catalyst. The remarkable decrease of the dissolution rates of the redox sensitive elements may be due to a catalytic effect of the UO_2(s) surface on hydrogen.

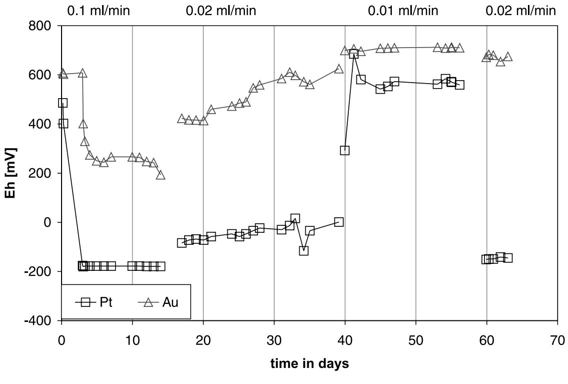

Fig. 11. The redox potentials measured with a Pt- and an Au-electrode after the fuel cell, for a 1 mM HCl test solution and different flow rates.

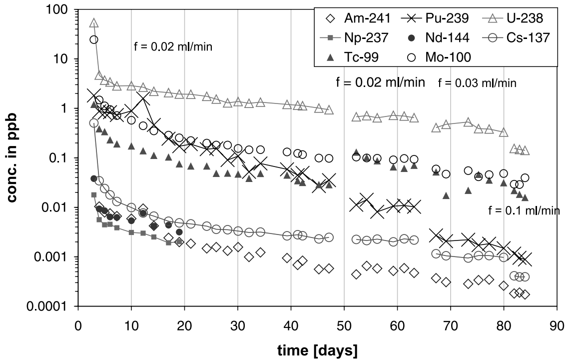

Fig. 12. Concentration of spent fuel components for a leaching test with a 10 mM $NaHCO_3$ solution saturated with H_2(g).

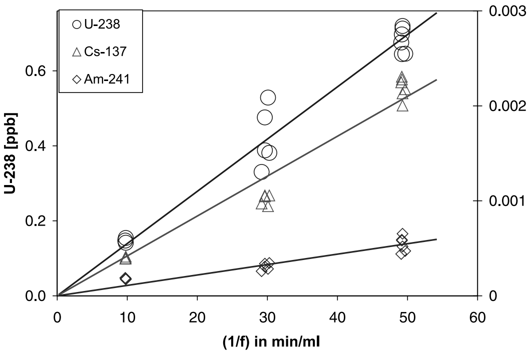

Fig. 13. Steady-state conditions are checked by plotting concentrations of dissolved fuel components vs. the inverse flow rate. Dissolution tests were performed with a 10 mM $NaHCO_3$ solution (pH 9.3) under reducing conditions.

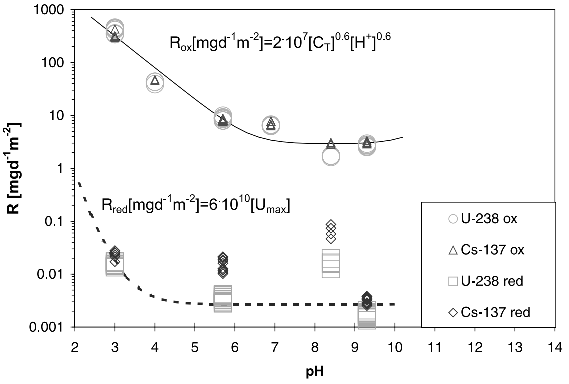

Fig. 14. Dissolution rates based on U-238 and Cs-137 for different pH under oxidizing and reducing conditions.

There are both experimental data on static leaching of spent fuel under 5 MPa hydrogen [18], as well as literature data (see [39] for a discussion), supporting this hypothesis.

In static dissolution tests Werme et al. [33] found that the fractional release of U dropped by up to three orders of magnitude for changing to reducing conditions in the presence of a Pd-catalyst. The fractional release of Cs appeared to be much less influenced by changing the redox conditions and dropped only by a factor 10. However, later on extensive calcite precipitation was detected in these fuel samples [6] and this may have partially influenced the results. In a flow-through experiment under hydrogen atmosphere, Bruno et al. [7] found dissolution rates of about 0.2 mg d^{-1} m^{-2} for $NaClO_4$ solutions in the pH range 6–11. For pH < 6 the dissolution rates were found to increase strongly. The fact that in the case of these experiments relatively high uranium concentrations were measured could possibly be due to the use of a peristaltic pump and to a less effective protection towards oxygen diffusion. Another possibility is that the radioactivity of the spent fuel activates hydrogen, and hereby causes an increase of the hydrogen radical concentration.

The dissolution rates under reducing conditions also seem to be almost pH independent for pH > 4. This would indicate a non-oxidative dissolution of the $UO_2(s)$ matrix, approaching the very low solubility of U(IV). The solution very near the spent fuel could be saturated with U and the dissolution rate hereby proportional to the solubility of U(IV). Thus the dissolution rates based on U-238 could be reasonably well fitted by a kinetic rate law of the form

$$R_{red}\ [\mathrm{mg\ m^{-2}\ d^{-1}}] = k(\mathrm{U_{max}}), \tag{2}$$

where (U_{max}) is the maximal U(IV) concentration in equilibrium with UO_2 (c) and $k = 6 \times 10^{10}$ [mg m^{-2} d^{-1} l mol^{-1}].

However, the rates of dissolution obtained for pH = 8.3 are slightly higher than the others (see Fig. 14). We believe this is due to the fact that these were the first measurements we carried out and they were possibly interrupted before reaching the reducing conditions in the fuel cell.

3.5. Anoxic conditions

Anoxic conditions were achieved by flushing a 1 mM $NaHCO_3$ test solution with Ar + 0.03% CO_2. Fig. 15 shows the dissolution rates for the 1 mM $NaHCO_3$ test solution under oxidizing, reducing and anoxic conditions.

Oxidizing conditions were established by flushing the test solution with Ar gas containing 20% O_2 and 0.3% CO_2. The CO_2 concentration was hereby ten times higher as under reducing and anoxic conditions. The pH of the solution was 7.3. However, dissolution rates are expected to be only slightly higher due to the increased CO_2 concentration.

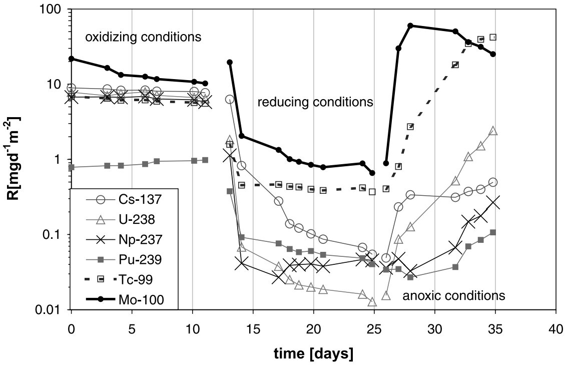

Fig. 15. Dissolution rates based on different monitors for a 1 mM $NaHCO_3$ test solution under oxidizing, reducing and anoxic conditions.

Prior to anoxic conditions, the test solution was flushed with $H_2 + 0.03\%\ CO_2$ for about 14 days during a leaching test under reducing conditions. The experiment indicates that low dissolution rates only can be obtained in the presence of H_2.

Although it could be switched to Ar-flushing without exposing the test solution to air atmosphere, both the redox potentials and the dissolution rates were increasing, approaching about the same values that were obtained under oxidizing conditions. Another reason for the increasing dissolution rates under anoxic conditions would be oxygen diffusion. New experiments with the whole flow-through experimental setup in Ar(g) atmosphere are under progress, to test this hypothesis.

In a static leaching experiment under anoxic conditions Grambow et al. [31] found a dissolution rate for UO_2 of 1.5 μg d^{-1} m^{-2}. The dissolution rate was hereby about five times lower than the rates the authors found for oxidizing conditions. These dissolution rates were thought to be very low and difficult to distinguish from a solubility value.

4. Conclusions

Dissolution rates of spent UO_2 fuel have been investigated under oxidizing, anoxic and reducing conditions. For oxidizing conditions, approximately congruent dissolution rates were found in the pH range 3–9.3 for nuclides of the elements U, Np, Ba, Tc, Cs, Sr and Rb. For these elements, steady-state conditions were found in the flow rate range 0.02–0.3 ml min^{-1}. The dissolution rates were about 3 mg d^{-1} m^{-2} for pH > 6. For pH < 6 the dissolution rates were strongly increasing for decreasing pH. A classical rate law of the form

$$R_{ox}\ [\mathrm{mg\ m^{-2}\ d^{-1}}] = k \cdot (C_T)^{0.6}(H^+)^{0.6},$$

where (C_T) and (H^+) is the total carbonate concentration and the proton concentration, respectively, and $k = 2 \times 10^7$ [mg m^{-2} d^{-1} l^2 mol^{-2}], could be used to predict dissolution rates for carbonate solutions in contact with air in the pH range 3–9.3. Incongruent dissolution was found for Zr, Mo, Ru, Rh and Pd as these elements form separate metallic alloy phases. The dissolution behavior of Zr, Mo, Y, Am and the lanthanides was strongly pH dependent. Zr and Mo showed only for high pH approximately congruent dissolution, whereas the trivalent species showed only for low pH approximately congruent dissolution.

Anoxic conditions were achieved by flushing the test solutions with Ar. Both the measured redox potential of the leaching solutions and the dissolution rates approached the same values as obtained under oxidizing conditions.

The dissolution rates of spent fuel in flow-through tests with $H_2(g)$ saturated solutions dropped by up to four orders of magnitude as compared to oxidizing conditions dissolution rates. Only the concentrations of U, Pu, Mo and Tc were high enough for reliable mass spectrometric determinations. Furthermore, Am-241 and Cs-137 could be measured by γ-spectrometry. Approximately congruent dissolution rates have been obtained for Am-241, U-238 and Cs-137 in the pH range 3–9.3. For these elements steady-state dissolution rates have been found in the flow rate range 0.02–0.3 ml min^{-1}. The dissolution rates based on U-238 could be fitted by a kinetic rate law where the rate was assumed to be proportional to the solubility of U(IV):

$$R_{red}\ [\mathrm{mg\ m^{-2}\ d^{-1}}] = k(U_{max}), \tag{3}$$

where (U_{max}) is the maximal U(IV) concentration in equilibrium with $UO_2(c)$ and $k = 6 \times 10^{10}$ [mg m^{-2} d^{-1} l mol^{-1}]. The lowest dissolution rate of about 0.002 mg d^{-1} m^{-2} was observed for a 10 mM $NaHCO_3$ solution.

At room temperature hydrogen is quite inert in the absence of a catalyst. The remarkable decrease of the dissolution rates of the redox sensitive elements may be due to a catalytic effect of the $UO_2(s)$ surface on hydrogen. Another possibility is that the radioactivity of the spent fuel activates hydrogen and hereby causes an increasing of the hydrogen radical concentration. This would explain why other authors did not see an effect of hydrogen on the dissolution rate of UO_2. However, a series of dissolution experiments with unirradiated UO_2 is planned to check the effect of hydrogen on the dissolution rate of UO_2. Furthermore, dissolution experiments will be made in a Ar atmosphere in order to minimize diffusion of oxygen in the system. By coupling an ion chromatograph to the ICP-MS, speciation analysis of actinides can be made for U concentrations down to 100 ppt [40]. Especially for low pH, this method can be used to check the oxidation state of U in the solution. Furthermore, experiments have started to do speciation analysis of Pu in order to get a better understanding of the redox conditions in the leaching solution [35].

Acknowledgements

This study was financed by the Swedish Nuclear Fuel and Waste Management Co (SKB).

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