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Simulation of radiation induced dissolution of spent nuclear fuel using the steady-state approach. A comparison to experimental data

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Abstract

Using the recently developed steady-state model for simulation of radiation induced dissolution of spent nuclear fuel in water we have estimated the rate of dissolution for relatively fresh fuel to 1.64×10^{-9} mol m^{-2} s^{-1}. A series of experiments have been performed on fuel fragments in deoxygenated water containing 10 mM HCO_3^-. The dissolution rates obtained from these experiments range from 2.6×10^{-10} to 1.6×10^{-9} mol m^{-2} s^{-1}. The leaching time in the experiments is 40 days or less and during this time the amount of released uranium increases linearly with time which indicates that the system has reached steady-state. The excellent agreement between the estimated dissolution rate and the dissolution rates obtained from the spent nuclear fuel leaching experiments indicates that the steady-state approach can indeed be used to predict the rate of spent nuclear fuel dissolution.

1. Introduction

The possible release of toxic and radioactive species from spent nuclear fuel in contact with water in a future deep repository is expected to depend mainly on the rate of dissolution of the UO_2 matrix [1]. In the reducing groundwater expected at the depth of a repository, UO_2 has very low solubility [2]. However, radiolysis of the ground water will produce reactive radicals and molecular products (e_{aq}^-, $H^\cdot$, H_2 (reductants) and $OH^\cdot$, H_2O_2 (oxidants)) [3] and thereby alter the reducing environment. Secondary reactions will produce $HO_2^\cdot$, $O_2^{\cdot-}$ and O_2 and with carbonate present in the ground water, $CO_3^{\cdot-}$ will be produced. $OH^\cdot$ and $CO_3^{\cdot-}$ are both strong one-electron oxidants (E^0=1.9 V and 1.59 V vs. NHE, respectively [4,5]) while $HO_2^\cdot$ and $O_2^{\cdot-}$ are fairly weak one-electron oxidants (depending on pH). H_2O_2 and O_2 on the other hand can act both as one- and two-electron oxidants.

The presence of carbonate affects the kinetics for UO_2 oxidation not only by converting $OH^\cdot$ into $CO_3^{\cdot-}$ but also since it forms soluble complexes with the oxidation product, UO_2^{2+} [6]. This facilitates continuous removal of oxidized UO_2 resulting in a constant surface area accessible to oxidation.

The kinetics for reactions between different oxidants and the spent fuel matrix (UO_2) has been studied quite extensively [7,8]. On the basis of these results it has been possible to assess the relative reactivity of the radiolytically formed oxidants towards the UO_2 surface. The relative importance of the different radiolysis products has been discussed for several years. However, it should be stressed that the relative reactivity is not the same as the relative importance or impact of the reactant. The latter being the product of the reactivity (rate constant for the surface reaction) and the surface concentration of the reactant. Very recently, it was shown that the molecular products, although in general being less reactive than some of the oxidizing radicals, have the highest impact (relative importance) for all types of radiation (except for very short irradiation time where the impact of radicals is significant) [9]. The rationale for

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this is simply that the concentration of molecular products is many orders of magnitude higher than that of radical products. In a system exposed to α-radiation, the relative impact of H_2O_2 was found to be 99.9–100% [9]. Hence, the only oxidant that should be accounted for in a safety assessment of a future deep repository is H_2O_2. At HCO_3^- concentrations higher than 1 mM the rate limiting step in the reaction between H_2O_2 and UO_2 has been shown to be oxidation while at lower concentrations dissolution of oxidized UO_2 influences the kinetics [8]. Consequently, the rate of spent fuel dissolution can be approximated by the rate of H_2O_2 consumption at the fuel surface in groundwater containing more than 1 mM HCO_3^-. The rate of H_2O_2 consumption is calculated from the rate constant and the surface concentration of H_2O_2. It has previously been shown that only 80% of the consumed H_2O_2 yields oxidized UO_2 [10]. The remaining 20% can probably be attributed to catalytic decomposition of H_2O_2. Therefore, the rate of dissolution corresponds to 80% of the rate of H_2O_2 consumption.

The geometrical dose distribution as well as the consumption of H_2O_2 in surface reactions and in homogeneous reactions in solution complicate the situation to some extent. However, keeping in mind the following boundary conditions, we can still reduce the complexity to some extent. (1) The rate of spent fuel dissolution can never exceed the rate of UO_2 oxidation and (2) the rate of H_2O_2 consumption can never exceed the radiolytic H_2O_2 production rate. The radiolytic H_2O_2 production rate is given by Eq. (1)

$$r_{\mathrm{H_2O_2}} = \int_{x=0}^{x_{\max}} \dot{D}(x) \times \rho \times G(\mathrm{H_2O_2})\mathrm{d}x, \tag{1}$$

where $\dot{D}(x)$ is the dose rate at distance x from the fuel surface, ρ is the density of water and $G(\mathrm{H_2O_2})$ is the radiation chemical yield for H_2O_2. The maximum rate of the reaction between H_2O_2 and the fuel surface corresponds to the steady-state. At steady-state, the rate of H_2O_2 consumption is identical to the rate of radiolytic H_2O_2 production. The steady-state surface concentration can be calculated from Eq. (2)

$$[\mathrm{H_2O_2}]_{\mathrm{s-s}} = \frac{\overline{r_{\mathrm{H_2O_2}}(\alpha)}\delta_{\max}(\alpha) + \overline{r_{\mathrm{H_2O_2}}(\beta)}\delta_{\max}(\beta)}{k_{\mathrm{H_2O_2}}}, \tag{2}$$

where $\bar{r}$ is the average production rate (Eq. (1)), δ is the maximum range of the radiation and$k_{\mathrm{H_2O_2}}$ is the rate constant for the reaction between H_2O_2 and the fuel surface.

By simulating H_2O_2 production using the geometrical dose distribution given above and H_2O_2 consumption in a surface reaction taking diffusion (one dimension) into account, we were able to show that steady-state surface concentration is approached in a very short time (minutes to hours) in view of the time span of interest for a deep repository [11]. Consequently, the use of the steady-state approach will simplify simulation of spent nuclear fuel dissolution significantly without loss of accuracy. It should be noted that reactions between H_2O_2 and solutes will also affect (reduce) the steady-state concentration.

In this work we have used the steady-state approach to simulate the rate of spent nuclear fuel dissolution for relatively fresh spent fuel for which experimental data are available. The experimental data have been published previously [12–14].

2. Methods

The spent fuel leaching experiments have been described in detail elsewhere [12–14]. PWR fuel (Ringhals DO-7-S14) was used in the experiments. The fuel rod was irradiated for 5 cycles during 1977–1983 experiencing an average linear power of 18 kW/m. The calculated average burn up is 40 MWd/kgU. Fuel fragments were transferred to a quartz vessel with approximately 60 cm^3 total volume. The vessel was placed in a lead shield into a glove box with argon atmosphere and connected to gas and solution sampling and analyzing systems. The vessel and gas sensor chamber were flushed with argon through a thin plastic tube inserted into the vessel via the sensor chamber. A volume of 30 cm^3 solution containing 10 mM $NaHCO_3$ was transferred through the same plastic tube to the vessel by applying argon overpressure to a stock solution reservoir. The tube was thereafter removed and the valve connecting the reaction vessel and sensor chamber closed. Small volumes (1–2 cm^3) of the test solution were at time intervals removed through a capillary tube for analysis. The concentration of uranium in solution was measured using a Scintrex UA-3 Uranium Analyser.

To simulate the rate of spent nuclear fuel dissolution, the geometrical dose distribution must be known. This can be calculated from the radionuclide inventory using a method recently published [15]. The radionuclide inventory for the fuel used in the calculation (as well as in the previous experiments) was obtained from OrigenArp 2.00 calculations. On the basis of the geometrical dose distribution taking α- and β-emitters into account, the average dose rate was calculated. From the average dose rate, the rate of H_2O_2 production and thereby the maximum rate of spent nuclear fuel dissolution was calculated.

3. Results and discussion

In each experiment 6–8 fragments were used and the total BET surface area exposed to the liquid was estimated to 7.5 cm^2. The geometrical surface area was calculated from the size of the fragments assuming spherical geometry and the BET surface area was calculated by multiplying the geometrical surface area by three [16]. Using the measured concentration and the solution volume, taking the amount removed with each sampling into account, the total amount of uranium released can be calculated. The calculated amounts for the experiments used in the comparison are presented in Table 1.

Table 1
Data from spent nuclear fuel dissolution experiments [13,14]

Time/days	n(U)/moles
Exp. 1 (ID 7.40.1)	
0	8.67×10^{-7}
0.78	1.55×10^{-6}
1.73	1.87×10^{-6}
2.82	1.86×10^{-6}
4.83	1.87×10^{-6}
6.83	2.34×10^{-6}
12.83	2.91×10^{-6}
Exp. 2 (ID 7.40.2)	
2.12	6.42×10^{-7}
5.08	8.59×10^{-7}
8.12	7.06×10^{-7}
12.08	1.16×10^{-6}
15.04	1.29×10^{-6}
43.04	1.77×10^{-6}
Exp. 3 (ID 7.40.3)	
0.02	1.64×10^{-7}
2.92	2.40×10^{-7}
5.92	4.09×10^{-7}
9.83	6.36×10^{-7}
11.87	7.56×10^{-7}
37.79	1.85×10^{-6}
Exp. 4 (ID 7.40.4)	
7.08	3.63×10^{-7}
16.13	7.15×10^{-7}
23.13	8.19×10^{-7}
27.20	9.06×10^{-7}
Exp. 5 (ID 7.40.9)	
5.83	3.30×10^{-7}
8.88	4.84×10^{-7}
11.79	6.10×10^{-7}
Exp. 6 (ID 7.40.12)	
0.96	6.60×10^{-8}
1.92	1.07×10^{-7}
4.92	1.33×10^{-7}
9.08	2.15×10^{-7}

In all the experiments the HCO_3^- concentration was 10 mM and no other solutes were added. Hence, the rate of dissolution is expected to be equal to the rate of oxidation and the surface reaction should be the only process consuming H_2O_2 in the system. For all six sets of experimental data the amount of uranium released increases linearly with time. Hence, the rate of dissolution is constant which implies steady-state conditions. However, the bulk concentrations of H_2O_2 are not constant during the experiments. The uranium release has a positive intercept, i.e. a significant amount of uranium is initially dissolved at a rate much higher than the steady-state rate. The rationale for this is most probably that the fuel fragments have a preoxidized layer which is immediately dissolved upon immersion of the solid. The rates of dissolution derived from the experiments (based on a surface area of 7.5 cm^2 in each experiment) are presented in Table 2.

As can be seen, the rate of dissolution varies significantly between the experiments. The average dissolution rate is 6.9×10^{-10} mol m^{-2} s^{-1}. The variation could partly be due to differences in surface areas since different fragments are used in the experiments. Furthermore, spent nuclear fuel is far from homogeneous and therefore the composition of the different fragments could also vary. From the simulations based on the radionuclide inventory we obtain an average α-dose rate of 0.23 Gy/s and an average β-dose rate of 0.0085 Gy/s in the liquid volumes limited by the maximum α- and β-range, respectively. The maximum α-range is 40 μm and the maximum β-range is 2.1 mm. The resulting steady-state rate for H_2O_2 production in the system is 2.05×10^{-9} mol m^{-2} s^{-1}. By taking the oxidative dissolution yield of 80% into account we estimate the maximum spent nuclear fuel dissolution rate to 1.64×10^{-9} mol m^{-2} s^{-1} (Eq. (3)). The relative contribution from α- and β-radiation to the dissolution rate is 47 and 53%, respectively.

Table 2
Steady-state dissolution rates

Exp.	Dissolution rate/mol m^{-2} s^{-1}
1	$(1.6 \pm 0.2) \times 10^{-9}$
2	$(4.1 \pm 0.8) \times 10^{-10}$
3	$(7.0 \pm 0.2) \times 10^{-10}$
4	$(4.1 \pm 0.6) \times 10^{-10}$
5	$(7.2 \pm 0.3) \times 10^{-10}$
6	$(2.6 \pm 0.3) \times 10^{-10}$
Simulated	1.64×10^{-9}

$$r_{\mathrm{diss}} = 0.8(\overline{r_{\mathrm{H_2O_2}}(\alpha)}\delta_{\max}(\alpha) + \overline{r_{\mathrm{H_2O_2}}(\beta)}\delta_{\max}(\beta)) \tag{3}$$

The estimated value is identical to the highest experimental dissolution rate and a factor of 2 higher than the average experimental dissolution rate. The agreement between experimental data and the simulation is astonishingly good indicating that the steady-state approach can indeed be used to predict the rate of spent nuclear fuel dissolution.

In long term leaching experiments performed under the same conditions, the rate of dissolution decreases with time [17]. For reaction times longer than one year the dissolution rate appears to become significantly reduced. A probable rationale for this behaviour which cannot be predicted from the simple steady-state approach used above is the increasing impact of noble metal particle catalyzed reduction of the solid phase by radiolytically produced H_2. [18]. This process can also be accounted for (Eq. (4))

$$r_{\mathrm{diss}} = 0.8(\overline{r_{\mathrm{H_2O_2}}(\alpha)}\delta_{\max}(\alpha) + \overline{r_{\mathrm{H_2O_2}}(\beta)}\delta_{\max}(\beta)) - k[\mathrm{H_2}]\varepsilon_{\mathrm{rel}} \tag{4}$$

In Eq. (4), k is the rate constant for uptake of H_2 from the solution by the noble metal particles, $[H_2]$ is the concentration of H_2 in solution and $\varepsilon_{\mathrm{rel}}$ is the fraction of the fuel surface covered by noble metal particles (sometimes referred to as ε-particles).

The dynamics of this process is currently under investigation.

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