

SKB

TECHNICAL

REPORT

90-08**Radiolytically induced oxidative
dissolution of spent nuclear fuel**Lars Werme¹, Patrik Sellin¹, Roy Forsyth¹¹ Swedish Nuclear Fuel and Waste Management Co (SKB)² Studsvik Nuclear

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RADIOLYTICALLY INDUCED OXIDATIVE DISSOLUTION OF
SPENT NUCLEAR FUEL

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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 author(s) and do not necessarily coincide with those of the client.

RADIOLYTICALLY INDUCED OXIDATIVE DISSOLUTION OF SPENT NUCLEAR FUEL

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ABSTRACT

The possible effects of radiolysis on the oxidative dissolution of spent nuclear fuel are discussed. A simple model for radiolytically controlled oxidation is proposed and numerical examples are given based on empirical data. The effects of solubility limits for some specific nuclides are also illustrated.

BACKGROUND

Deep granitic groundwaters are expected to be reducing. Under these conditions the spent fuel matrix, to approximately 97 % UO_2 , will be stable. However, there are some uncertainties concerning the influence of the radiolysis, in particular alpha-radiolysis, on the redox conditions in the very near field. Radiolysis produces equivalent quantities of oxidizing and reducing species, the reducing species being predominantly hydrogen. The relatively low reactivity of hydrogen, coupled with a relatively high diffusivity, may allow hydrogen to escape from the system before reacting leaving the more reactive oxidizing species behind. This may well result in an increased redox potential in the very near field and UO_2 may not be the most stable solid, but transforms involving oxidation to U(VI) secondary phases. Experiments have shown that at the rate of transformation, the matrix bound radionuclides may be mobilized and released. Depending on the solubilities of the radionuclides, their individual releases will be controlled by the rate of matrix transformation or by mass transport constraints.

INTRODUCTION

In order to measure the matrix oxidation/alteration rate, it is necessary to identify a soluble element, which is released at the rate of UO_2 matrix alteration, i.e. an element which is expected to be in solid solution with UO_2 . Experimental studies in Sweden as well as elsewhere have shown that for oxidative dissolution of UO_2 , the uranium concentration in solution rapidly reaches an apparent saturation level of a few mg/l in carbonate containing groundwater (ca 2 mM HCO_3^-) independent of contact time [1 - 5]. (See figure 1.) Thus, the uranium release itself cannot serve as an indicator of matrix alteration. In fact, the releases of most radionuclides mobilized from the fuel when contacted with water have been found to be controlled by their respective solubilities. As an example, plutonium concentrations as a function of contact time are shown in figure 2. In groundwater, the fraction of plutonium released is almost a factor of 100 lower than the fractional release of uranium, while in deionized water the fractional plutonium release exceeds that of uranium by at least a factor of 10 at prolonged tests. The latter observation indicates an ongoing fuel alteration after the leachant has been saturated with uranium. (A more detailed discussion of the uranium and plutonium behaviours can be found in e.g. refs. [1,2,4,6].) Of the soluble elements some, like cesium, are known to be selectively released (see e.g. ref. [1]). However, the release of strontium appears to be of particular interest. It cannot be completely ruled out that also strontium is partly selectively released, but most observations indicate that it is released congruently with the matrix alteration [7] and is, consequently, a monitor of the matrix alteration rate. If there are any possible contributions from segregated material, the strontium release would represent an upper limit for the matrix alteration rate.

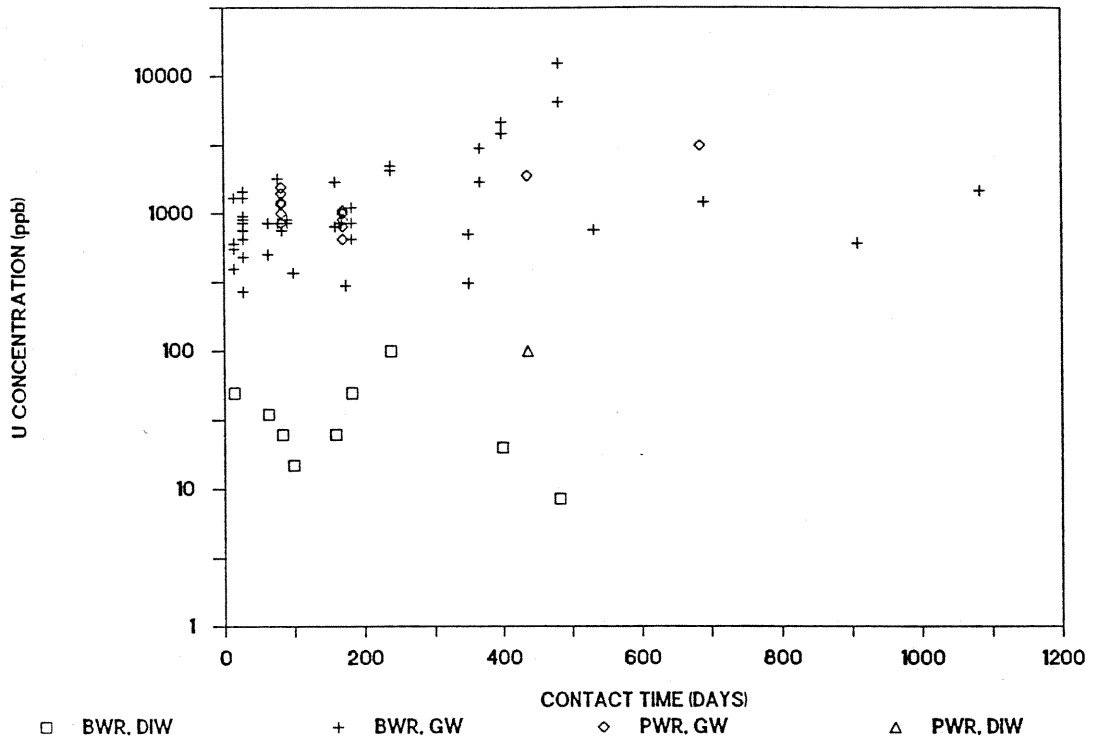


Figure 1: Uranium concentrations as a function of contact time. BWR = Boiling water reactor, PWR = Pressurized water reactor, GW = Groundwater, DIW = deionized water.

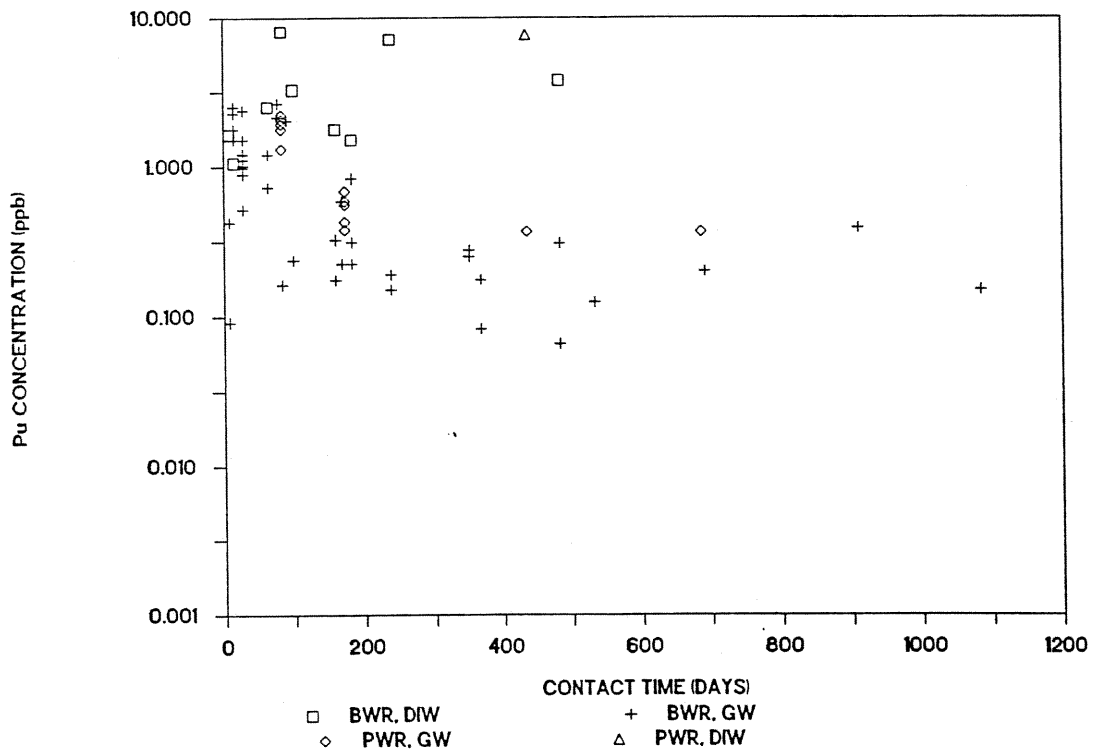


Figure 2: Plutonium concentrations as a function of contact time. Same abbreviations as in figure 1.

The cumulative release of strontium versus cumulative contact time is shown in figure 3. Figure 3 shows that the cumulative fractional release of strontium is independent of whether sequential or static leaching has been performed. In a sequential leaching, the leachant is renewed at preset interval, while in a static test, the same leachant is used throughout the total exposure time. Thus, in a sequential test, the uranium release is many times higher than in a static test, since the leachant has been saturated with uranium in each sequence. However, the strontium release appears to be independent of the cumulative uranium release and depend only on the cumulative contact time. This is even more pronounced in the tests performed in deionized water, where it is found that the strontium release is the same as in groundwater, while the cumulative uranium release can be almost a factor of 1000 lower. The release rate of strontium versus cumulative strontium release (i e cumulative time) is shown in figure 4.

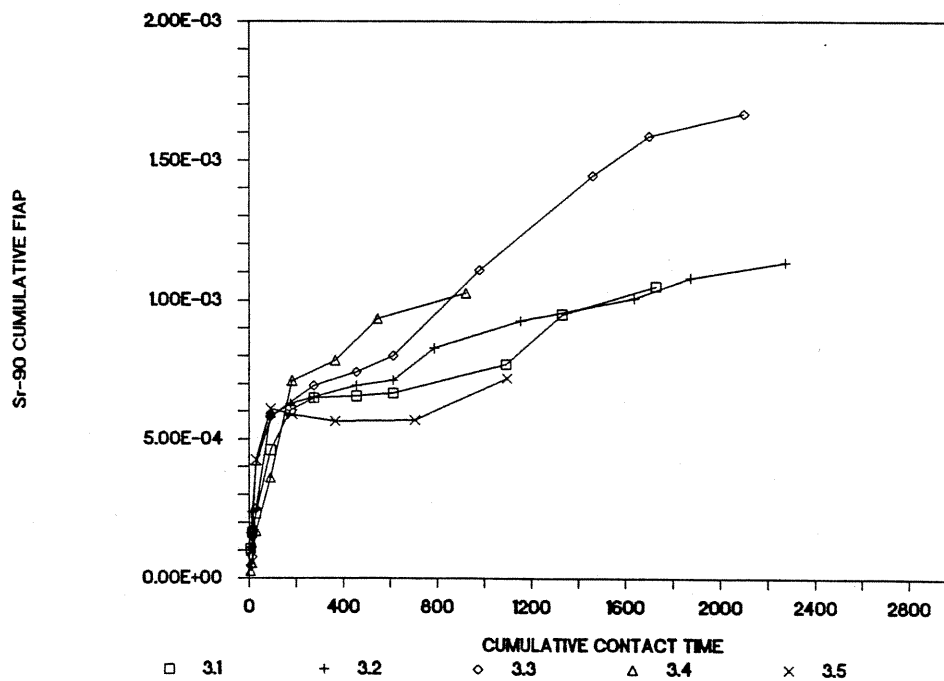


Figure 3: Cumulative strontium release from boiling water reactor (BWR) fuel as a function of cumulative contact time. 3.1 = sequential tests in deionized water, 3.2 and 3.3 = sequential tests in synthetic groundwater, 3.4 and 3.5 = static tests in synthetic groundwater.

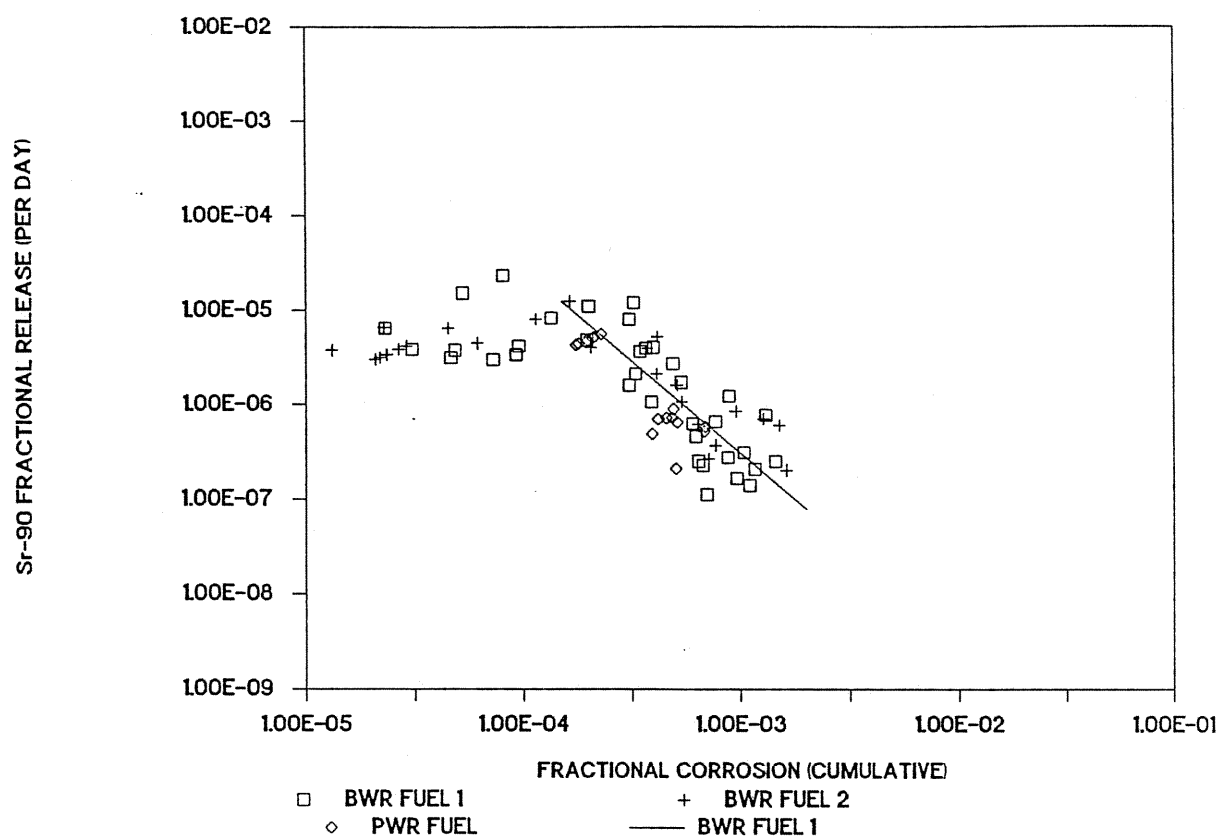


Figure 4: Fractional release rates of strontium as a function cumulative fractional corrosion (reaction progress). The solid line represents a least square fit to the BWR data.

EXPERIMENTAL EVIDENCE

The results shown in figures 1 to 4 have been obtained for oxidizing conditions. No efforts were made to exclude atmospheric oxygen from the system. It is therefore reasonable to assume that there is a substantial contribution of dissolved atmospheric oxygen to the oxidation of the UO_2 matrix. The size of the contribution from radiolytically produced oxidants is of course difficult to determine from such experiments. There is some experimental evidence that radiolytically produced radicals may actually have a major impact on the oxidation of UO_2 under aerated conditions through the formation of O_2^- radicals [8].

Experiments under reducing conditions have also been performed. In these studies, reducing conditions were obtained by bubbling a gas mixture of 6 % H₂ in argon through the leach solution in the presence of a palladium catalyst. The measured uranium concentrations in these experiments are markedly lower (normally at the analytical detection limit of a few $\mu\text{g/l}$) than what is found for oxidizing conditions (a few mg/l). As expected, appreciable decreases in the measured concentrations of other redox sensitive elements were also found. The strontium release is also lower, although only by about a factor of ten. The results for one long-term exposure of PWR fuel are shown in figure 5. As can be seen in figure 5, in the analysis of the material plated out on the palladium catalyst most of the uranium, plutonium and curium was recovered.

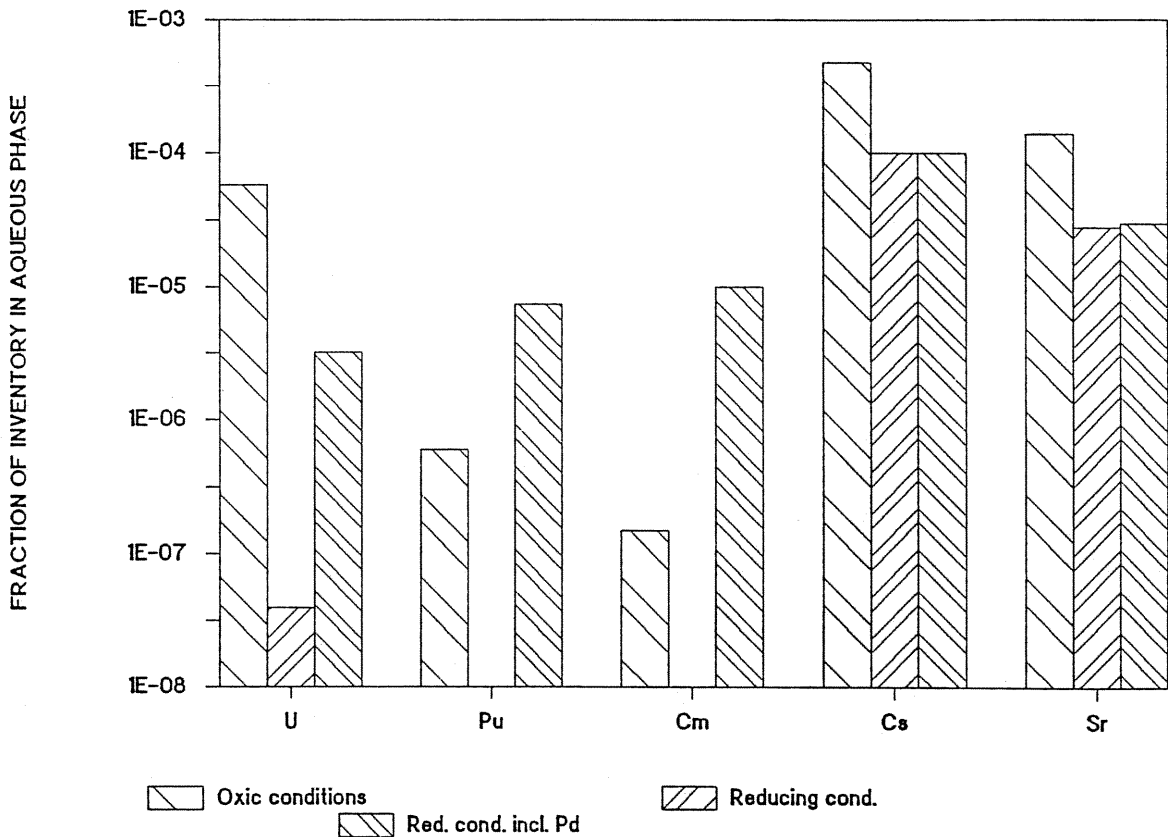


Figure 5: Comparison between fractional releases of radionuclides from PWR fuel (ca 43 MWd/kgU) for oxidizing and reducing conditions. The results for reducing conditions are presented both with and without the contributions from the palladium mesh.

It should be emphasized that although the observed leachate concentrations for both oxidizing and reducing conditions have been confirmed in a number of experiments, the plate out on the Pd mesh has been analysed in a few experiments only. It is therefore to some extent an open question how these results are to be interpreted.

It is not unreasonable, that despite the overall reducing conditions, oxidative dissolution may take place at the fuel surface while the reduction reaction takes place at the catalyst thus maintaining low concentrations in the bulk solution. This oxidative dissolution may be caused either by radiolysis products or by residual oxygen. Nor can sorption be excluded, but seems less likely since U(VI) is expected to form anionic species, predominantly uranyl-carbonates in the groundwater, which are known to sorb less effectively than the cationic species formed by plutonium. Furthermore, no sorption of strontium was observed. In a leach experiment with bentonite present, substantial sorption was found for all cationic species, including cesium and strontium [9]. It is worth noting that all the experiments are performed on fresh fuel, where there are appreciable contributions from beta- and gamma-radiolysis, while in a repository, the fuel will be 1000 years or older before coming into contact with water.

In an attempt to assess the contribution of alpha-radiolysis to the dissolution of spent fuel, high burnup (42 MWd/kgU) and low burnup (0.5 MWd/kgU) BWR fuel has been leached. The alpha dose rate from the low burnup fuel was less than 1 % of that of the high burnup fuel (0.04 rad/s and 25 rad/s respectively). Both fuel types had comparable beta and gamma contributions to the alpha irradiated water layer (160 rad/s for the high burnup fuel and 210 rad/s for the low burnup fuel). No significant differences in the strontium release rates for the two fuels were found for either oxidizing or reducing conditions. This is also in accordance with calculations, which show that with the model

used, the results were less sensitive to variations in alpha dose rate than to variations in other parameters [10]. Thus a tentative conclusion from this study could be that for both fuels, beta and gamma radiolysis products are dominating any possible oxidation of the fuel surfaces under oxygen-free conditions.

At the time for canister break-through, alpha-radiolysis will dominate. It is therefore possible that the rate of alpha-radiolytic oxidation under repository conditions is well below the rates observed even under oxygen-free conditions in the laboratory. Thus, it appears to be reasonable to assume that the measured strontium release rates under reducing experimental conditions represents a conservative upper limit for the corrosion rate under repository conditions.

MODEL

The alpha-radiolysis dose rate and its variation with time is shown in figure 6. The data are based on calculations carried out by Lundgren [11] for storage times of 40 and 10^5 years and data from ref. [12]. For a BWR fuel rod with a burnup of 33 MWd/kgU, the dose rates at 40 and 10^5 years are 28 rad/s and $7.5 \cdot 10^{-2}$ rad/s, respectively. The simple analytical expression for the variation of dose rate with time at intermediate times and after 10^5 years has been derived from the alpha-decay curves of ^{241}Am , ^{239}Pu , ^{240}Pu and ^{237}Np and can be expressed as follows:

$$R_{\alpha}(t) = 25.3 \cdot e^{-t \cdot \ln 2 / 433} + 2.2 \cdot e^{-t \cdot \ln 2 / 6570} + 1.1 \cdot e^{-t \cdot \ln 2 / 2.4 \cdot 10^4} + 0.04 \cdot e^{-t \cdot \ln 2 / 2.1 \cdot 10^6} \quad (1)$$

Christensen and Bjergbakke [12] have shown that if Fe^{2+} is readily available, radiolysis will produce H_2 and Fe(III) . This is also the situation with the highest total yield of hydrogen.

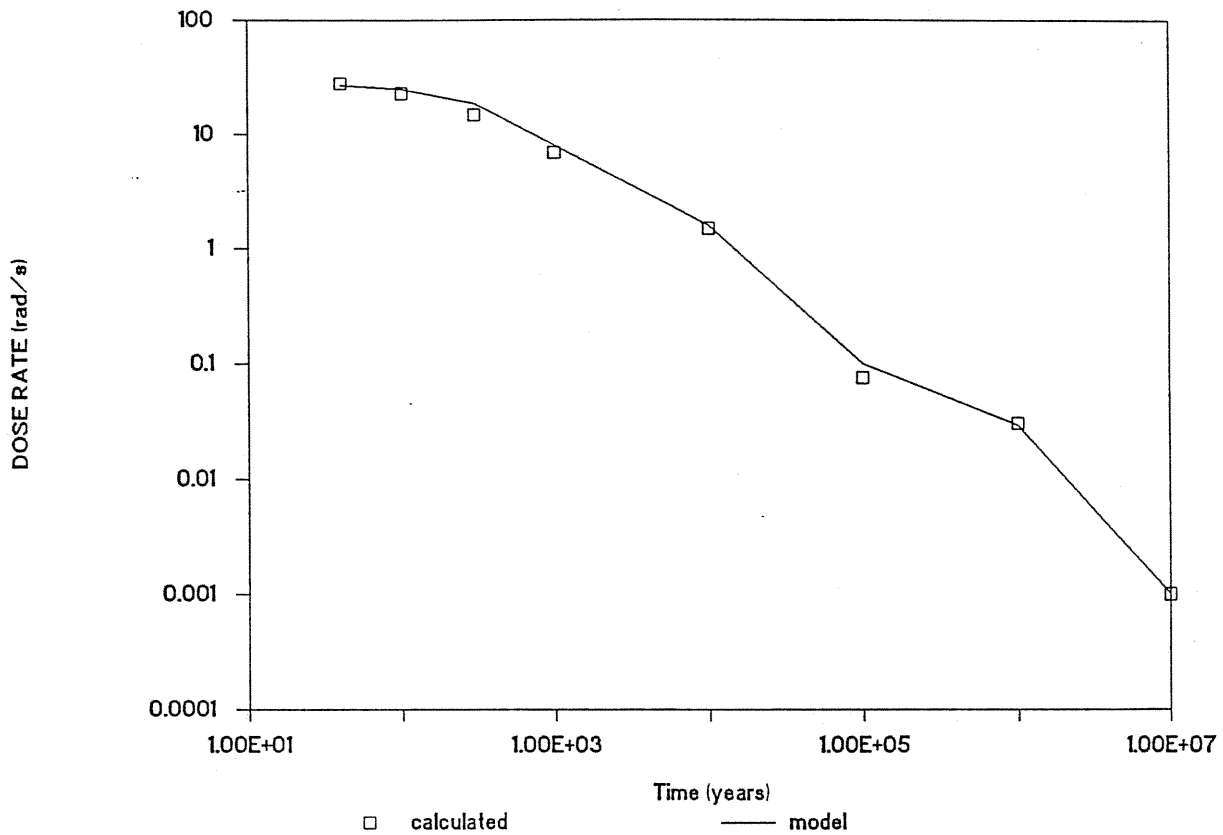


Figure 6: Variation of alpha dose rate with time. Symbols represent data from refs. [10 and 11]. Solid line data calculated using Eq. (1).

The calculations also show that the hydrogen production rate and, hence, the production rate of Fe(III) is proportional to the alpha dose rate. If the oxidation of UO_2 would be as effective as the oxidation of Fe^{2+} , the normalized oxidation rate of spent fuel could be expressed as:

$$r_{\text{OX}}(t) = k_1 \cdot R_\alpha(t) \quad (2)$$

The normalized amount of oxidized fuel can then be expressed as:

$$M(t) = \int r_{\text{OX}}(t) dt = k_1 \cdot \int R_\alpha(t) dt \quad (3)$$

or:

$$\begin{aligned}
M(t) = k_1 \cdot [& 25.3 \cdot 433 \cdot (e^{-Tb \cdot \ln 2 / 433} - e^{-t \cdot \ln 2 / 433}) + \\
& 2.2 \cdot 6570 \cdot (e^{-Tb \cdot \ln 2 / 6570} - e^{-t \cdot \ln 2 / 6570}) + \\
& 1.2 \cdot 2.4 \cdot 10^4 \cdot (e^{-Tb \cdot \ln 2 / 2.4 \cdot 10^4} - e^{-t \cdot \ln 2 / 2.4 \cdot 10^4}) + \\
& 0.03 \cdot 2.1 \cdot 10^6 \cdot (e^{-Tb \cdot \ln 2 / 2.1 \cdot 10^6} - e^{-t \cdot \ln 2 / 2.1 \cdot 10^6})] \quad (4)
\end{aligned}$$

where Tb is the time for canister break-through.

Very little is known about radiolysis in heterogeneous systems. However, it is reasonable to assume that reactions involving a solid uranium phase are slower than the reaction rates in the homogeneous system containing Fe^{2+} . Following the calculations by Christensen and Bjergbakke, the normalized oxidation rate of the spent fuel 1000 years after disposal would be about $0.9 \cdot 10^{-4} \text{ a}^{-1}$. This must be considered as a very conservative upper limit for the fuel oxidation rate. Using this rate, the relative amount of oxidized fuel as a function of time will be as shown in figure 7.

The rate of $0.9 \cdot 10^{-4} \text{ a}^{-1}$ is comparable to what is observed in spent fuel corrosion tests with 15 years old spent fuel, if the strontium release is assumed to be a monitor of matrix oxidation/alteration. At prolonged tests, the strontium release rate has been found to be about $1.1 \cdot 10^{-4} \text{ a}^{-1}$ under oxidizing conditions. Under reducing conditions (H_2 in the presence of a Pd catalyst), strontium release rates of $1.1 \cdot 10^{-5} \text{ a}^{-1}$ are measured. The relative amount of oxidized fuel for these conditions, as a function of time will be as shown in figure 8.

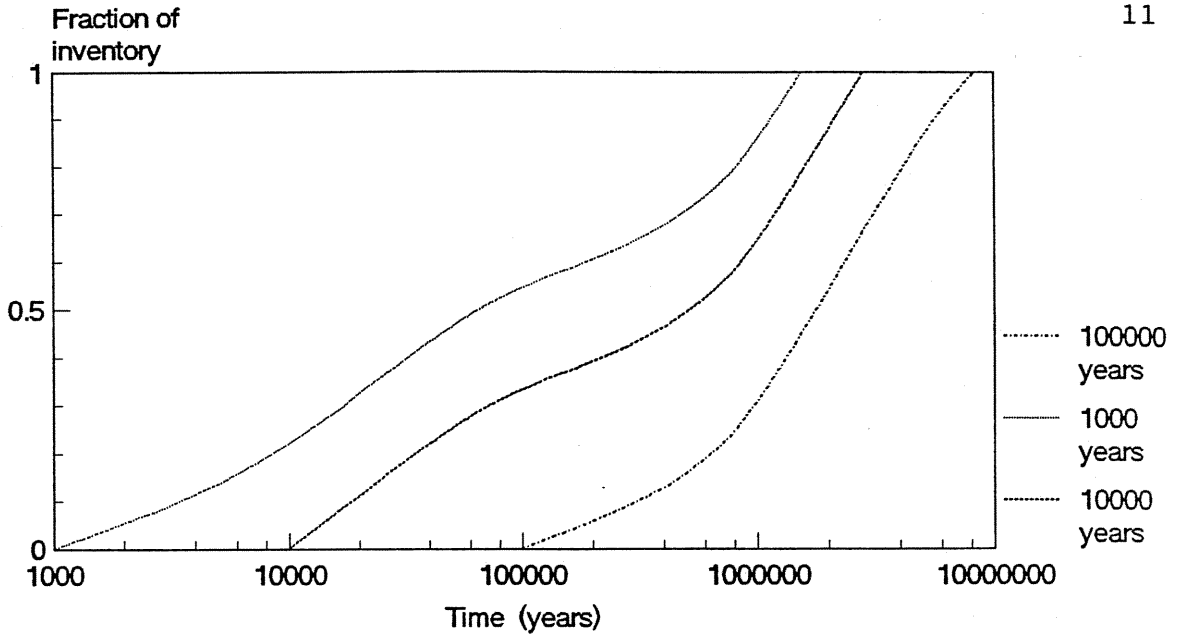


Figure 7: Fractional alteration of the fuel matrix as a function of time (in years) for canister life-times of 10^3 , 10^4 and 10^5 years. Alteration rate base on calculations in ref. [12].

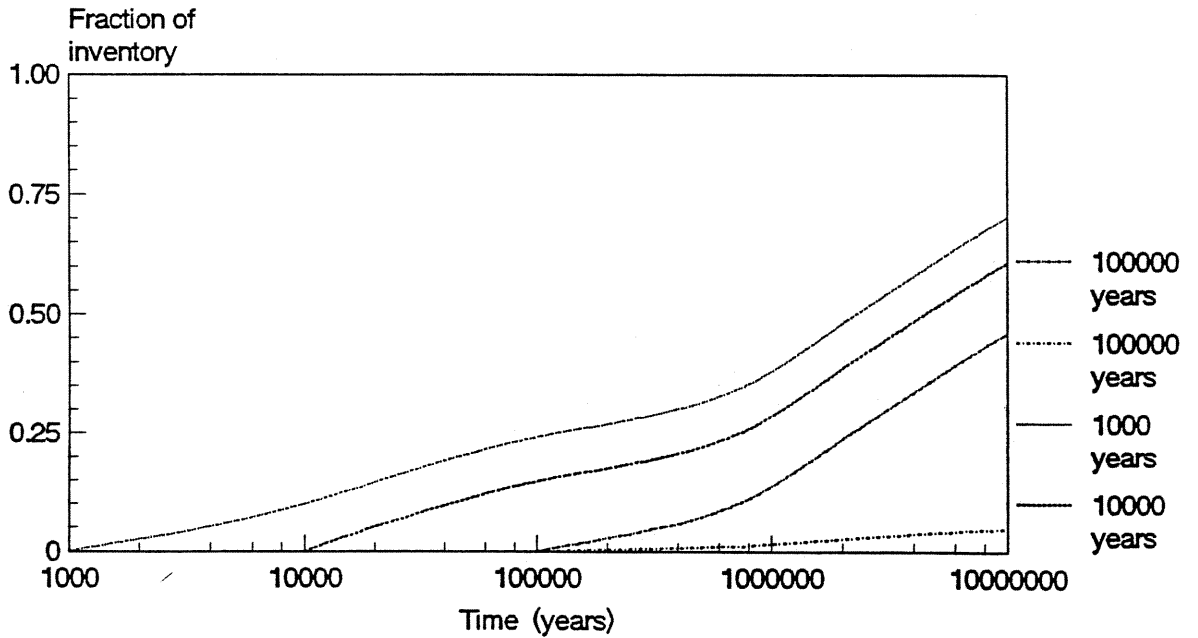


Figure 8: Fractional alteration of the fuel matrix as a function of time (in years) for canister life-times of 10^3 , 10^4 and 10^5 years. Alteration rate base on empirical data for oxidizing conditions (three upper curves). Lower curve: empirical data for reducing conditions and canister life-time = 10^5 years

DISCUSSION

Alpha-radiolysis is a surface phenomenon. The curves in figures 7 and 8 are plotted assuming that the fuel surface area is constant with time, or rather, that the possible surface area increase caused by fuel oxidation will not lead to increased alpha dose rates to the water. It remains to be demonstrated that this is actually the case. A total disintegration of the fuel into individual UO_2 grains corresponds to a surface area increase of about a factor of 200. At which rate such a process may occur is not known, nor is the actual surface area active in the radiolysis process under the experimental conditions. However, in one experiment where powdered and sieved fuel (7.2 g) was leached in a small amount of water (6.9 g) in a sealed gold capsule, the strontium release rate, as well as the uranium concentration were both found to be comparable to what was found in the standard leach tests using about 16 g fuel and 200 g water. The fuel surface area in the gold capsule experiment was estimated to be a factor of 50 to 100 higher than in the standard experiments. Thus, it appears that the overall oxidation rate in the laboratory experiments is not depending on the apparent fuel surface area. A surface area increase of at least a factor of 50 does not result in an appreciable increase in radiolytic oxidation rate and, therefore, it may be justified to extrapolate the laboratory oxidation rates as given by the strontium dissolution rates to very long times.

The fuel oxidation rate will put an upper limit on the release rates of soluble radionuclides. For sparingly soluble elements, their respective solubility limits will control the release. As an example, figure 9 shows the release (in [Bq/Canister]) of one soluble element, cesium, and two solubility limited elements, plutonium and neptunium. As solubility limits for Pu and Np, respectively, $2 \cdot 10^{-11}$ M and $1.2 \cdot 10^{-6}$ M were chosen. The equivalent water flow was assumed to be 1 l per canister and year. The fuel alteration rate has been assumed to be $1.1 \cdot 10^{-5} \text{ a}^{-1}$

The long half-life of neptunium results in a constant release in Bq over one hundred thousand years. The apparent decrease in release in Bq for plutonium is an artifact, caused by plutonium concentration being constant, while the more short-lived isotopes decay leading to decrease in release in radioactivity.

As the radiolytically induced oxidation/alteration rate gradually decreases, it will eventually reach a level where it is lower than the dissolution rate of UO_2 . When this will happen depends on factors such as the solubility of UO_2 and the water flow rate at the waste package. The water flow rate or water exchange rate is to some extent site specific and also depends on the repository design. Once these are known, UO_2 dissolution can easily be incorporated into the present model.

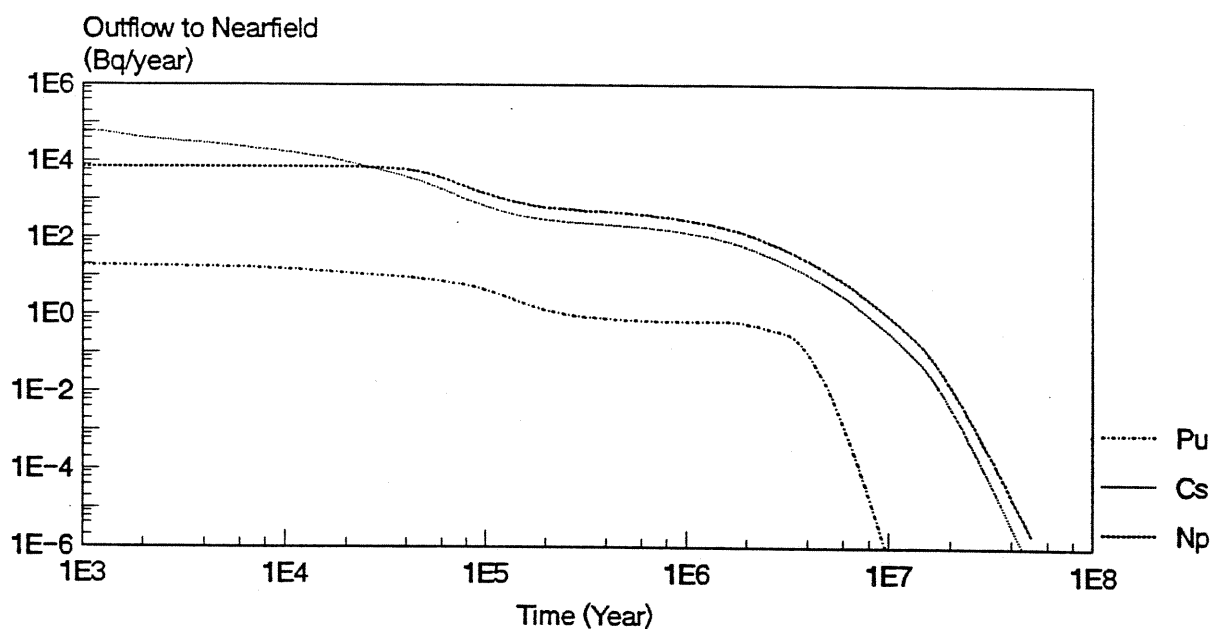


Figure 9: Releases in [Bq/Canister] for Cs (upper curve), Np (middle curve) and Pu (lower curve) as a function of time in years.

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¹ Starprog AB

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