



Modelling the radiolytic corrosion of α -doped UO_2 and spent nuclear fuel



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HIGHLIGHTS

- A model is adapted to simulate the corrosion rates measured on α -doped UO_2 .
- Simulated corrosion rates are in good agreement with the published rates.
- The corrosion rate is determined by the radiolytic production rate of H_2O_2 .
- The accumulation of O_2 leads to an increase in corrosion rate in a closed system.
- The corrosion rate decreases to a negligible level by including H_2 effect.

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ABSTRACT

A model previously developed to predict the corrosion rate of spent fuel (UO_2) inside a failed waste container has been adapted to simulate the rates measured on a wide range of α -doped UO_2 and spent fuel specimens. This simulation confirms the validity of the model and demonstrates that the steady-state corrosion rate is controlled by the radiolytic production of H_2O_2 (which has been shown to be the primary oxidant driving fuel corrosion), irrespective of the reactivity of the UO_2 matrix. The model was then used to determine the consequences of corrosion inside a failed container resealed by steel corrosion products. The possible accumulation of O_2 , produced by H_2O_2 decomposition, was found to accelerate the corrosion rate in a closed system. However, the simultaneous accumulation of radiolytic H_2 , which is activated as a reductant on the noble metal (ϵ) particles in the spent fuel, rapidly overcame this acceleration leading to the eventual suppression of the corrosion rate to insignificant values. Calculations also showed that, while the radiation dose rate, the H_2O_2 decomposition ratio, and the surface coverage of ϵ particles all influenced the short term corrosion rate, the influence of the radiolytically produced H_2 was the overwhelming influence in reducing the rate to negligible level (i.e., $<10^{-20} \text{ mol m}^{-2} \text{ s}^{-1}$).

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1. Introduction

If nuclear energy is to play an important role in alleviating the risk of global climate change, it must be demonstrated that the high level waste can be safely disposed of. The approved approach for the long-term management of used nuclear fuel in Canada is

disposal in a deep geologic repository (DGR) [1,2]. As accepted internationally, the repository concept is based on multiple barriers including the fuel bundles, durable metal containers, a clay buffer and seals around the container, and a deep geologic formation [3]. A key barrier is the corrosion-resistant container which is expected to isolate the used fuel for a very long time [4,5]. However, it is judicious to examine the consequences of container failure and the exposure of used fuel bundles to groundwater. In the anoxic conditions anticipated in a DGR, H_2O radiolysis resulting from the radiation fields associated with the used fuel within a failed container will be the only source of oxidants. The radiolysis product, H_2O_2 , has been shown to be the primary oxidant driving fuel corrosion [6,7]. Oxidation of fuel (U^{IV}) will produce the oxidized form (U^{VI})

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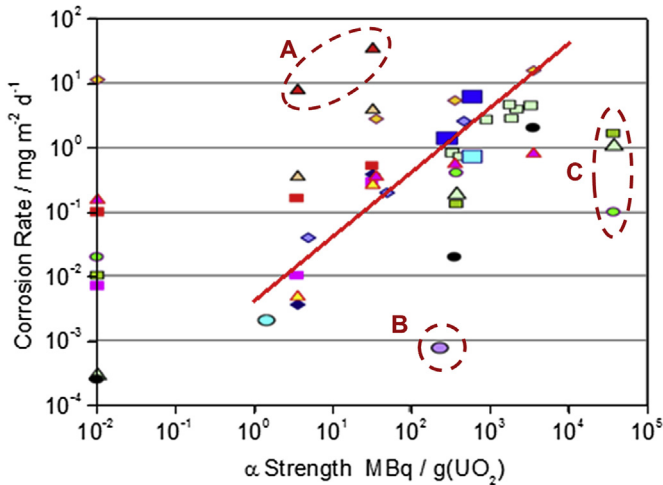


Fig. 1. Corrosion rates of α -doped UO_2 , non-doped UO_2 ($0.01 \text{ MBq g}^{-1} (\text{UO}_2)$), SIMFUEL and some spent fuels (from Ref. [17], with permission). The red line indicates a linear least squares fit to the data from Ref. [18] without including values marked A, B and C, which are discussed in the text. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

with a considerably higher solubility, leading to the release of radionuclides [8].

Since α -radiolysis of H_2O is the dominant source of oxidants for spent fuel oxidation/dissolution (corrosion) inside a failed waste nuclear container, the influence of the α -dose rate on the corrosion of UO_2 materials has been extensively studied [9–16]. The corrosion rates as a function of α -dose from a range of studies have been discussed in detail and summarized [17]. These measurements were conducted on a number of specimens including ^{233}U -doped UO_2 , ^{238}Pu -doped UO_2 , ^{225}Ac -doped UO_2 , UO_2 fuel pellets, SIMFUEL and spent fuels. Fig. 1 shows that, while significant variability exists, a clear trend of increasing corrosion rate with increasing alpha source strength was established. It was suggested that for alpha source strengths below $\sim 1 \text{ MBq g}^{-1} (\text{UO}_2)$, the influence of α -radiolysis became insignificant, the fuel dissolution rate becoming chemically controlled with U released in the unoxidized U^{IV} state.

Within this compilation, three sets of data, marked A, B and C, cannot be considered to fit the linear relationship. For A, corrosion rates were calculated based on electrochemical impedance spectroscopy measurements which required the compensation of the resistance in low conductivity materials. This led to large errors and an overestimation of the rates. The value labelled B was measured

$$\text{Corrosion Rate (mg (UO}_2\text{) m}^{-2}\text{ d}^{-1}\text{)} = 4.35 \times 10^{-3} \times \text{Activity (MBq g}^{-1}\text{ (UO}_2\text{))}$$

The errors associated with the use of this fit have been discussed elsewhere [18].

In this study, an attempt is made to use these data to validate the model we have developed for fuel corrosion inside a failed waste container [19–22]. The model is then used to evaluate a number of scenarios which could occur within a failed container. Of particular interest is the influence of O_2 , which can be produced by both decomposition of H_2O_2 and water radiolysis. In many of the experiments performed to produce the rates plotted in Fig. 1, the system was open and/or the solution purged with inert gas, making it possible that O_2 formed within the experiment could have influenced the corrosion rate measured. Although inadvertently achieved, this could have simulated the conditions achievable within a failed container possibly resealed by the accumulation of container corrosion products. The consequences of such a scenario are also addressed in this study.

2. Description of models

2.1. Conversion of α -source strength to α -dose rate

In Fig. 1 the corrosion rates are plotted as a function of alpha-source strength. The specific alpha-source strength is converted to the alpha-dose rate to the water layer adjacent to the UO_2 surface, which is used in the model to calculate the rate of production of radiolytic species. The rate of radiolytic production for species i can be calculated according to equation (1),

$$R_i (\text{mol m}^{-3} \text{s}^{-1}) = D_R \times g_i \times \rho_{\text{H}_2\text{O}} \quad (1)$$

where D_R is the dose rate representing the rate of energy deposition per unit of mass, g_i is the g -value of species i (the number of moles formed per joule of radiation energy absorbed), and $\rho_{\text{H}_2\text{O}}$ is the density of water.

For α -radiation, the dose rate near the solid surface and the energy fraction transferred into the solution can be approximately estimated from geometric considerations. Since the transfer range of α -emissions in UO_2 is $\sim 14 \mu\text{m}$, only a fraction of the α -particles within this range can reach the adjacent liquid to form radiolytic products [17]. For a $1 \text{ MBq g}^{-1} (\text{UO}_2)$ doped UO_2 , the energy deposited in the UO_2 layer with a thickness of $14 \mu\text{m}$ is $1.425 \times 10^{-8} \text{ J cm}^{-2} \text{ s}^{-1}$, according to equation (2),

$$\text{Total Energy Deposition in a } 14 \mu\text{m } \text{UO}_2 \text{ layer (corresponding to } \frac{1 \text{ MBq}}{\text{g (UO}_2\text{)})} = C_1 \times \text{typical energy of an } \alpha \text{ particle} \times C_2 \times \text{transfer range of } \alpha \text{ particles in } \text{UO}_2 \quad (2)$$

in a clay environment known to contain reducing species leading to the unexpectedly low values. The values labelled C were measured on ^{238}Pu -doped specimens, and it has been suggested, but not proven, that the low rates indicate a stabilizing influence of Pu on the UO_2 matrix. The line in Fig. 1 shows a fit to the data (excluding the data marked A, B and C) used by the Nuclear Waste Management Organization (Toronto, Canada) in repository performance assessment calculations [18] yielding the relationship,

In which $C_1 (= 10.97 \times 10^6 \text{ Bq cm}^{-3})$ is a conversion coefficient changing $\text{MBq g}^{-1} (\text{UO}_2)$ to $\text{Bq cm}^{-3} (\text{UO}_2)$; the typical energy of an α particle is $5.8 \times 10^6 \text{ eV}$; $C_2 (= 1.6 \times 10^{-19} \text{ J eV}^{-1})$ is a conversion coefficient changing electron volts to joules, and the transfer range of α particles in UO_2 is 0.0014 cm . Given the various depths of location of α particles in UO_2 , it can be calculated that only 18.8% of this energy can be absorbed by the adjacent H_2O [17].

The geometrical distribution of α -dose rate in a H_2O layer has been found to follow an exponential decay with distance from the

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