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An improved model for the corrosion of used nuclear fuel inside a failed waste container under permanent disposal conditions

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An improved model for nuclear fuel corrosion inside a failed waste container has been developed. The model considers the influence of the α-radiolysis products using a full radiolytic reaction set, and demonstrates that H_2O_2 is the dominant oxidant. Corrosion of the fuel is modelled considering both the direct oxidation of UO_2 by H_2O_2 and the galvanically-coupled oxidation by H_2O_2 reduction on noble metal (ε) particles. Corrosion has been found to be very sensitive to the corrosion products of steel container, Fe^{2+} and H_2. The surface coverage of ε-particles can significantly influence the dissolution rate.

1. Introduction

The safety assessment of deep geological disposal of used nuclear fuel requires a fundamental understanding of the processes controlling fuel corrosion and the release of radionuclides to the geosphere [1]. The development of source-term models to describe the processes involved in spent fuel dissolution has been the focus of considerable international effort [2–5]. The key process controlling the long-term release of radionuclides is corrosion of the UO_2 matrix [6]. In its reduced form (U^{IV}) the UO_2 matrix has an extremely low solubility in groundwater. However, the corrosion rate is very sensitive to the redox conditions since the solubility of the oxidized form (U^{VI}) is orders of magnitude higher [1,7]. Inside a failed waste container, the redox conditions at the fuel surface are controlled by both the oxidants/reductants produced by the radiolysis of the groundwater and the corrosion products of the steel container [8]. The radiolytic oxidants are expected to have a much larger influence on redox conditions than their reducing counterparts, at least during the early stages of disposal [9], and H_2O_2 has been shown to be the primary oxidant driving fuel corrosion [10,11]. However, the anaerobic corrosion of the steel container, sustained by H_2O reduction, will produce the potential redox scavengers, Fe^{2+} and H_2 [12].

A range of experimental studies has been conducted to determine how steel corrosion products would influence the fuel corrosion process. These studies have been recently reviewed [13] and are briefly discussed below. Ollila and co-workers [14–16] performed dissolution experiments on UO_2 doped with the α-emitter ^{233}U (to simulate the dose rates expected after 3000–10,000 years of disposal) in the presence of anaerobically corroding iron but found no evidence for irradiation-enhanced dissolution. These and similar experiments [3,14,15,17] suggested a significant reductive influence of the steel corrosion products and showed that both radiolytic oxidants and oxidized U^{VI} were reduced at the fuel surface. Corrosion studies using irradiated spent fuel segments [18–21] also showed that dissolved H_2 (in the concentration range 1–42 mmol L^{-1}) inhibited fuel dissolution. Cera et al. [22] observed in a long-term fuel leaching experiment that even radiolytically produced H_2 could inhibit fuel dissolution. The inhibiting effect of H_2 on UO_2 dissolution has been subsequently modelled by Eriksen and Jonsson [23] and Eriksen et al. [24].

In electrochemical experiments Broczkowski et al. observed a suppression of the corrosion potential by H_2 leading to a decrease in extent of surface oxidation on UO_2 specimens (SIMFUEL) doped to simulate the non-radioactive characteristics of spent fuel [25–27]. The extent of this effect was found to depend on the number density of noble metal particles in the SIMFUEL pellets and the concentration of dissolved H_2. It was proposed that fuel oxidation/dissolution was suppressed by H_2 oxidation on these particles galvanically coupled to the fission-product-doped UO_2 matrix. The kinetic parameters for reactions on UO_2 involving H_2 have

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been investigated [28–31] to facilitate the modelling of fuel dissolution rates.

The development of radiolytic models (in particular for α-radiolysis) for spent fuel corrosion has recently been reviewed [9]. Poinssot et al. [4] modelled fuel corrosion assuming that α-dose rate was uniform within a 45 μm thick water layer at the fuel surface, and that only half of the radiolytic oxidants reacted with the fuel, the remainder being consumed by other unidentified processes. A series of kinetic models, which included the influence of diffusive transport, were developed for both γ and α radiolytic processes by Christensen et al. [32] and Christensen [33], and a similar approach was adopted by Poulesquen and Jegou [34]. Since kinetic information for the reaction of radiolysis products with the fuel surface was unavailable, these models assumed that the heterogeneous reactions could be mimicked by an equivalent series of homogeneous reactions occurring within a thin layer of solution at the fuel surface. A mixed potential model based on electrochemical parameters for fuel corrosion was also developed [35,36]. This model included an attempt to model both the corrosion of the fuel and the steel vessel as well as a range of additional homogeneous redox reactions and adsorption/desorption/precipitation processes. The model also included reactions occurring on noble metal particles but not the influence of H_2. Jonsson et al. [37] developed a comprehensive model which integrated the available kinetic data and tried to account for the geometrical distribution of radiation dose rate and the effects of the oxidant scavengers Fe^{2+} and H_2, fuel burn up, and ground water chemistry. The maximum rate of spent fuel dissolution under Swedish repository conditions was calculated and it was concluded that a H_2 pressure of 0.1 bar (78 μmol L^{-1}) would be sufficient to completely suppress the corrosion of 100-year old LWR fuel even if the influence of Fe^{2+} was neglected. When the expected [Fe^{2+}] in a Swedish repository (∼36 μmol L^{-1}) was included, its effect and that of the radiolytically produced H_2 alone were calculated to be sufficient to effectively inhibit fuel corrosion.

These studies have revealed many of the key features required in models for the radiolytic corrosion of spent fuel. The spatial distribution of radiolytic species is of particular importance for α-radiolysis since all the α-particle energy is deposited within a few tens of micrometers of the fuel/solution interface. Consequently, mass transport becomes important in coupling the homogeneous aqueous reactions and heterogeneous processes involved. This is especially important if the influence of container corrosion products, Fe^{2+} and H_2, on the redox conditions at the fuel surface are to be quantitatively modelled.

Previously [38], a preliminary model, involving a series of homogeneous and heterogeneous reactions, was developed to determine the influence of redox conditions on the radiolytic corrosion of spent fuel. The model also attempted to account rudimentarily for the separation of the two corroding interfaces at the fuel and the steel vessel surfaces. Consistent with the claims of Jonsson et al. [37], the model predicted that the corrosion of UO_2 could be suppressed by the steel corrosion products, Fe^{2+} and, in particular, H_2.

However, this model contained many approximations and limitations and has been improved in a number of ways: (i) A complete set of α-radiolytic reactions has been included. Previously, the α-radiolysis process was simplified with H_2O_2 considered the only radiolysis product. Inclusion of a full reaction set allows this simplification to be evaluated; (ii) A less arbitrary approach to account for the decomposition of radiolytically-produced H_2O_2 has been adopted, since this process appears to be the major route for H_2O_2 consumption on a UO_2 surface [10,39]; (iii) An attempt to incorporate the influence of fuel burnup is included, since burnup will not only influence the dose rate but also affect the surface reactivity of the fuel [40]; (iv) Instead of treating the oxidative dissolution (corrosion) of UO_2 as a general surface reaction, an attempt is made to take into account anodic dissolution supported by H_2O_2 reduction on both the UO_2 and noble metal particle surfaces, the latter being a product of the in-reactor fission process; and (v) the reactions between H_2 and H_2O_2 and between H_2 and UO_2^{2+} catalyzed on noble metal particles have been added. As in the previous model it is assumed that the groundwater contains sufficient carbonate/bicarbonate and any formation of corrosion product deposits is omitted, thus making the predicted dissolution rate conservative.

Presently, as is the case with other models, our model is 1-dimensional and considers only the corrosion of a planar fuel surface. However, this is a precursor for the eventual development of 2-D and 3-D models involving customized geometry to account for the fractured nature of the spent fuel and the complex fuel bundle geometry. Within such structures the local accumulation of radiolysis species is likely to occur and externally produced Fe^{2+} and H_2 may have limited access to reactive locations within fractures, porous grain boundaries and fuel bundles. Such geometric effects are expected to have a significant influence on the overall ability of container corrosion products to influence fuel corrosion and radionuclide release.

2. Model description

During in-reactor irradiation, the UO_2 fuel pellet undergoes a number of compositional changes involving the formation of rare earth (RE^{III}) elements and noble metal (ε) particles [8,38]. From a corrosion perspective, the fuel can be considered as a conductive (RE^{III}-doped) and chemically reactive matrix containing ε-particles which could act as either cathodes or anodes depending on the prevailing solution redox conditions. The reaction set used to describe the fuel corrosion process is modified compared to that used previously, as numbered and illustrated in Fig. 1. The current model includes: (1) a complete reaction set for the α-radiolysis of water including the generation of, and the interactions between, the radiolysis products; (2) the oxidative dissolution (corrosion) of UO_2 supported by H_2O_2 reduction on both the UO_2 surface (reaction 2a) and noble metal particles (reaction 2b); (3) the reduction of oxidized surface species (U^V/U^{VI}) by H_2 oxidation on noble metal particles (reaction 3a) and of dissolved UO_2^{2+} either by reaction with H_2 in solution (reaction 3b) or with H_2 catalyzed on the fuel surface (reaction 3c); (4) the reaction of H_2O_2 with H_2 catalyzed by noble metal particles; (5) the scavenging of H_2O_2 in homogeneous solution by reaction with Fe^{2+}; and (6) the decomposition of H_2O_2 to O_2 and H_2O (not shown in Fig. 1). In the model the rates of these processes are described by a series of one dimensional diffusion–reaction equations as described previously [38] .

2.1. Water radiolysis

Since it is reasonable to assume containment preventing contact of the fuel with groundwater will be maintained over the period when γ/β radiation fields are significant (a few hundred years), only α-radiolysis is considered as a source of oxidants [6]. The penetration depth of α-particles emitted by spent fuel into water is very short and a high concentration of radiolysis species is expected at the fuel/water interface. Due to the fractured nature of spent fuel, the accumulation of aqueous radiolysis species may occur locally within cracks, fission gas tunnels and porous grain boundaries. These features are not considered in this model which focuses on the general corrosion of a uniform fuel surface.

A range of studies have calculated the dose rate profiles of α-radiation for different types of fuels using different approaches [41–44]. The α dose rate in water in contact with a spent fuel