

Modeling the Radiolysis Effect on CSNF Dissolution Kinetics

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INTRODUCTION

It has often been assumed that radiolysis of water will have a minimal effect on the dissolution of commercial spent nuclear fuel (CSNF) under oxidizing conditions. This may be true after long times, such as when the majority of the ^{137}Cs and ^{90}Sr have decayed and reduced the dose from the fuel by three to four orders of magnitude. However, for fresh CSNF as used by researchers internationally to determine dissolution rates, the radiolytic contribution may be significant enough to increase the dissolution rate by two orders of magnitude over air-saturated conditions alone. [1] The objective of this work is to provide a quantitative estimate of the radiolytic products produced and determine the effect on UO_2 and CSNF dissolution rates.

DESCRIPTION OF THE ACTUAL WORK

Previous work has been performed to develop a detailed model showing the dose from CSNF to water as a function of type of radiation, fuel particle size (surface to volume ratio), and fuel-to-water ratio. [2] A second model is being developed following the methodology of Pastina and LaVerne [3] that shows the effect this calculated dose has on water chemistry.

The initial model accounted for 16 chemical species (e.g., H^+ , H_2O_2 , O_2^- , OH) formed by radiolysis of water in the absence of any carbonate species. The concentration of each species is determined first by establishing their formation as a function of dose and the applicable G-values. Next, the concentrations as a function of time are calculated by solving 16 simultaneous differential equations that include 79 chemical reactions among those species. A FORTRAN program using ODEPACK [4] was written to solve the differential equations and calculate the concentrations for each species as a function of time.

Comparison of the results from the initial model with those of Pastina and LaVerne [3] showed excellent reproducibility. The model is currently being expanded to include carbonate species, which are significant in most groundwaters that may react with CSNF in geologic repositories, and reactions of each species (if the rate constant is known) with aqueous UO_2^{2+} . Continued development of the model will include temperature dependence, important especially for thermal

decomposition of H_2O_2 , and interactions of each species with the CSNF matrix.

Single-pass flow-through (SPFT) tests are being run to measure the dissolution rate of UO_2 doped with various quantities of ^{90}Sr to replicate the β dose from CSNF of various burnups and different decay times. In addition to determining the dissolution rate, the effect of radiolysis, matrix chemistry, surface area to volume ratio, and carbonate are being investigated. The goal is to combine the model and experimental work to develop an understanding of CSNF dissolution and how the rate will change as the dose decreases due to radioactive decay.

RESULTS

The model predicts the chemistry of the aqueous solution around the fuel given the dose for the conditions modeled by Miller et al. [2] Since the SPFT tests on CSNF typically use grain-size particles to eliminate the contribution from gap and grain boundary inventories, the dose for this scenario was used for this work. The results generated by the current model (without carbonate reactions or species) for the dose to water from CSNF with a burnup of 41,200 MWd/t and a 23 year decay time are shown in Figure 1.

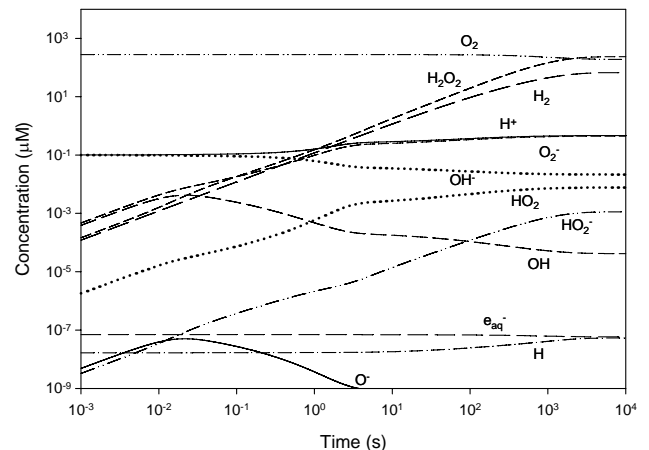


Fig. 1. 23 year old CSNF (41,200 MWd/t) with an α dose of 1700 Gy/hr and a β/γ dose of 4800 Gy/hr.

The results using the dose to water from the same sized individual grains of unirradiated UO_2 are shown in Figure 2. In both cases, the initial dissolved O_2 concentration is calculated as the concentration of O_2 in water in equilibrium with air having $p\text{O}_2=0.2$ atm. The concentration of H_2O_2 at 10^4 seconds for the fresh CSNF case is greater than 3 orders of magnitude higher than for the unirradiated UO_2 case. Similarly, the concentration of both OH and O_2^- are more than 2 orders of magnitude greater for the CSNF case. As shown in previous research these oxidizing species are major contributors to spent fuel dissolution. [5] It is clear that even under oxidizing conditions, the effect of radiolysis on production of other highly oxidizing radicals and molecules is significant for fresh CSNF. Given the effect these species have on fuel dissolution, [1,5] it is highly likely that the dissolution rate of CSNF 300 to 400 years from now when the ^{137}Cs and ^{90}Sr have decayed will be significantly less than presently modeled.

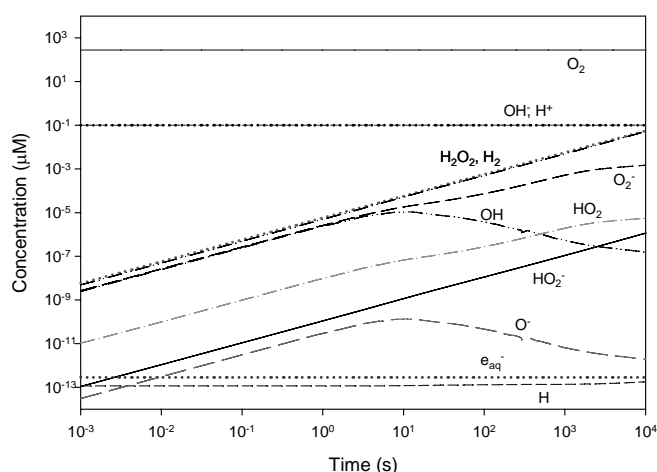


Fig. 2. Unirradiated UO_2 grains with an α dose of 0.163 Gy/hr and a β/γ dose of 0.0108 Gy/hr.

ACKNOWLEDGEMENTS

The research was performed under appointment of the Office of Civilian Radioactive Waste Management Graduate Fellowship Program administered by Oak Ridge Institute for Science and Education under a contract between the U.S. Department of Energy and the Oak Ridge Associated Universities.

This work was sponsored in part through the Source Term Strategic Thrust Area of the Office of Science and Technology and International within the U.S. Department of Energy Office of Civilian Radioactive Waste Management.

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