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A multiphase interfacial model for the dissolution of spent nuclear fuel

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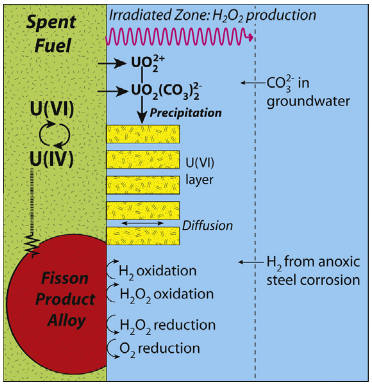
HIGHLIGHTS

- This model accounts for chemistry, temperature, radiolysis, U(VI) minerals, and hydrogen effect.
- The hydrogen effect dominates processes determining spent fuel dissolution rate.
- The hydrogen effect protects uranium oxide spent fuel from oxidative dissolution.

GRAPHICAL ABSTRACT



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ABSTRACT

The Fuel Matrix Dissolution Model (FMDM) is an electrochemical reaction/diffusion model for the dissolution of spent uranium oxide fuel. The model was developed to provide radionuclide source terms for use in performance assessment calculations for various types of geologic repositories. It is based on mixed potential theory and consists of a two-phase fuel surface made up of UO_2 and a noble metal bearing fission product phase in contact with groundwater. The corrosion potential at the surface of the dissolving fuel is calculated by balancing cathodic and anodic reactions occurring at the solution interfaces with UO_2 and NMP surfaces. Dissolved oxygen and hydrogen peroxide generated by radiolysis of the groundwater are the major oxidizing agents that promote fuel dissolution. Several reactions occurring on noble metal alloy surfaces are electrically coupled to the UO_2 and can catalyze or inhibit oxidative dissolution of the fuel. The most important of these is the oxidation of hydrogen, which counteracts the effects of oxidants (primarily H_2O_2 and O_2). Inclusion of this reaction greatly decreases the oxidation of U(IV) and slows fuel dissolution significantly. In addition to radiolytic hydrogen, large quantities of hydrogen can be produced by the anoxic corrosion of steel structures within and near the fuel waste package.

The model accurately predicts key experimental trends seen in literature data, the most important being the dramatic depression of the fuel dissolution rate by the presence of dissolved hydrogen at even relatively low concentrations (e.g., less than 1 mM). This hydrogen effect counteracts oxidation reactions and can limit fuel degradation to chemical dissolution, which results in radionuclide source term values that are four or five orders of magnitude lower than when oxidative dissolution processes are operative. This paper presents the scientific basis of the model, the approach for modeling used fuel in a disposal system, and preliminary calculations to demonstrate the application and value of the model.

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1. Introduction

The geologic disposal of nuclear wastes utilizes multiple natural and engineered barriers to isolate radionuclides from the biosphere. The nuclear waste form is the core barrier to radionuclide mobilization, as its dissolution rate will determine the radionuclide source terms for near- and far-field transport calculations.

Of particular importance to current nuclear waste management strategies are the large inventories of used uranium oxide fuel from power plants. For example, in the U.S. there is approximately 23 billion curies of long-lived radioactivity in commercial used oxide fuel stored at 75 sites in 33 states [1]. The direct disposal of existing inventories of used oxide fuel in geologic repositories is a primary waste management strategy throughout the global community [2,3]. Used fuel destined for direct disposal in a repository is referred to as "spent fuel" in this paper.

A number of process-oriented models that can be used to calculate the radionuclide source term in a geologic repository have been developed and tested against experimental data. For example, five models quantifying the dissolution behavior of the spent fuel matrix were selected for comparison to a central experimental data base as part of the European Commission MICADO project on quantifying model uncertainties [4]. These models included: (1) the matrix alteration model (MAM), which was developed as part of the European Union Spent Fuel Stability project, and accounts for water radiolysis, solution chemistry and surface complexation kinetics, (2) a model developed by KTH Royal Institute of Technology, Sweden that accounts for water radiolysis, diffusion and homogeneous kinetics at the spent fuel surface, (3) a model developed by SUBATECH, Ecole des Mines de Nantes, France, which also accounts for water radiolysis and diffusion, but deals with interfacial reactions using electrochemistry rather than surface complexation, (4) a model developed by CEA, France, which accounts for oxidizing radiolytic species produced near the fuel surface, but neglects reducing species and the recombination of radicals, and (5) another CEA model consisting of a complete radiolytic model and accounts for dose rate gradients and diffusion similar to the SUBATECH model [4–10]. Additionally, there is the well-established Mixed Potential Model (MPM) developed as part of Canadian repository program [11–15]. The MPM accounts for radiolytic hydrogen peroxide generation, diffusion, the role of secondary phases and describes interfacial reactions at the fuel surface using mixed potential theory [12].

One of the key results from these previous experimental and modeling studies has been that the dissolution rate of spent fuel can be strongly influenced by the so-called "hydrogen effect" (e.g., [4–10,16–31]). This term refers to the dramatic decrease in the dissolution rates of spent fuel and simulated fuels observed when tests are performed with various concentrations of dissolved hydrogen (e.g., [4–10], [16–31]). As will be discussed below, the hydrogen effect can dominate all the other processes affecting spent fuel dissolution.

Since hydrogen has been shown to decrease fuel dissolution rates, it is conservative to neglect this effect in source term models. However, based on the large amount of experimental data demonstrating the importance of this effect [16–31], ignoring the role hydrogen may prove to be overly conservative and unrealistic for some repository scenarios. Of the models mentioned above, three account for role of hydrogen in determining the dissolution rate of the fuel [4]: the MAM accounts for the hydrogen effect as homogeneous reactions in solution [6], the SUBATECH model accounts for hydrogen through its electrochemical effects at the fuel surface [4], and the KTH model contains catalytic reaction sites for hydrogen, which are associated with the fission product alloy phase (epsilon phase) present on the fuel surface [9].

In this report we discuss the development of a new spent fuel dissolution model that is based on the Canadian MPM of Shoesmith and King [11] and King and Kolar [12–14]. This new model, referred to as the Fuel Matrix Dissolution Model (FMDM), was first described by Frey and Jerden [32,33] and was developed based on fundamental principles to quantify the effects of dose rate, temperature, and important chemical species on spent fuel dissolution rates. As discussed below, the FMDM accounts for hydrogen reactions by quantifying their effects on the electrochemical corrosion potential of the fuel. This is accomplished by including hydrogen reactions on both the UO_2 fuel grains and the noble metal fission product alloy particles also referred to as the epsilon phase or noble metal particles (NMP).

The FMDM is being developed as part of the U.S. Department of Energy (DOE), Used Fuel Disposition Program (UFD). The initial version of the model has been integrated into the UFD program's generic repository performance analysis framework to facilitate further development of the FMDM as a science-based, source term model [34].

Since the FMDM is based on fundamental thermodynamic and electrochemical principles, it can be applied to a diverse range of geologic and engineered environments, provided the pertinent redox reactions and rate parameter values are included. This paper presents FMDM results for redox reactions and environmental conditions expected for clay/shale and crystalline rock repositories.

2. Model development and implementation

2.1. Thermodynamic basis

Radionuclides in spent fuel can be defined in terms of two inventory fractions: (1) the gap and grain boundary fraction, which is often assumed to become available for transport instantaneously when the fuel is contacted by groundwater, and (2) a matrix fraction, which becomes available for transport at the same fractional rate that the fuel dissolves. The FMDM calculates the fuel dissolution rate that controls the release of radionuclides in the matrix fraction. An instant release fraction model is used to calculate release of radionuclides in the gap and grain boundary fraction. The two models are coupled through the area of the matrix and grain boundaries that are contacted by groundwater over time. The releases calculated by the two models are combined to provide radionuclide source terms that can be used in performance assessment calculations [34].

In the absence of oxidants, uranium dioxide spent fuel is sparingly soluble, and the dissolution rate is low. When oxidants are present, fuel matrix degradation proceeds by a faster oxidative dissolution mechanism. The oxidative dissolution of spent fuel has been measured to be approximately four orders of magnitude higher than chemical dissolution in relatively dilute, near-neutral aqueous solutions [35]. The primary value calculated in the MPM and FMDM is the corrosion potential at the fuel surface that is established by the contributing redox reactions. The value of the corrosion potential is used to determine if the matrix dissolves by oxidative dissolution in addition to chemical dissolution.

The FMDM accounts for both oxidative and chemical dissolution and determines which is operative based on the surface potential. The reactions used in the FMDM to quantify the oxidative and chemical dissolution processes are shown in Table 1 (reactions A and L). These include reactions affecting the dissolved hydrogen concentration that are not included in the MPM. Figs. 1 and 2 provide part of the thermodynamic basis for the FMDM and were plotted using the program "the Geochemist's Workbench" (GWB) [36], with the thermochemical database "data0.ymp.R5" [37].