USED-FUEL DISSOLUTION STUDIES IN CANADA

L.H. Johnson, N.C. Garisto and S. Stroes-Gascoyne
Atomic Energy of Canada Limited
Whiteshell Nuclear Research Establishment
Pinawa, Manitoba, Canada ROE 1LO

ABSTRACT

Studies of the release of radionuclides from used UO_2 fuel are reviewed, and their relevance to the radionuclide release model used in the performance assessment of used-fuel disposal in Canada is discussed. The model describes two processes. The first is the rapid leaching of a small percentage of the inventory of specific fission products, such as Cs-135 and I-129, from the fuel-sheath gap and UO_2 grain boundaries upon contact with groundwater. This is followed by a slow, uranium-solubility-controlled dissolution of the UO_2 grains. The data on fission-product release in leaching experiments are reviewed, indicating how the instant-release term has been derived. Studies of used-fuel and UO_2 dissolution, including α-radiolysis experiments, are being performed to provide supporting data for the solubility-controlled dissolution mechanism. These studies are reviewed and their role in establishing the range of redox conditions within which the solubility-controlled dissolution model may be applied is discussed.

INTRODUCTION

The environmental and safety assessment of used nuclear fuel disposal in an underground vault requires information on the mechanisms and rates of release of radionuclides from used-fuel bundles after groundwater breaches the containers and the fuel cladding, and contacts the used fuel[1,2]. In the Canadian Nuclear Fuel Waste Management Program, the assessment is being carried out using the probabilistic safety assessment code, SYVAC: Systems Variability Analysis Code[3,4,5]. The objective of the used-fuel and UO_2 dissolution studies described in this paper is to supply SYVAC with source-term models for the release of radionuclides from used fuel, and with associated data, in the form of input parameter distribution functions that take uncertainty and variability into account[6]. These studies include leaching and dissolution experiments on used CANDU fuel, as well as fundamental investigations of UO_2 electrochemical behavior for a range of solution chemistry conditions, in both the presence and absence of radiation fields.

THE RADIONUCLIDE RELEASE MODEL

The release of radionuclides from used fuel, and their subsequent migration through buffer material and into the geosphere, are represented in SYVAC by one-dimensional transport equations, which take into account diffusion, convection, sorption, radioactive decay and buildup[1,2]. The boundary conditions for these equations at the waste-container/buffer interface (the source boundary conditions) depend on the mechanism of release of radionuclides from the used fuel.

Two different boundary conditions, representing two release modes that operate on very different time scales, are used in the release model:

(i) An instant release of a fraction of the inventory of some radionuclides, upon container failure and contact of the fuel by groundwater[6,7].

(ii) A slow, solubility-controlled, congruent release of radionuclides due to the dissolution of the fuel matrix itself[6,8]. For this release mode, the uranium concentration at the waste-container/buffer interface is assumed to be constant and equal to the solubility of uranium under the expected vault conditions (i.e., a constant concentration boundary condition). The solution of the transport equations with this boundary condition can be used to calculate the used-fuel dissolution rate. The rate at which a particular radionuclide is released from the used fuel, the so-called solubility-controlled source term, is then given by the product of the used-fuel dissolution rate and the fractional abundance of the radionuclide in the used fuel. The validity of the solubility-controlled dissolution model depends on the groundwater flow rate in the vault, and on the chemical stability of UO_2 and its exact dissolution mechanism under the geochemical conditions existing in the vault[8,9].

Our experimental programs to determine the input parameter distributions for this radionuclide release model are described in the following sections.

FISSION-PRODUCT LEACHING

Rapid release of a small fraction of the inventory of fission products, such as Cs-137 and I-129, is observed upon exposure of used fuel to water[10]. The total fractional release of these radionuclides within the first few days of leaching has been estimated from correlations with the stable xenon release during in-reactor irradiation[11]. The quantity available for rapid release upon breaching of the fuel sheath is referred to as the gap inventory. The relationship between the stable xenon and Cs-137 and I-129 gap inventories is shown in Fig. 1.

Following the initial rapid leaching of the gap inventory, fission-product release rates decrease gradually until the majority of the fission products are released in conjunction with the dissolution of the uranium. This transition occurs over a period of weeks to months, depending on the fuel power history. In many cases, Cs-137 fractional release rates remain 3 to 5 times higher than those of other radionuclides. This is also likely to be true for I-129, although no data are available beyond the first few days of

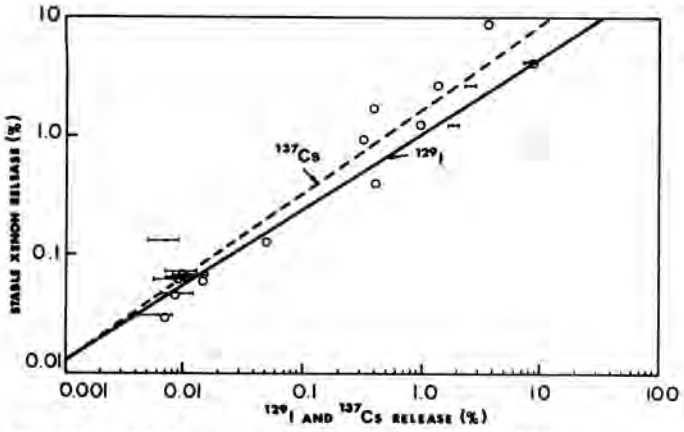

Fig. 1. Relationship between measured stable xenon release and I-129 release and CS-137 release during leaching at 25°C.

leaching. In certain cases, such as for fuel with high linear-power ratings, for which leaching data are shown in Fig. 2, the fractional release rate of Cs-137 remains two orders of magnitude higher than that of the uranium, even after seven years. This is thought to be indicative of fission-product removal by grain-boundary leaching. Other evidence for leaching of grain boundaries is discussed by Johnson et al.[11] It is clear that it is not yet possible to determine when the leaching of the gap inventory is complete and when the grain-boundary leaching mechanism becomes dominant, nor is it known how long the latter will continue to dominate fission-product release kinetics.

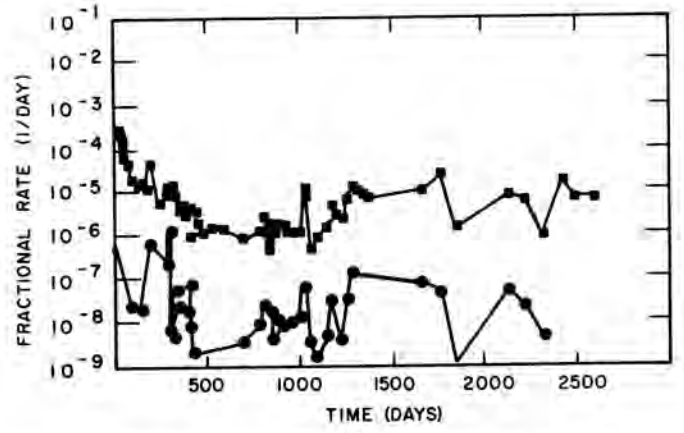

Fig. 2. Fractional release rate of Cs-137 (■) and uranium (●) from used fuel in air-saturated distilled water at 25°C.

It is not surprising that the gap and grain-boundary release contributions cannot be effectively separated, since they are linked together in terms of the diffusion, grain-growth and gas-bubble formation mechanisms that influence their location in the fuel after irradiation. As fission-gas bubbles accumulate at grain boundaries, they eventually join to form tunnels. When these tunnels intersect a crack, the gas is released to the fuel-sheath gap. Whether or not the cesium and iodine in these interconnected bubbles move physically into the gap by volatilization, they are available for release upon penetration of the fuel sheath by groundwater. This *release may take* several days, or possibly more, since water must percolate through grain-boundary tunnels with diameters of approximately 1 μm[12] in order to dissolve fission-product deposits. At the same time, grain boundaries that are not yet connected to the gap are attacked by the groundwater, initiating the release of fission products associated with closed porosity.

Because grain-boundary leaching has been shown to be important on the time frame of laboratory experiments, it seems reasonable that the gap and grain-boundary inventories should be combined to give a single release parameter, which is referred to as the instant-release fraction. A parameter distribution function describing the instant-release fraction for the radionuclides Cs-137, Cs-135, I-129 and Se-79 has been derived by Johnson and Joling[7]. A maximum value of 10% is assumed, with the most probable release fraction being 2.2%.

Studies are underway to determine the kinetics of grain-boundary leaching under a variety of conditions, and to establish whether other radionuclides are released by this mechanism at a rate greater than the overall dissolution rate of the UO_2 grains.

A qualitative picture of how the release of fission products such as Cs-137, Cs-135 and I-129 may proceed is shown in Fig. 3. The diagram is based on data obtained from a large number of experiments. Although the final dissolution rate of $\sim 10^{-7}$ d^{-1} is similar to that observed in experiments with CANDU and light-water-reactor fuel, the gap and grain-boundary release curves are only approximate, and may vary greatly depending on the fuel microstructure. Control of fission-product and actinide releases by dissolution of the UO_2 grains is discussed in the next section.

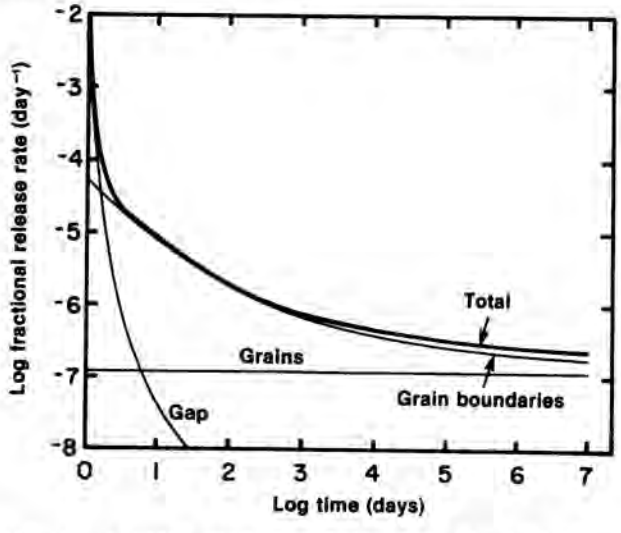

Fig. 3. Fission-product release from UO_2 fuel in water, oxidizing conditions.

SOLUBILITY-CONTROLLED DISSOLUTION

The principal controlling factor in the release of radionuclides from used fuel is expected to be the rate of dissolution of UO_2, since >90% of the radionuclide inventory is contained within the UO_2 grains. Under conditions where UO_2 is thermodynamically stable, it is assumed in the fuel-dissolution model that the rate of release of a specific radionuclide is proportional to the product of the uranium release rate (which is controlled by the uranium solubility) and the fractional abundance of that radionuclide in the UO_2 grains.

It should be emphasized that the release of radionuclides from used fuel may not be limited by uranium solubility if UO_2 is not a thermodynamically stable solid under vault conditions[8,9]. For example, the formation of uranium solids that proceeds through an initial UO_2 dissolution step could invalidate the concept of a solubility-controlled, radionuclide release rate. It is therefore necessary to know the effects of groundwater chemistry and groundwater radiolysis on the stability of the used-fuel matrix.

A variety of studies are in progress to determine the effects of redox chemistry and radiolysis on UO_2 and used-fuel dissolution. Because of the large difference between the solubility of uranium under oxidizing and reducing conditions, a difference of several orders of magnitude between the dissolution rates under these two conditions might reasonably be expected. This has not been observed in used-fuel dissolution experiments, probably due to the importance of grain-boundary leaching in short-term experiments, and to difficulties in controlling redox conditions. Fission-product release from used fuel under reducing conditions is being measured in an effort to clarify the role of redox chemistry in used-fuel dissolution.

A complicating factor in used-fuel dissolution is radiolysis, caused by the emission of α-particles from the fuel surface. This may lead to oxidative dissolution under disposal conditions, rendering the solubility-controlled model based on UO_2 stability invalid. However, electrochemical and X-ray photoelectron spectroscopic (XPS) studies[13] indicate that although UO_2 is rapidly oxidized in oxygenated water through the sequence $UO_2 \rightarrow UO_{2+x} \rightarrow UO_{2.25} \rightarrow UO_{2.33}$, no significant dissolution occurs until a composition close to $UO_{2.33}$ is reached. This suggests that a solubility model may be applied to the dissolution of used fuel in a disposal vault, if it can be shown that under these conditions oxidation does not proceed beyond a composition of $UO_{2.25}$[14,15].

Studies of the effects of α-radiolysis of water on the oxidation of UO_2 are being undertaken to provide information on the applicability of the solubility-controlled dissolution model for used fuel. Preliminary electrochemical studies at room temperature[16] indicate that the corrosion potential of a UO_2 electrode in deoxygenated water increases to the value observed in oxygenated water when the electrode is placed adjacent to a water film undergoing α-radiolysis at a rate approximately fifty times greater than that produced by a used-fuel surface. Whether the lower radiolysis rate produced by used fuel can produce significant oxidation is not known.

Calculations suggest that the production of hydrogen peroxide, due to α-radiolysis of groundwater by used fuel, may occur at a rate sufficient to maintain oxidizing conditions at the fuel/water interface for tens of thousands of years[17,18]. Implicit in these calculations are certain assumptions that are of crucial importance in the evaluation of whether or not α-radiolysis will result in sufficient oxidation of used fuel to negate the application of the UO_2 solubility model. One assumption is that the hydrogen produced by radiolysis will not reduce the oxidized film on UO_2, thus counteracting the oxidative effect of the H_2O_2[2]. The actual situation will depend on the relative kinetics of the oxidation and reduction reactions, which must be established for the specific disposal conditions. There are indications that oxidation of UO_2 by H_2O_2 is much more rapid than reduction of U(VI) solution species or oxidized UO_{2+x} surfaces by hydrogen[16,19]. A second assumption is that recombination of H_2 and H_2O_2 is negligible. Calculations suggest that β-radiolysis should catalyze recombination to some degree[20], and it is likely that metal and metal-oxide surfaces will also have the same effect. Finally, the effect of groundwater species that will consume H_2O_2, thus protecting the UO_2 from oxidation, may be important. For example, the provision of a Fe^{2+} source, either within the used-fuel container, or in the surrounding buffer material, may be a suitable method of minimizing the overall impact of radiolysis.

The effects of groundwater chemistry and α-particle dose rate on UO_2 oxidation are being investigated using electrochemical and XPS techniques. Particular emphasis will be placed on studies using α-particle dose rates similar to those produced by used fuel, in the presence and absence of groundwater constituents, such as Cl^- and Fe^{2+}.

CONCLUSIONS

The framework for modelling the release of radionuclides from used fuel has been developed and is now well-established. This framework enables the incorporation of the results of detailed leaching and dissolution experiments into the SYVAC assessment code used for estimating the potential environmental impact of used-fuel disposal in a geological waste-disposal vault. The experiments indicate which release mechanisms should be considered in the model and provide quantitative data for the assessment. This is an ongoing process; the data derived from the experimental studies is being continuously updated as more results become available.

At present the model consists of (i) an instant-release source term that accounts for both the gap and grain-boundary releases and (ii) a solubility-controlled source term representing release due to the dissolution of the fuel matrix. The experimental research program offers some support for this model.

To improve our understanding of radionuclide release from used fuel, it is important to focus further effort on several key areas; in particular: radionuclide release under reducing conditions, the effects of α-radiolysis, and the effects of groundwater composition (e.g., Cl^-, Fe^{2+} concentrations) on radionuclide release. These studies will provide data on radionuclide release under the expected vault conditions and will lead to the development of methods to mitigate the effects of radiolysis by controlling the near-field redox conditions.

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