

SOURCE TERM MODELS FOR THE ASSESSMENT OF NUCLEAR FUEL WASTE

DISPOSAL IN CANADA

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ABSTRACT

Models for the release of radionuclides from nuclear fuel wastes are described, and their relevance to the performance assessment of high-level waste disposal concepts is discussed. The experimental basis for the models is outlined, and the geochemical conditions controlling the release of radionuclides from nuclear fuel wastes are analyzed. Both used fuel and vitrified fuel recycle wastes are discussed.

INTRODUCTION

The Canadian concept for nuclear fuel waste disposal is based on immobilization of the waste, followed by its emplacement in a vault, deep underground, in stable plutonic rock¹. Two options are being considered: (i) direct disposal of intact, used CANDU fuel and (ii) disposal of wastes that would arise from reprocessing this fuel. Laboratory and field experiments are being carried out to evaluate the feasibility of the geological disposal concept, by identifying the main processes that may influence the environmental impact of a nuclear fuel waste disposal vault. The major disposal features being evaluated are (i) the durability of the waste forms, (ii) the corrosion resistance of the waste containers and (iii) the isolation and retardation capabilities of the buffer materials placed around the containers and of the massive geological formation².

The environmental assessment of nuclear fuel waste disposal involves assimilation of the laboratory and field data accumulated in these studies, to produce an estimate of the potential impact of a disposal vault on man and the environment^{3,4}. In this paper, we briefly outline the assessment methodology and expand upon one aspect of the data assimilation process, namely, the incorporation of radionuclide release mechanisms in the assessment.

THE ASSESSMENT METHODOLOGY

The computer program SYVAC (Systems Variability Analysis Code) has been developed in Canada for the environmental and safety assessment of nuclear fuel waste disposal concepts^{5,6}. SYVAC contains modules representing submodels for the vault, the geosphere (i.e., the massive rock formation surrounding the vault) and the biosphere (i.e., the environment accessible to man in every day life)⁴.

The SYVAC vault submodel represents the container failure, the release of radionuclides from the waste forms, and the transport of radionuclides into the geosphere. The geosphere submodel represents migration from the vault to the biosphere. The biosphere submodel determines concentrations of radionuclides in the biosphere and calculates the dose consequence due to these radionuclides. The geosphere and biosphere submodels of SYVAC will not be discussed further in this paper.

The two distinctive features of the SYVAC assessment method are:

- (i) The solution of the transport equations is based on generating response functions for each of the submodel modules as a function of the input parameters. The associated convolution integral then gives the output from a module for a given input. This procedure enables easy linkage of the modules into a total system assessment code and allows for a high degree of flexibility in the submodels (e.g., in the waste-form release models) that can be incorporated in SYVAC.
- (ii) SYVAC specifically addresses the problem of parameter variability and uncertainty associated with long-term assessments. Sources of uncertainty include errors in measuring parameter values and extrapolating them in space and time, as well as approximations made in deriving the mathematical models used to describe the real system. All this is taken into account by representing the parameters as distributions rather than as single values. Values sampled for each parameter from their distributions characterize a possible initial state of the system, and define a release scenario. Repeated random sampling of scenarios and estimation of consequence result in a histogram of frequency of occurrence versus the consequence estimate⁷. The main consequence calculated is the maximum annual effective radiation dose to an individual within a specified time. Other possible consequences, such as the potential impact of toxic elements (associated with nuclear fuel wastes) that will be in the disposal vault, are being considered as well¹⁰. A subsequent sensitivity analysis, i.e., a calculation of the effect of changes in the values of input parameters on the resulting consequence, assists in identifying important parameters and processes, and indicates where further research is required.

SOURCE TERMS AND THE SYVAC VAULT SUBMODEL

Radionuclide transport through the buffer is modelled in the SYVAC vault submodel by a one-dimensional, convection-diffusion equation, which takes into account sorption and radioactive decay and buildup⁸. This transport equation is subject to initial conditions, and boundary conditions at the container/buffer interface (i.e., source boundary condition) and at the buffer/geosphere interface (i.e., exit boundary condition).

The initial conditions are approximated by zero concentrations in the buffer, for all radionuclides.

The source boundary condition determines the rate of release of radionuclides from the waste-form. It provides the only coupling between detailed waste-form dissolution and leaching experiments and the environmental assessment. Hence, modelling of radionuclide release from used fuel and from high-level vitrified wastes simply involves definition of source boundary conditions for solving the transport equations in the buffer. The response function method, used in SYVAC for solving the transport equations, allows SYVAC to handle a wide variety of source boundary conditions, including time-dependent flux and concentration boundary conditions.

The exit boundary condition couples transport in the buffer to transport in the geosphere. Its physico-chemical significance is discussed in Refs. [7,11] and is beyond the scope of the present paper.

The solution of the transport equations gives the flux of radionuclides in the buffer as a function of time. We refer to the radionuclide flux at the waste form/buffer interface as the "source term".

THE BASIC GEOCHEMICAL PARAMETERS FOR THE VAULT

The processes represented by the vault submodel all depend, to some degree, on the geochemical conditions in the vault. Independent, random sampling of parameters, representing container failure time, radionuclide release rates and sorption coefficients, does not fully express this correlated dependence. However, the dependence of the vault processes on the geochemical conditions can be accounted for by using the following procedure:

- (i) define the major geochemical parameters (if any) controlling each process, e.g., pH, T, etc.,
- (ii) provide parameter distribution functions for these basic geochemical parameters, under the expected vault conditions, and
- (iii) derive models expressing the functional dependence of the vault processes on these parameters.

An example of this procedure is shown below for the used-fuel dissolution model. This model consists of two components (see discussion in the next section): (i) short-term release, which does not depend strongly on the geochemical conditions, and (ii) long-term release, which is largely controlled by the solubility of the UO_2 matrix and is, therefore, strongly dependent on the geochemical conditions in the vault: the temperature, pH and redox potential of the groundwater, as well as on the groundwater composition^{12,13}.

Temperature

The temperature in the vault will depend on the history of the used fuel, the emplacement geometry of the used-fuel containers, and the time after emplacement. Present vault design studies assume a maximum temperature at the container/buffer interface of $100^\circ C$ ¹⁴. However, the solubility of UO_2 has been studied as a function of temperature for a wider temperature range: $25-200^\circ C$ ¹⁵.

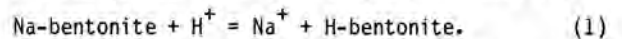
pH

The exact value of the pH, redox potential and groundwater composition in the vault will depend on the nature of the geological formation in which the vault is built.

An estimate of the probable range of pH values can

be obtained from analyses of deep groundwaters. The pH values of deep groundwaters typically fall in the neutral to slightly basic pH range^{16,17}. Although the pH of groundwater in the vault could increase by¹⁸ interaction with concrete or cement-based grouts, it is expected to stay within the neutral to slightly basic range, due to the dominant effect of bentonite-based buffer materials in controlling the near-field pH¹⁹.

Bentonites buffer pH in the mildly basic region, due to exchange reactions involving H^+ , for example,



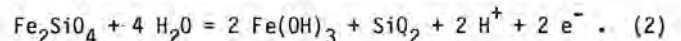
The effect of bentonites on groundwater pH is somewhat weaker in saline groundwaters, where the H^+ exchange is suppressed due to the high cation activity²⁰. In view of all these observations, the near-field pH is assumed to be in the range 5 to 10.

Redox Potential

An exact definition of the near-field redox conditions, in terms of a single redox potential, E, is very difficult to obtain, because aqueous redox systems are often not in equilibrium. Thus, the potentials measured in natural groundwaters are often mixed potentials, which are generally difficult to relate to a single, dominant redox couple^{21,22}. Nevertheless, redox potential is a useful parameter, and an approximate range of E values can be defined for the near-field region. Such a range provides an indication of the redox conditions, keeping in mind the difficulties associated with its interpretation.

Iron-containing minerals in the rocks and buffer materials surrounding the vault are expected to play a major role in controlling the near-field redox conditions. Several Fe^{2+}/Fe^{3+} reactions are also capable of effectively reducing actinides and technetium from high to low oxidation states, where their solubilities are significantly lower than those observed in oxidizing waters^{23,24}. In particular, at elevated temperatures, both kinetic and thermodynamic factors favor oxidation of Fe^{2+} with subsequent crystallization of hematite. The effects of this reaction can be observed in the field, where it leads, for example, to coprecipitation of uraninite and hematite in vein-type uranium deposits²⁵. Consequently, the Fe^{2+}/Fe^{3+} couple is of major interest in used-fuel dissolution and radionuclide migration.

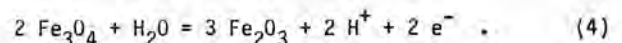
Olivines and oxides are common host materials for iron in igneous rocks. They are also being considered as buffer redox additives²⁶. Iron-rich olivines (e.g., fayalite) participate in redox reactions, such as



The E/pH equilibrium line for reaction (2) is

$$E = B - A \cdot pH . \quad (3)$$

where $B = 0.513 V$ and $A = 0.05916 V$ at $25^\circ C$. Another common redox couple in igneous rocks is the magnetite/hematite couple. Hematite is reduced to magnetite in the following reaction:



Although the magnetite/hematite couple is not likely to be completely reversible at low temperatures, a prolonged contact of deep groundwaters with both minerals tends to bring their E values close to the magnetite/hematite equilibrium redox potential¹⁶. Even the presence of iron silicates tends to establish the

magnetite/hematite redox potential since hydrolysis of silicates yields ferrous hydroxide, which gradually converts to magnetite. Thus, the redox potential of groundwaters in contact with rocks containing magnetite and hematite, or fayalite, is approximated by the magnetite/hematite equilibrium redox potential, i.e., equation (3) with the values of A and B given in Table I.

TABLE I
Redox Parameter Values (V)

Parameter	T ^o C	
	25	100
A	0.05916	0.07404
B(magnetite/hematite)	0.210	0.200
B(UO ₂ /U ₄ O ₉)	0.448	0.411
B(U ₄ O ₉ /U ₃ O ₇)	0.514	0.505

A complicating factor in estimating the near-field E value is radiolysis of water following container failure. Experimental evidence indicates that radiolysis could produce oxidizing conditions, which are detrimental to the performance of the vault. The addition of buffer redox additives may, therefore, be necessary, to maintain reducing conditions and to minimize radionuclide release and transport²⁰.

Preliminary results indicate that the oxidation of UO₂ due to γ -radiolysis²⁷ is suppressed by the presence of the Fe²⁺/Fe³⁺ couple²⁸. A similar effect is expected for α -radiolysis²⁸. However, to allow for some extension of the redox potential range due to radiolysis, we assume that the redox potential in the vault extends from the magnetite/hematite E-pH boundary to the U₄O₉/U₃O₇ boundary (see Table I) and includes the UO₂/U₄O₉ boundary. Thus, the magnitude of B (i.e., the redox potential at a pH of zero) is approximately 0.2 to 0.5 V.

Additional experimental and modelling effort is required to support this choice of redox conditions. Several studies are underway on the oxidative dissolution of UO₂ in the presence of α -radiolysis products²⁹, and others are being planned, in particular: (i) a study of the mechanism of the mitigating effect of the Fe²⁺/Fe³⁺ couple on the effects of radiolysis and the possibility for a catalytic effect of Fe²⁺ on peroxide decomposition, and (ii) a comparison of the rate of peroxide production by α -radiolysis close to the used fuel with the rate at which Fe²⁺ could diffuse through sheath defects into the cracked fuel, counteracting the oxidative effect of H₂O₂.

Groundwater Composition

The composition of deep groundwaters varies widely from site to site. The concentrations of complexing anions that enhance the solubility of UO₂ are of primary importance in models for the release of radionuclides from used fuel. Thus, the major species of interest are (i) carbonate and phosphate anions, which are strong uranium complexing agents in the E-pH range of interest¹², and (ii) chloride and sulfate anions, which are weaker complexing agents, but can be found in fairly high concentrations in deep groundwaters and are important complexing agents for relatively high oxidation potential and low pH values.

The radionuclide release model for used fuel, described below, has been derived for total carbonate,

phosphate, sulfate and chloride concentrations of up to 10⁻², 2 x 10⁻⁶, 10⁻², and 1.0 mol·kg⁻¹, respectively. The concentration ranges are representative of granitic groundwaters containing relatively high concentrations of potential complexing agents^{17,30,31}.

THE RELEASE MODEL FOR USED FUEL

The release of radionuclides from used fuel is a complex process. Two escape mechanisms, which operate on very different time scales, are expected to control the rate at which radionuclides will enter the groundwater system: (i) an instant release of a fraction of the inventory of some radionuclides and (ii) a slow, solubility-controlled, congruent release of radionuclides, due to the dissolution of the fuel matrix itself²⁰.

Instant Release

The instant release model represents a fast release of a fraction of the inventory of some fission products (e.g., iodine, cesium) from the fuel/sheath gap and the grain boundaries of the fuel, upon container and sheath failures, and contact of the fuel with groundwater. This so-called "instant release fraction" determines the source boundary condition, by defining the magnitude of a δ -function-shaped flux pulse released from used fuel at the used fuel/buffer interface. The instant release fraction depends strongly on the power history of the used fuel. It has been determined for CANDU fuel by Johnson and Joling³². On average, < 10% of the cesium and iodine inventories is found in the fuel/sheath gap and at the grain boundaries.

Solubility-Controlled Release

The use of a solubility-limited dissolution model for the release of radionuclides from used UO₂ fuel requires information concerning the solubility of UO₂ in the environment of an underground vault. This solubility defines a constant concentration boundary condition for the solution of the diffusion-convection equation that describes the transport of uranium species away from the used fuel. The solution of this equation gives the flux of dissolved uranium species at the fuel/buffer interface, i.e., the UO₂ dissolution rate. The rate at which a particular radionuclide is released from the used fuel, the solubility-controlled source term, is given as a product of the uranium dissolution rate and the fractional abundance of the radionuclide in the used fuel¹³. This congruent release model¹³ is supported by long-term leaching experiments^{33,34} that show that the long-term fractional releases of cesium, technetium, strontium and uranium are comparable, in spite of the widely varying chemical properties of the leached elements.

Ideally, direct experimental determinations of the UO₂ solubility for all possible groundwater conditions in a vault are desirable. However, the experimental difficulties involved make such measurements impractical. Therefore, thermodynamic calculations of UO₂ solubilities must be used. Such calculations can be performed using complex equilibrium programs. As it is desirable to avoid incorporating an equilibrium program into SYVAC and having to repeat the equilibrium calculation thousands of times for various geochemical input conditions, a simple and explicit mathematical expression has been developed for the solubility of UO₂, S_{UO₂}, as a function of the geochemical conditions (pH, carbonate, phosphate, sulfate and chloride concentrations, temperature, and redox potential) based on thermodynamic principles¹³. This expression agrees with the results of thermodynamic equilibrium programs

based on a full uranium data base to within 5%¹³. It was derived for the groundwater conditions defined in the previous section and is valid within the E-pH region where UO_2 is the thermodynamically stable solid.

However, α -radiolysis of groundwater may enhance the oxidative dissolution of the fuel and invalidate the UO_2 solubility-controlled release model. Electrochemical and X-ray photoelectron spectroscopic (XPS) studies indicate that, although UO_2 is rapidly oxidized in oxygenated water through the sequence $UO_2 \rightarrow UO_2^{+} \rightarrow U_4O_9 \rightarrow U_3O_8$, no significant dissolution occurs until a composition close to U_3O_8 is reached³⁵. Consequently, a solubility model, based on U_4O_9 solubility, 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 approximately U_4O_9 ^{36,37}.

An expression for the solubility of U_4O_9 , $S_{U_4O_9}$,

has therefore been derived as well. It was found to be related to the solubility of UO_2 by

$$S_{U_4O_9} = S_{UO_2} \cdot 10^{(E - \bar{E})/2A} \quad (5)$$

where \bar{E} is the redox potential along the UO_2/U_4O_9 stability line, E is the redox potential of the groundwater, and A is the Nernst constant¹³.

RELEASE MODELS FOR HIGH-LEVEL VITRIFIED WASTES

Silicate glasses are excellent solvents for the large majority of actinides and fission products occurring in the waste streams from fuel reprocessing. Sodium borosilicate glasses have been chosen as the 'first generation' waste form in the U.S.A. and in France. Research and development in Canada have concentrated on sodium borosilicate and sodium calcium aluminosilicate glass compositions. Because glass is not a thermodynamically stable material, a combination of kinetic modelling and experimentally based approaches has been used to model radionuclide release.

Sodium Borosilicate Glasses

Preliminary experiments show that the durability of a sodium borosilicate glass, as defined by its rate of dissolution in water, increases with increase in silica content³⁸. Two reference sodium borosilicate glasses have been studied: Glass 200, with a molecular formula $Na_2O \cdot B_2O_3 \cdot 4SiO_2$ (64.62% wt. SiO_2), and Glass 204, $Na_2O \cdot B_2O_3 \cdot 8SiO_2$ (78.51% wt. SiO_2). In terms of composition and durability, Glass 200 lies approximately in the centre of the spectrum of glasses considered internationally for waste immobilization purposes³⁹. Glass 204 represents the upper compositional limit that can be readily produced by conventional Joule melting (a process for the production of immobilized waste).

In a recent review of the leaching and dissolution properties of glasses intended for waste immobilization, Grauer⁴⁰ has concluded that the only significant release mechanism observed to date is that of congruent matrix dissolution. Our own experience supports this view. In the Canadian waste management concept¹, in which the glassy waste form is supposed to be closely surrounded by a clay/sand buffer material, the waste form will be in contact with only a small volume of water, which is almost static. Under this condition, the water should saturate very rapidly with respect to silica (<10 days at 100°C), and the glass dissolution products should increase the pH to a moderately basic value.

A series of models has been produced that describe the dissolution of a sodium borosilicate glass at constant temperature and pH⁴¹. When applied to the above disposal conditions, the model suggests that the glass should dissolve at a constant rate, independent of the glass surface area/water volume ratio (SA/V).

Experimental work shows that the glass does indeed dissolve at a constant rate, with only a small effect due to SA/V ratio. The release model for sodium borosilicate glass is then a constant dissolution rate. The 'instant' release term for Glass 200 is insignificant. Preliminary experimental results for Glass 204 indicate that there is an 'instant' release of approximately $3.5 \times 10^{-3} \text{ g} \cdot \text{cm}^{-2}$, while the long-term release rate is approximately $2.6 \times 10^{-4} \text{ g} \cdot \text{cm}^{-2} \cdot \text{day}^{-1}$ at 100°C⁴². The presence of clay and/or granite rock was found to have no significant effect on the dissolution rates of the glasses⁴³.

The experimental methods used to date were developed principally for use in screening tests of the durability of glass compositions, and are not sufficiently sensitive to allow reliable measurements of glass dissolution rates at the lower end of the range of temperatures anticipated in a disposal vault. In addition, in experiments with high levels of fission product and actinide loading in the glasses surface films form on the dissolving glasses. Mechanical disturbance of these films during measurements of dissolution rates has led to erratic results.

An improved method of measuring dissolution rates, using the "Radioactive Sealed Leach Testing Apparatus," is being developed at the Whiteshell Nuclear Research Establishment (WNRE). In this method, the dissolution experiment takes place inside a sealed tube, and the progress of the experiment is monitored from the outside by γ -ray counting. There is no intrusion into the experiment, which also is not disturbed mechanically or by temperature cycling. A prototype has operated for two years⁴⁴. This method will be used to obtain dissolution data on the higher waste-loaded glasses, over the temperature range 15 to 100°C, currently assumed for the disposal vault¹⁴.

The glass dissolution models used in the interpretation of data have been based on the assumption that the dissolution reactions are not affected by the presence of films or layers on the surface of the glass. When applied to glasses that form surface layers, these models may be invalid, or unduly conservative in their forecasts of release. Models have also been developed that take account of the presence of a surface layer, based on the Wallace-Wicks 'Savannah River Model' approach⁴⁵. These models assume that the intrinsic properties of the surface layer do not change during dissolution. However, preliminary observations suggest that they will not completely describe published experimental data⁴⁶. Models describing the effects of layers with variable properties are being investigated at WNRE, and methods are being developed to incorporate individual solubility limits for sparingly soluble radionuclides into the release models (7).

Sodium Calcium Aluminosilicate Glasses

Sodium calcium aluminosilicate glasses were developed at the Chalk River laboratories of Atomic Energy of Canada Limited for waste immobilization in the late 1950s⁴⁷. When placed in contact with a finite volume of water, they apparently cease to dissolve after a period of time (~100 days at a SA/V ratio of 0.1 cm^{-1} at 100°C), because a mineralized layer forms

on the glass surface⁴⁸. Similar behaviour has also been observed for glasses containing ¹³⁷Cs. When placed in water previously saturated with aluminosilicate glass dissolution products, no weight loss is observed. Also, within the accuracy of the experiment ($\pm 1.5\%$), no radioactive release takes place either. The accuracy of the experiment is currently being improved. The release model for sodium calcium aluminosilicate glasses is then first-order dissolution, followed at long times, by a constant concentration of dissolved species in the water contacting the wasteform.

CONCLUSIONS

The assimilation of the results of the experimental program into models for the environmental assessment is an ongoing process. The models are being critically reviewed and updated as more experimental results become available. The source terms presented in this report are the result of such a process.

To further improve the scientific quality of the source terms, a particular effort is needed:

- (1) to study the possibility of mitigating the effects of radiolysis by using redox additives in the vault,
- (2) to study the combined effect of groundwater, buffer, container material and radiation field on radionuclide release,
- (3) to quantify the effect of 'sinks' (such as sorption and precipitation) downstream from the waste form, on the radionuclide release rate, and
- (4) to compare predictions based on the release models with available experimental results.

These issues are being addressed by a combined experimental and theoretical effort at the Whiteshell Nuclear Research Establishment.

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