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The solubility limits of radionuclide dissolution

Authors: J. F. Kerlask, UK

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Los Alamos National Laboratory
Los Alamos, New Mexico 87545

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SOLVENT LIMITS ON RADIOPHOTOID DISSOLUTION

L. W. Ferris,
Lawrence Radiation Laboratory,
Livermore, CA 94550 USA

Abstract

This paper examines the effects of solubility in limiting dissolution rates of a number of important radionuclides from the repository. Two simple dissolution models were used for calculations that would be characteristic of a waste mountain repository. A saturation-limited dissolution model in which the water flowing through the repository is assumed to be saturated with each waste element is very conservative in that it overestimates dissolution rates. A diffusion-limited dissolution model in which elemental dissolution rates are limited by diffusion of waste elements into water flowing past the waste is more realistic, but it is subject to some uncertainty at this time. Dissolution rates of some elements (Pu, Am, Sr, Te, Cr, Sn) are always limited by solubility. Dissolution rates of other elements (Cs, Sr, C) are never solubility limited. The release would be limited by dissolution of the bulk waste form. The elements Al, Be, Na, Rb show solubility-limited dissolution under some conditions.

Introduction

The most likely mechanism for release of radionuclides from a geologic repository is transport in water along flow paths to the accessible environment. To meet the standards regulations and requirements of the Environmental Protection Agency (EPA) and Nuclear Regulatory Commission (NRC), it will be necessary to mathematically model the transport of radionuclides in water through the repository and the surrounding rock. This is an extremely complex problem and requires additional work. In this paper, the radionuclides are assumed to be the waste element that controls the concentrations of radionuclides in water near the waste. This paper describes two simple solubility-limited dissolution models that can be used to calculate the release rates of radionuclides from a solid waste form into water as dissolved species.

The primary purpose of this work is to estimate the effect of element solubilities on dissolution rates of elements from a solid waste form. A number of experimental investigations have indicated that solubility may control the process of dissolution of radioactive elements. However, the quantitative limitations of these studies remain incomplete. To simplify the approach, a first model is a saturation-limited dissolution model in which water flowing through the repository, assumed to be saturated with each element. This is a very conservative model because it is highly unlikely that adequate contact exists between the water and waste for these conditions. A second model is a diffusion-limited dissolution model in which element saturation is assumed at the waste water interface and dissolution is limited by diffusion of the element into water flowing past the waste. This model requires assumptions about waste
siners water flow characteristics and are element diffusion-related issues. It is subject to more uncertainty. The model accounts for the effects of other parts of the engineered barrier system or of components such as spent-fuel cooling in the waste-element dissolution

In the model, we assume that the dissolution rate for each element is limited by the dissolution rate for the bulk waste form. The dissolution rate is a function of the rate of change of the concentration of the element in the solid phase with respect to time. The fractional dissolution rate is the rate at which the element is dissolved per unit of time, and this rate is assumed to be a function of the bulk fraction of the waste form. The fractional dissolution rate is the bulk fractional dissolution rate. Assumptions on the solubility and the rate of release are made for that element. The procedure assumes that elements that are not soluble will disperse at the same rate as the bulk waste form. Under certain circumstances, this assumption may not be valid. When spent fuel is disposed in the waste form, both iodine and cesium could be released at rates greater than the bulk waste-form fractional dissolution rate, but this problem has not been addressed in this analysis.

The two solubility-limited dissolution models have been applied to calculations of waste-element dissolution rates from solid waste forms at the Hanford Nuclear Waste Storage Investigations (HANWASI) potential site for a repository at Yucca Mountain, Nevada. The present target repository for a repository at Yucca Mountain is the site of the nuclear waste repository at Yucca Mountain. The unsaturated zone at Yucca Mountain is above the static water level on the Hanford Site Test Site was used to estimate waste-element solubilities [3]. The recharge rate of water at Yucca Mountain, which was used to calculate water flow rates and velocities, was obtained from a US Geological Survey estimate [4]. Calculations have been done for both spent fuel and high-level waste.

**Saturation-Limited Dissolution Model**

For the saturation-limited dissolution model, the flow rate of water through the repository area was estimated using an assumed maximum thermal gradient for the repository and an assumed water retention rate. A 10-year timescale was used for the calculations. The waste form's repository would require 114 m$^3$ for each MTHA. The recharge rate of water through the unsaturated zone at Yucca Mountain was estimated as 1 m$^3$ per year [4]. At this rate, a water flow of 114 m$^3$ per year would pass through the horizontal area of 114 m$^2$ that is associated with each MTHA of waste. The saturation-limited dissolution model assumes that each element is at its solubility limit at this quantity of water or is limited by dissolution of the bulk waste form, whichever assumption gives the lower dissolution rate. From these assumptions, the fractional dissolution rate of an element is calculated as:

\[
F_s = \frac{Q}{V}
\]

\[
F_s = \frac{1}{P}
\]

where $Q$ is the water flow rate (in m$^3$ per year), $V$ is the solubility (M), $P$ is the molecular weight of the element, and $F_s$ is the fractional dissolution rate assumed for the bulk waste form (1 year), and $F_s$ is the fractional dissolution rate of the element as
calculated. After the value of $F_a$ is estimated other quantities of concern can be calculated as

$$F_a = F_a^h$$

and

$$F_a = F_a^w$$

where $F_a^h$ is the element concentration rate in MTHM year$^{-1}$, $F_a$ is the radon-222 activity content in the element in the waste (Ci g$^{-1}$), $F_a^w$ is the element radionuclide release rate in MTHM year$^{-1}$, and $C_a$ is the concentration of the element in water entering the repository (M). If $F_a^w > F_a$ then the concentration equals the solubility that is $C_a = S$; however, if $F_a^w < F_a$ the concentration is assumed to be controlled by bulk dissolution of the waste, and $C_a = 0$. The concentrations of specific isotopes such as $^{238}$U or $^{90}$Sr in the water are needed for transport calculations. They can be calculated as

$$C_{a_j} = C_{a_j}^w M_j w_j$$

where $C_{a_j}$ is the concentration of isotope $j$ in the waste (M), $M_j$ is the molecular weight of the isotope $j$, and $w_j$ is the mass of isotope $j$ in the waste (g MTHM). The radon-222 activity release rate of isotope $j$ can be calculated as

$$F_{a_j} = F_{a_j}^w M_j w_j$$

where $F_{a_j}^w$ is the radon-222 activity content of isotope $j$ in the waste (Ci g$^{-1}$). Values of $F_{a_j}^w$ and $w_j$ were obtained from the compilation of Crann and Alexander [5]. These data are a function of time after discharge from the reactor because of the different decay rates of the various isotopes of each element.

**Diffusion-Limited Dissolution Model.**

In the diffusion-limited dissolution model, waste elements are assumed to be saturated at the interface between the waste and water flowing past. Dissolution is assumed to be the result of the waste elements dissolving into the water. The rate of element dissolution is defined as

$$C = C_0 \text{erfc}[x 2(Dt)^{1/2}]$$

where $D$ is the apparent diffusion coefficient of the element in water and \( \text{erfc}(x) \) represents the complementary error function of $x$ [6]. A penetration depth $\delta(x)$ can be defined such that the average concentration within $\delta$ of the surface is $C_0$. From this relation, $\delta$ can be approximated [6] as

$$\delta = (DL)^{1/2}$$

where the contact time is related to the velocity and waste length as $\delta = v t$. The diffusion-limited dissolution model assumes that the dissolution rate can be calculated from the quantity of the element that has diffused into the water by its passage through the solid waste or as the quantity removed by dissolution of the bulk waste form whichever is smaller.
These equations show the rate of dissolution of an element as a function of the fraction dissolved. The rate can be expressed as

\[ \frac{dF}{dt} = \frac{F}{t} \]

or

\[ \frac{dF}{dt} = \frac{F}{t} \]

where \( F \) is the fraction dissolved, \( F_0 \) is the initial fraction dissolved, and \( F_\infty \) is the equilibrium fraction dissolved. In the case of an isotopic element, the fraction dissolved is equal to the equilibrium fraction dissolved.

In the case of a radionuclide, the radionuclide release rate \( F \) is the fraction of the radionuclide that is dissolved and released into the environment. The radionuclide release rate can be expressed as

\[ \frac{dF}{dt} = \frac{F}{t} \]

where \( F \) is the fraction of the radionuclide dissolved and released, \( F_0 \) is the initial fraction of the radionuclide dissolved, and \( F_\infty \) is the equilibrium fraction of the radionuclide dissolved.

All dissolved species were assumed to have an apparent diffusion coefficient of \( 1 \times 10^{-9} \text{ m}^2 \text{ s}^{-1} \). This value results from assuming an effective diffusion coefficient \( D' \) of \( 1 \times 10^{-9} \text{ m}^2 \text{ s}^{-1} \) for the radionuclide in water, with constant porosity \( \phi \) and tortuosity \( \Psi \) defined so that

\[ D = D' \phi \Psi = \phi D' \]

The porosity of the rock surrounding the waste form was assumed to be 10\% \( (\phi = 0.1) \). The velocity of water flowing through the waste was taken as the recharge rate \( (v \text{ m year}^{-1}) \) divided by the porosity of the rock. This gives \( v = 1 \times 10^{-9} \text{ m year}^{-1} \) using the following values of the parameters in Eq. 16:

- A porosity of 10\%
- A water velocity of \( 1 \times 10^{-9} \text{ m year}^{-1} \)
- A temperature of 100°C
- A radionuclide release rate of \( 1 \times 10^{-9} \text{ m year}^{-1} \)
- A radionuclide concentration of \( 1 \times 10^{-9} \text{ m year}^{-1} \)

Based on these assumptions, the radionuclide release rate \( F \) is calculated from Eq. 16:

\[ F = \frac{dF}{dt} = \frac{F}{t} \]

The one-dimensional diffusion solution for a cylindrical waste form introduces some error into the results, however, the error is not large compared to uncertainties in solubilities and the one-dimensional solution simplifies the analysis.

**Results**

Calculations were done for 13 waste elements and the PMI spent fuel waste elements. As more elements are added to the reactor, the spent fuel content increases, and the results for the nominal model parameters that were described in the previous sections were recalculated. The solubilities were calculated using the EQUISOL computer program for the radionuclides used and estimated from recent reviews. The oxidation conditions were assumed to lead to higher solubilities than would occur under reducing conditions.
Table I

<table>
<thead>
<tr>
<th>Element</th>
<th>Solubility in Water from Yucca Mountain</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hp</td>
<td>$3 \times 10^{-3}$</td>
</tr>
<tr>
<td>U</td>
<td>$3 \times 10^{-9}$</td>
</tr>
<tr>
<td>Pu</td>
<td>$1 \times 10^{-4}$</td>
</tr>
<tr>
<td>Am</td>
<td>$1 \times 10^{-6}$</td>
</tr>
<tr>
<td>Cm</td>
<td>$1 \times 10^{-6}$</td>
</tr>
<tr>
<td>Th</td>
<td>$1 \times 10^{-9}$</td>
</tr>
<tr>
<td>Ra</td>
<td>$2 \times 10^{-6}$</td>
</tr>
<tr>
<td>Cs</td>
<td>Large</td>
</tr>
<tr>
<td>Sr</td>
<td>$6 \times 10^{-6}$</td>
</tr>
<tr>
<td>Y</td>
<td>Large</td>
</tr>
<tr>
<td>Lr</td>
<td>$1.5 \times 10^{-3}$</td>
</tr>
<tr>
<td>Sm</td>
<td>$1 \times 10^{-3}$</td>
</tr>
<tr>
<td>Nd</td>
<td>$1.0 \times 10^{-2}$</td>
</tr>
<tr>
<td>Sm</td>
<td>$2 \times 10^{-9}$</td>
</tr>
</tbody>
</table>
Elemental Rate Limitation - Bulk Dissolution Rate

<table>
<thead>
<tr>
<th>Saturated Model</th>
<th>Diffusional Model</th>
<th>Saturated Model</th>
<th>Diffusional Model</th>
</tr>
</thead>
<tbody>
<tr>
<td>F, Fe</td>
<td>Sr, Ba</td>
<td>Sr, Ba</td>
<td>Sr, Ba</td>
</tr>
<tr>
<td>Sr</td>
<td>Sr, Ba</td>
<td>Sr, Ba</td>
<td>Sr, Ba</td>
</tr>
<tr>
<td>Act</td>
<td>Th, U</td>
<td>Th, U</td>
<td>Th, U</td>
</tr>
<tr>
<td>Th</td>
<td>Th, U</td>
<td>Th, U</td>
<td>Th, U</td>
</tr>
</tbody>
</table>

Bulk fractional dissolution rate \( F_r = 1 \times 10^{-4} \) year

Not solubility limited for the few times after discharge

A measure of the effect of solubility on limiting dissolution of specific radionuclides can be obtained by examining the ratio of the radionuclide dissolution rate (in \( \text{mCi} \text{ yr}^{-1} \)) to the EPA limit for that radionuclide (in \( \text{mCi} \text{ yr}^{-1} \)). Table II lists radionuclides ordered by these ratios along with values of the ratio for WM spent fuel using diffusion-limited model dissolution rates. Radionuclides near the top of the list have high dissolution rates and low EPA release limits. Solubility is not providing an effective restraint in recharge for these radionuclides. Results for WM high-level waste are similar to those in Table III except that some of the activities are dropped to lower positions in the lists.

Effects of Varying Model Parameters

The effects of varying three of the model parameters: bulk fractional dissolution rate, water recharge rate, and element solubilities were examined. The nominal value of \( F_r \) was \( 1 \times 10^{-4} \text{ yr} \). Calculations were

**Radionuclide and Dissolution Rate EPA Limit (\( \text{yr}^{-1} \)) for Various Decay Times**

<table>
<thead>
<tr>
<th>Radionuclide</th>
<th>102 yr</th>
<th>103 yr</th>
<th>104 yr</th>
<th>105 yr</th>
</tr>
</thead>
<tbody>
<tr>
<td>( ^{137}\text{Cs} )</td>
<td>1 G</td>
<td>( 1.4 \times 10^{-3} )</td>
<td>( 1.4 \times 10^{-3} )</td>
<td>( 1.4 \times 10^{-3} )</td>
</tr>
<tr>
<td>( ^{90}\text{Sr} )</td>
<td>( 6.8 \times 10^{-1} )</td>
<td>( 1.6 \times 10^{-2} )</td>
<td>( 1.6 \times 10^{-2} )</td>
<td>( 1.6 \times 10^{-2} )</td>
</tr>
<tr>
<td>( ^{60}\text{Co} )</td>
<td>( 1 \times 10^{-3} )</td>
<td>( 1 \times 10^{-3} )</td>
<td>( 1 \times 10^{-3} )</td>
<td>( 1 \times 10^{-3} )</td>
</tr>
<tr>
<td>( ^{40}\text{K} )</td>
<td>( 1 \times 10^{-4} )</td>
<td>( 1 \times 10^{-4} )</td>
<td>( 1 \times 10^{-4} )</td>
<td>( 1 \times 10^{-4} )</td>
</tr>
<tr>
<td>( ^{241}\text{Am} )</td>
<td>( 1 \times 10^{-4} )</td>
<td>( 1 \times 10^{-4} )</td>
<td>( 1 \times 10^{-4} )</td>
<td>( 1 \times 10^{-4} )</td>
</tr>
<tr>
<td>( ^{35}\text{S} )</td>
<td>( 1 \times 10^{-5} )</td>
<td>( 1 \times 10^{-5} )</td>
<td>( 1 \times 10^{-5} )</td>
<td>( 1 \times 10^{-5} )</td>
</tr>
<tr>
<td>( ^{90}\text{Sr} )</td>
<td>( 1 \times 10^{-5} )</td>
<td>( 1 \times 10^{-5} )</td>
<td>( 1 \times 10^{-5} )</td>
<td>( 1 \times 10^{-5} )</td>
</tr>
<tr>
<td>( ^{228}\text{Ra} )</td>
<td>( 1 \times 10^{-6} )</td>
<td>( 1 \times 10^{-6} )</td>
<td>( 1 \times 10^{-6} )</td>
<td>( 1 \times 10^{-6} )</td>
</tr>
</tbody>
</table>

*Short-lived daughters of \( ^{137}\text{Cs} \), \( ^{90}\text{Sr} \), \( ^{228}\text{Ra} \), and short-lived decay products of 220Ra have not been included.
For the diffusion-limited model the total release rate of radioactivity from the solid waste form by dissolution inc. 10E65 WTEW yr is not affected strongly by changes in water recharge or element solubilities. This occurs because most of the radioactivity release comes from elements that are not solubility-limited. Thus elements such as Mo, Ta, K, Cs, and Sr contribute most to the total radioactivity release. Changes in $F_p$, however, directly affect the elements that are not solubility-limited. Thus, reducing $F_p$ significantly reduces the total radioactivity release from the solid waste form. For the saturation-limited model all three parameters affect the total radioactivity release rate, particularly for minor elements. Reducing water recharge solubilities or $F_p$ reduces the total radioactivity release rate.

**Discussion**

The two models proposed here attempt to improve on that approximation by accounting for limits imposed by the solubilities of the different elements. The saturation-limited model assumes that the total quantity of water passing through the repository area is saturated with each waste element, which is very conservative in that it overestimates dissolution rates of elements that are limited by solubility. This occurs because the model fails to recognize that there is only limited contact between the waste and the total quantity of water that would pass through the repository. The saturation model is limited by the assumption that all elements are independent of the saturation limit.

The diffusion-limited dissolution model assumes that waste-element dissolution is limited by diffusion into water flowing past the solid waste form. This model is more physically realistic since it accounts for a mechanism to transport waste elements from the solid into the adjacent water. However, in
accounting for the role the model requires information on the radionuclide distribution in the water waste interaction between the element and the medium of the waste. The flux past the waste was estimated by these elements in the concentration with the solid waste. Significant of the simulations for the diffusion-limited model most of the radionuclides released from the solid waste come from elements that do not exhibit significant dissolution.

The ordering of radionuclides presented in Table II: high-solubility radionuclides released from the solid waste at high rates relative to the background radiation. These are radionuclides that must be retarded by other mechanisms such as sorption. At 1000 years and later, isotopes of Sr, Nd, and Sr, need the least. The elements Ra and its chemical analog Ba are sorbed strongly, while Np and Pu are sorbed moderately, well on tuff from Yucca Mountain [3]. However, Cs is sorbed poorly. No data are available for sorption of C, probably as carbonate or N. Thus, the high solubility and poor sorption of Cs present a potential problem for performance assessment. This condition could change if reducing conditions are encountered along flow paths to the environment.

References


