

## Mathematical Modeling for Leaching and dissolution of Solidified Radioactive Waste in a Geologic Repository

Chang-Lak Kim, Kwang Sub Choi, Chan-Hee Cho, Jhinwung Kim and In Suk Suh

Korea Advanced Energy Research Institute

(Received April 13, 1988)

### 지하 처분장에서의 방사성폐기물 고화체의 용출 및 용해에 대한 수학적 모형 분석

김창락 · 최광섭 · 조찬희 · 김진웅 · 서인석

한국에너지연구소

(1988. 4. 13 접수)

#### Abstract

A source term model describes mathematically the source of radionuclides as they begin slow migration and decay in deep groundwater. Various source term models based on mass-transfer analysis and measurement-based source term models are reviewed. Generally, two processes are involved in leaching or dissolution: (1) chemical reactions and (2) mass transfer by diffusion. The chemical reaction controls the dissolution rates only during the early stage of exposure to groundwater. The exterior-field mass transfer may control the long term dissolution rates from the waste solid in a geologic repository. Mass-transfer analyses rely on detailed and careful application of the governing equations that describe the mechanistic processes of transport of material between and within phases. If used correctly, source term models based on mass-transfer theory are valuable and necessary tools for developing reliable predictions.

#### 요 약

지중매몰된 방사성핵종들이 지하수계를 통해 이동을 하는 Source를 수학적으로 표시하는 Source Term 모형이 필요하다. 물질전달식 또는 측정식에 근거한 여러 Source Term 모형을 비교 분석하였다. 일반적으로 용출 또는 용해에는 (1) 화학반응, (2) 확산 등에 의한 물질이동의 두 가지 작용이 관여한다. 화학반응은 고화체가 지하수에 노출된 후 초기의 짧은 기간 동안에만 용해율을 조절한다. 외부로의 물질전달율이 지하 처분장에서 방사성폐기물 고화체로부터의 장기간에 걸친 핵종유출율을 조절하는 역할을 한다. 물질전달 이론을 적용할 때는, 필요로 하는 물질이동 현상을 기술할 수 있는 식을 선택해야 한다. 적절히 사용했을 경우, 물질전달 이론에 입각한 Source Term 모형은 핵종유출율의 신뢰할 만한 예측을 위한 귀중한 도구이다.

## 1. Introduction

The safe disposal of radioactive waste has been a matter of national concern. The disposal methods, such as an intermediate depth disposal of low- and intermediate-level radioactive waste and a deep underground disposal of high-level radioactive waste, are being studied in depth.

In a geologic nuclear waste repository, the radioactive waste will be isolated from the biosphere by several barriers. These barriers are often categorized as waste form, engineered barriers, and natural barriers; and using the proper engineered barriers insures the additional safety margin. Assurance on the long term safety of the disposal system becomes the basic regulatory requirement for a geologic repository.

A commonly used solidification technique for low- and intermediate-level radioactive wastes is cementation. Glasses have long been recongized as potentially suitable host matrices for the immobilization of high-level radioactive waste, and borosilicate glasses have been chosen as "first generation" waste forms in several countries including the United States, France, and Germany.

Reliable prediction of long-term rates of release of radionuclides from solid waste to groundwater in a geologic repository will be necessary for the final acceptance of a repository design. Therefore, a part of an assessment of the safety of a deep geologic repository for isolating radioactive waste is a predictive model for the rate of release of radionuclides from the repository to the surrounding repository site. This is often called a "source term" model in that it mathematically describes the source of radionuclides as they begin slow migration and decay in deep groundwater. A source term model is either a "leach model" or a "dissolution model", or both. "Leaching" usually denotes liquid extraction of a component from a solid without destroying the solid in the process. The term "dissolution" probably arose from the

matrix dissolution of the glass. Therefore whether the term "leach" or the term "dissolution" is used, what is of interest is the rate of release of radionuclides from a waste form - in which they are initially immobilized - to become available for transport.

There have been extensive laboratory tests on the rate of dissolution of individual constituents from solidified waste form into deionized water and simulated groundwater.<sup>1-8)</sup> Most of the data have been obtained with a small sample of simulated waste in a static liquid leachant, although some tests have been made with a slow flow of the leachant through the test container.

Various correlations of the time-dependence of the leach rate were proposed<sup>2,4,8-11)</sup> and these correlations based on laboratory leach data have been extrapolated to predict the performance of the waste form in a repository during several thousand years.<sup>4)</sup> Moreover various combinations of Fick's second law of diffusion with boundary conditions or other phenomena such as chemical reactions have been proposed.<sup>14 28)</sup>

In this paper we will review various source term models based on mass-transfer analysis and measurement-based source term models. The purpose of the present study is to propose a mathematically described source term for the long-term reliable prediction of a repository performance.

## 2. Leach/Dissolution Models

### 2.1. Measurement-Based Models

Beginning over twenty years ago, laboratory leach experiments have been performed on borosilicate glass and other candidate waste forms. Leaching was described mathematically by Douglas *et al.*<sup>12)</sup> for the loss of sodium or other alkali from common commercial glasses immersed in distilled water. The cumulative release  $F(t)$  is

$$F(t) = a \cdot t^{1/2} + b \cdot t \quad (1)$$

where  $a$  and  $b$  are constants and  $t$  is time. This ex-

pression was proposed to account for simultaneous diffusive release ( $a \cdot t^{1/2}$ ) and release due to dissolution of the glass matrix ( $b \cdot t$ ).

To calculate the total released radioactivity from a single glass block as a function of thermal history of the repository, Altenhein *et al.*<sup>9)</sup> proposed an empirical expression for the cumulative release  $F(t)$

$$F(t) = k(T) \cdot t^n \quad (2)$$

where  $k$  is the rate constant ( $\text{g/cm}^2\text{-d}^n$ ) and  $n$  varies with the type of reaction mechanism. The temperature dependence of  $k$  was given by the Arrhenius equation:

$$K(T) = I e^{-E/RgT} \quad (3)$$

where  $I$  = frequency factor ( $\text{g/cm}^2\text{-d}^n$ ),

$E$  = activation energy (J/mole),

$Rg$  = gas constant (8.3146 J/mole °K),

and  $T$  = absolute temperature (°K).

The leach rate  $L(t)$  is

$$L(t) = \frac{dF(t)}{dt} = n I e^{-E/RgT} \cdot t^{n-1} \quad (\text{g/cm}^2\text{-d}) \quad (4)$$

Westsik *et al.*<sup>2)</sup> proposed an empirical equation for leach rate same as eq.(4) derived from short-term leaching experiments of borosilicate glass waste form. They determined the temperature dependence of  $k$  by fitting experimental data.

To describe the cumulative amount leached, Côté *et al.*<sup>8)</sup> developed a semi-empirical expression by combining the general forms for the cumulative release

$$F(t) = k_1(1 - e^{-k_2t}) + k_3\sqrt{t} + k_4t \quad (5)$$

The first term,  $k_1(1 - e^{-k_2t})$ , is the general form based on the kinetics of exchanges of species between the surface of waste form and the aqueous solution. In the case where the initial surface exchanges are fast relative to the time span of the data being considered, this term can be reduced to the constant  $k_1$ . The second term,  $k_3\sqrt{t}$ , is the general form representing the transport of species

by diffusion. The third term,  $k_4t$ , is the general form representing leaching due to a slow mobilizing chemical reaction or to structural breakdown of the waste form matrix.

To apply the empirical correlation of laboratory leach data to predicting waste performance in a repository, Macedo *et al.*<sup>13)</sup> proposed a repository analogue that a specific volume of groundwater is associated with each well-stirred volume of waste fragments. For a waste solid surrounded by a large volume of wet rock, they assumed that the leachant volume  $V$  is the volume of voids initially inside the waste container, which will become filled with water when the waste container fails. The volumetric flow through this well-mixed container of waste fragments and void water was assumed as the upstream Darcy velocity of groundwater multiplied by the projected cross-sectional area  $A$  of the solid waste. When liquid in contact with the waste is at concentration  $N_i$ , the expected fractional dissolution rate  $f_i$  is

$$f_i = \frac{N_i V}{m_i Tr A} \quad (1/\text{sec}) \quad (6)$$

where  $m_i$  is the mass of species  $i$  in the waste solid per unit surface area of solid, and  $Tr$  is the contact time of groundwater. At low groundwater velocity the equivalent contact time of groundwater was assumed as

$$Tr = \frac{d^2}{KD} \quad (7)$$

where  $K$  is the retardation coefficient,  $d$  is the waste diameter, and  $D$  is the diffusion coefficient in groundwater in the rock pore.

## 2.2. Diffusion Models

The rate of mass transfer by diffusion is emphasized in many analyses because it is found to be the phenomenon that controls the net rate at which most of the species in a waste solid dissolve. Godbee *et al.*<sup>14)</sup> proposed a leaching model based on bulk diffusion from a semi-infinite

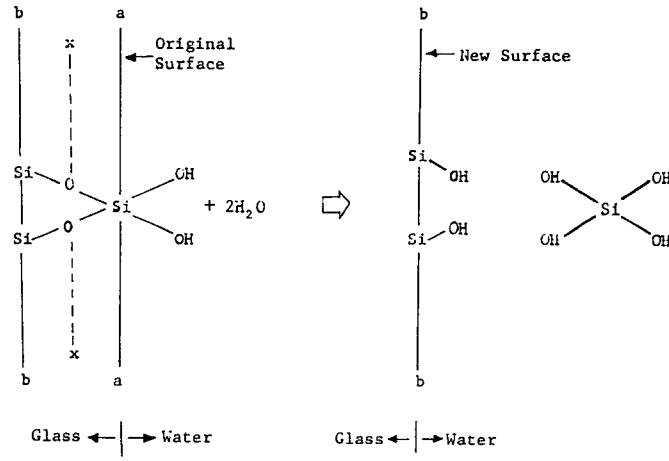


Fig. 1. Harvey's Hypothesis-Diffusion of Water into a Glass

medium of waste composite. If a species is present in the matrix in its mobile form only, a mass balance shows that the net rate of transfer is expressed by Fick's second law of diffusion (taking the interface as origin). It was assumed that diffusion takes place in the liquid filling the pores of the waste composite.

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial z^2} \tag{8}$$

When the groundwater velocity is high enough to maintain zero surface concentration,

$$L(t) = C_i \left( \frac{D}{\pi t} \right)^{1/2} \tag{9}$$

where D is the diffusion coefficient of the species for the waste composite, and C<sub>i</sub> is the initial concentration throughout the matrix.

This was further elaborated by invoking Fick's second law of diffusion with a moving surface boundary condition. For a semi-infinite medium, bulk diffusion with surface dissolution (i.e. a moving boundary) yields an expression<sup>15)</sup>

$$F(t) = C_i S \sqrt{BD} \left[ \left( t + \frac{1}{2B} \right) \text{erf} \sqrt{Bt} + \left( \frac{t}{\pi B} \right)^{1/2} e^{-Bt} + t \right] \tag{10}$$

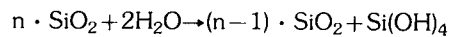
where F(t) is the cumulative release at time t (g), S is the surface area (cm<sup>2</sup>), U is the moving boundary velocity or degradation rate (cm/sec),

$$B = \frac{U^2}{4D}, \text{ moving boundary constant (1/sec),}$$

and erf(u) = error function

$$= \frac{2}{\sqrt{\pi}} \int_0^u e^{-z^2} dz.$$

Harvey *et al.*<sup>16,17)</sup> used a hypothesis that the dissolution of glass is a consequence of the diffusion of water into it (See Figure 1). If two molecules of water diffuse into the glass and react with oxygen bridges at x-x, then a new glass surface is created at b-b, and silica is expelled into solution as Si(OH)<sub>4</sub>. In this ideal case



More generally let q molecules of water diffuse into the glass, and a molecule of SiO<sub>2</sub> be released (q ≥ 2). The cumulative release of glass at time t due to water diffusion into a dissolving glass of a semi-infinite length is

$$F(t) = S \rho \left[ \sqrt{\frac{D}{\alpha}} \text{erf} \sqrt{\alpha t} + \frac{\phi t}{2} + \frac{\phi}{2} \right]$$

$$\left\{ \left( t - \frac{1}{2\alpha} \right) \operatorname{erf} \sqrt{\alpha t} + \sqrt{\frac{t}{\pi \alpha}} e^{-\alpha t} \right\} \quad (11)$$

Where  $\phi$  is the velocity at which the plane interface is moving due to the glass dissolution,  $D$  is the diffusion coefficient of water in the glass,  $\rho$  is the density of the glass, and  $\alpha = \phi^2/4D$ .

Chambré *et al.*<sup>18,19)</sup> analyzed the molecular diffusion of the dissolved species through groundwater continuum in the tortuous pathways formed by pores and fractures in the surrounding medium. They considered a prolate spheroidal waste solid embedded in a porous medium. The fractional dissolution rate  $f_i$  of the species  $i$  at steady state is

$$f_i = \frac{\beta \epsilon DN_i^*}{n_i} \quad (1/sec) \quad (12)$$

where  $D$  is the species diffusion coefficient in pore liquid,  $\epsilon$  is the porosity of the surrounding rock,  $n_i$  is the bulk density ( $\text{g/cm}^3$ ) of the species in the waste, and  $N_i^*$  is the concentration of the species in the surface liquid. For a bounding calculation,  $N_i^*$  is chosen as the saturation concentration.  $\beta$  is a geometrical parameter that can be calculated from the waste-form dimensions. For a sphere of radius  $R$

$$\beta = \frac{3}{R^2} \quad (13)$$

For a prolate spheroidal waste of semi-minor axis  $b$  and eccentricity  $e$

$$\beta = \frac{3e}{b^2 \ln[\coth(\alpha_s/2)]}, \quad \alpha_s = \cosh^{-1}(1/e) \quad (14)$$

Diffusive-convective mass transfer of the dissolved species through the concentration boundary layers was analyzed by Chambré *et al.*<sup>18,19)</sup> to predict the limiting dissolution rate of low-solubility species. The fractional dissolution rate  $f_i$  of the elemental species  $i$  from a long cylinder of radius  $R$  was obtained at steady state:

$$f_i = \frac{8N_i^* \epsilon \sqrt{DU}}{(\pi R)^{3/2} n_i}, \quad \frac{UR}{D} > 4 \quad (1/sec) \quad (15)$$

where  $U$  is the pore velocity of groundwater before it comes near the waste. For a waste cylinder of finite length  $H$ , end effects are accounted for by multiplying the right-hand side of eq.(15) by a correction factor  $(1 + R/H)$ .

The equation for the time-dependent fractional dissolution rate of decaying radioelements was also obtained by Chambré *et al.*<sup>18,19)</sup>

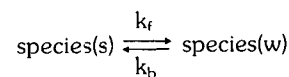
$$f_i = \frac{8 \epsilon N_i^* \sqrt{DU}(1+R/H)}{(\pi R)^{3/2} n_i} \left\{ \frac{e^{-\lambda E[m^2(\tau)]}}{m(\tau)} + D_a \int_0^\tau e^{-D_a \tau'} \frac{E[m^2(\tau')]}{m(\tau')} d\tau' \right\} \quad (16)$$

where  $\lambda$  is the decay constant of the species,  $D_a$  is the Damköhler number, a dimensionless group defined as  $D_a = K \lambda R/U$ ,  $K$  is the retardation coefficient,  $E[x]$  is the complete elliptic integral of the second kind,

$$m(\tau) \equiv [1 - e^{-4\tau}]^{1/2}, \quad \text{and } \tau \equiv Ut/KR.$$

### 2.3. Kinetics Model

Pescatore *et al.*<sup>20,21)</sup> presented a network dissolution model using a chemical kinetics approach. In this leaching model for glass waste form, surface phenomena were described based on the kinetics of exchanges of a species between the surface of the solid (s) and the aqueous solution (w):



where  $k_f$  and  $k_b$  are two phenomenological constants describing the kinetics of attack of glass by water and re-deposition of dissolved silicon species back onto the glass, respectively. The instantaneous silicon leach rate per unit area,  $L(t)$  can be expressed as

$$L(t) = k_f - k_b C(t) = L_0(1 - C/C_{sat}) \quad (17)$$

where  $C(t)$  denotes the concentration of a species

in a volume  $V$  of aqueous solution contacting a waste glass specimen of surface area  $S$ , and  $L_0 \equiv k_f$ ,  $C_{sat} \equiv k_f/k_b$ .

With simplifying assumption of no radioactive decay, the mass balance is

$$\frac{dC(t)}{dt} = \gamma L(t) - \Omega C(t) \quad (18)$$

where  $\gamma = S/V$  and  $\Omega =$  the leachant renewal frequency.

Substituting eq.(17) into eq.(18) and solving for  $C(t)$  yields

$$C(t) = \frac{C_{sat}}{1 + \Omega C_{sat} / \gamma L_0} \left[ 1 - e^{-(\Omega + \frac{\gamma \cdot L_0}{C_{sat}})t} \right] \quad (19)$$

For static leach testing,  $\Omega = 0$ . Substituting eq.(19) with  $\Omega = 0$  into eq.(17) yields

$$L(t) = L_0 e^{-\frac{\gamma \cdot L_0}{C_{sat}} t} \quad (20)$$

If  $C(t) \approx C_{sat}$ , then  $L(t) \approx 0$ .

**2.4. Diffusion and Kinetics Models**

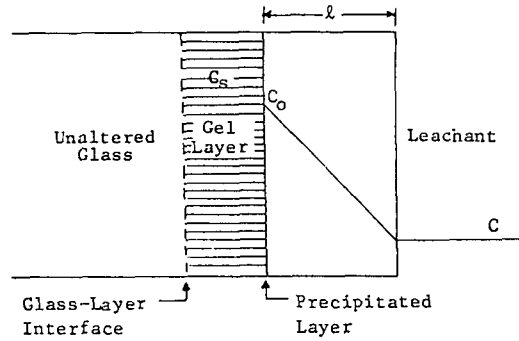
For the case where a species is present in both an immobile and a mobile form initially in a state of chemical equilibrium, leaching of the mobile form will establish a difference in chemical potential. This will drive the reaction to transform the immobile form of the species into a mobile form. Côté *et al.*<sup>8)</sup> proposed the following mass balance for a mobile species of initial concentration  $C_{eq}$  being produced at a rate  $k[C_{eq} - C(z,t)]$ :

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial z^2} + k[C_{eq} - C] \quad (21)$$

The leaching rate was expressed as

$$L(t) = C_T(D_e k) \left[ \text{erf} \sqrt{kt} + \frac{e^{-kt}}{\sqrt{\pi kt}} \right], \quad (g/cm^2 - \text{sec}) \quad (22)$$

where  $C_T$  is the total initial concentration (mobile + immobile), and  $D_e$  is the effective diffusion



**Fig. 2. Protective Layer Model**

coefficient defined as  $D_e = D/(C_T/C_{eq})^2$ .

Walace *et al.*<sup>22)</sup> assumed that three processes involved in glass leaching: (1) interdiffusion, (2) matrix diffusion, and (3) surface layer formation. The interdiffusion process involved the diffusion of hydronium ions into the glass matrix accompanied by the simultaneous diffusion of alkali ions out. This generates an alkali-depleted silica-rich layer in the leachant. After a sufficiently long period, these processes will reach a steady state so that the rate of diffusion of alkali ions through the precipitated layer is equal to the rate of dissolution from the surface of the gel layer (See Figure 2). The rates  $L$  are give by

$$L = k(C_s - C_0) \quad \text{dissolution} \quad (g/cm^2 - \text{sec}) \quad (23)$$

$$L = \frac{D}{\ell} (C_0 - C) \quad \text{diffusion} \quad (g/cm^2 - \text{sec}) \quad (24)$$

where  $k$  is a rate constant (cm/sec),  
 $D$  is the diffusion coefficient of silicale in the layer (cm<sup>2</sup>/sec),  
 $\ell(t)$  is the thickness of the precipitated layer at  $t$  (cm),  
 $C(t)$  is the silicate concentration of the leachant (g/cm<sup>3</sup>),  
 $C_0$  is the silicate concentration in the solution next to the gel layer (g/cm<sup>3</sup>),  
 and  $C_s$  is the silicate concentration in a saturated solution in the medium (g/cm<sup>3</sup>).  
 The thickness of the precipitated layer  $\ell(t)$  is proportional to the amount of silica leached  $F(t)$

up to time  $t$  in the leachant of volume  $V$ :

$$\ell(t) = q F(t) \quad (25)$$

where  $q$  is a proportionality constant.

These equations can be combined with the fact that  $L(t) = \frac{dF(t)}{dt}$  to yield the following:

$$\frac{dF}{dt} = \frac{kC_s(1 - \eta F)}{1 + \xi F} \quad (26)$$

$$\text{where } \eta = \frac{1}{C_s} \frac{S}{V} \text{ and } \xi = \frac{kq}{D}.$$

For an open system where the products of leaching do not accumulate, i.e.,  $C=0$  or  $V = \infty$ ,

$$F + \frac{\xi}{2} F^2 = k C_s t \quad (27)$$

Kuhn *et al.*<sup>23)</sup> assumed that surface layers can control leaching. If the dissolution rate  $L$  is an intrinsic function of solution concentration  $C$ , it should have a form such as

$$L = L_0/(1 + k C) \quad (28)$$

where  $k$  is a constant describing the impediment to the reaction caused by the accumulation in solution of reaction product and  $L_0$  is a constant. Across a protective layer, the dissolution rate of a reaction product out to a flowing leachant can be related to the layer thickness ( $\ell$ ) and to a diffusion coefficient ( $D$ ) in the layer, according to

$$L = \frac{D}{\ell} (C_p - C) \quad (29)$$

where  $C_p$  is the concentration of the reaction product in the layer at the glass interface and  $C$  is the concentration at the leachant interface. If the thickness of the layer is assumed to remain proportional to the depth of glass reacted ( $x$ ), a constant  $\delta = \ell/x$ .

For a flowing leach test,  $C \rightarrow 0$ . Then from eq.(28) and eq.(29)

$$L = 2 L_0/(1 + \sqrt{1 + x/x_0}) \quad (30)$$

where  $x_0 = D/4k \delta L_0$

For a static leach test

$$L = 2 L_0[1 + k C + \sqrt{(1 + k C)^2 + (4 \delta L_0/D)x}] \quad (31)$$

The effect of the low rate of diffusion into the surrounding porous or fractured media is to cause a rapid build-up of the concentration of the dissolved species in the surface liquid. As saturation of each species is approached, the net rate of solid-liquid reaction decreases to match the slow rate that the dissolved species can diffuse from the surface liquid. Without assumptions as to which process is controlling, Zavoshy *et al.*<sup>24)</sup> solved the equations for the time-dependent dissolution rate from the surface of a waste solid into surrounding saturated porous media, using experimentally determined surface-liquid reaction rate as a boundary condition. Assume a spherical waste solid surrounded by porous rock containing groundwater, with groundwater pore velocity low enough that mass transfer through the porous rock is controlled by molecular diffusion of dissolved species through the tortuous liquid pathways in the rock. Neglecting radioactive decay,

$$K \frac{\partial C}{\partial t} = D \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 \frac{\partial C}{\partial t}), \quad t > 0, \quad R < r < \infty \quad (32)$$

with initial condition

$$C(r,0) = 0, \quad R < r < \infty \quad (33)$$

Where  $C(r,t)$  is the concentration of dissolved species in groundwater,

$K$  is the retardation coefficient,

$D$  is the diffusion coefficient in the liquid,

$r$  is the radial distance from the waste center,

and  $R$  is the radius of the waste form.

As a boundary condition at the waste-liquid interface, the diffusive mass transfer rate of dissolved species is equal to the dissolution rate by the solid-liquid reaction:

$$-\epsilon D \frac{\partial C(R,t)}{\partial r} = j_0 \left[ 1 - \frac{C(R,t)}{C_s} \right], t > 0 \quad (34)$$

where  $\epsilon$  is the porosity of the surrounding medium,  $C_s$  is the saturation concentration of the dissolved species, and  $j_0$  is the experimental forward reaction rate of the species per unit external surface area. The remaining boundary condition is

$$C(\infty, t) = 0, t > 0. \quad (35)$$

The time-dependent dissolution rate at the outer surface of the waste is

$$L(t) = j_0 \frac{1 + \theta e^{\tau} \operatorname{erfc} \sqrt{\tau}}{1 + \theta} \quad (36)$$

where the dimensionless time  $\tau$  is defined as

$$\tau = \frac{(1 + \theta)^2 D t}{KR^2} \quad (37)$$

The dimensionless flux ratio  $\theta$  is defined as

$$\theta = \frac{j_0 R}{\epsilon D C_s} \quad (38)$$

and can be interpreted as

$$\theta = \frac{\text{forward reaction rate per unit area at } R}{\text{steady-state diffusive mass transfer rate at } R}$$

One can interpret the forward reaction rate  $j_0$  in terms of a reaction-rate constant  $k$ :

$$j_0 = k C_s \quad (39)$$

which results in

$$\theta = \frac{kR}{\epsilon D} \quad (40)$$

At steady state,

$$L(\infty) = \frac{j_0}{1 + \theta} \quad (41)$$

For  $\theta \gg 1$ ,  $L(\infty) \simeq \epsilon D C_s / R$ . Under this condition, the net dissolution rate is controlled by molecular diffusion in the exterior field. For  $\theta \ll 1$ , the net dissolution rate is controlled by the solid-

liquid reaction and is equal to  $j_0$ .

### 2.5. Modified Diffusion Models

In a wet-rock repository the waste is dissolved by groundwater flowing slowly in the porous or fractured rock. Under this condition the rate of diffusive transport of dissolved species away from the waste surface into the surrounding groundwater can be slow enough for low-solubility species to limit the net rate of dissolution. Chambré *et al.*<sup>25,26</sup> analyzed the time-temperature dependent diffusion-controlled dissolution model. The surface temperature of the waste package is time dependent, on account of the time variable heat release of the waste. Since solubility and the diffusion coefficient of diffusing species are assumed known functions of temperature, they in turn depend on time. They are respectively  $C_s(t)$  and  $D(t)$ . This analysis applies also to isothermal conditions where these parameters are constant in time. Chambré *et al.* derived the time-dependent diffusive mass transfer rate from a spherically shaped waste form of radius  $R$ , imbedded in a porous medium, in the absence of water convection. The concentration  $C(r,t)$  of the diffusing species, in absence of precursors, is governed by

$$\frac{\partial K(t) C(r,t)}{\partial t} = D(t) \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial C}{\partial r} \right) - K(t) \lambda C, R < r < \infty, t > 0 \quad (42)$$

where  $K(t)$  is the retardation coefficient.

The initial condition is

$$C(r,0) = 0, r > R \quad (43)$$

and the boundary conditions are

$$C(R,t) = C_s(t), t \geq 0 \quad (44)$$

$$C(\infty,t) = 0, t \geq 0 \quad (45)$$

The dissolution rate per unit surface area from the spherical waste form into the exterior field is

$$L(t) = -D(t) \epsilon \frac{\partial C(R,t)}{\partial r} \quad (46)$$



Then,

$$L(t) = \frac{D(t)C_{s_0} \epsilon e^{-\lambda t}}{R K(t)} \left[ \tilde{f}'(\tau(t)) + \frac{1}{\sqrt{\pi}} \frac{\tilde{f}(0)}{\sqrt{\tau(t)}} + \int_0^{\tau(t)} \tilde{f}'(\tau(t) - \eta) \frac{d\eta}{\sqrt{\eta}} \right] \quad (47)$$

where

$$\frac{D(t)}{K(t)} = \frac{D_0}{K_0} g(t) \quad (48)$$

$$K(t) C_s(t) = C_{s_0} f(t) \quad (49)$$

$$\tau(t) = \frac{D_0}{K_0 R^2} \int_0^t g(t') dt', t \geq 0 \quad (50)$$

$$\tilde{f}(\tau) = f(t(\tau)) e^{\lambda t(\tau)} \quad (51)$$

and  $\tilde{f}'(\tau)$  denotes differentiation with respect to the variable  $\tau$ . The dimensionless functions  $f(t)$  and  $g(t)$  represent the known time dependence of  $K(t) \cdot C_s(t)$  and  $D(t)/K(t)$  respectively. In order to reduce eq.(42) to a constant coefficient equation the transformation with respect to  $\tau(t)$  is introduced.

For a uniform and time-invariant temperature field

$$g(t) = 1, f(t) = K(t) = K_0, t \geq 0.$$

Then, the dissolution rate is

$$L(t) = \frac{D_0 C_{s_0} \epsilon}{R} \left[ 1 + \sqrt{\frac{K_0 R^2}{\pi D_0 t}} e^{-\lambda t} + \sqrt{\frac{\lambda K_0 R^2}{D_0}} \operatorname{erf} \sqrt{\lambda t} \right] \quad (52)$$

This was further elaborated by Kim<sup>27,28)</sup> who used the leach time  $T$  to account for the initial inventory  $M^0$  in each waste form. The dissolution rate of a species given in eq.(47) or eq.(52) is correct during the leach time of the species. After the leach time, the dissolution rate is zero. Then, eq.(52) is modified as

$$L(t) = \frac{D_0 C_{s_0} \epsilon}{R} \left[ 1 + \sqrt{\frac{K_0 R^2}{\pi D_0 t}} e^{-\lambda t} \right]$$

$$+ \sqrt{\frac{\lambda K_0 R^2}{D_0}} \operatorname{erf} \sqrt{\lambda t} \cdot |h(t) - h(t-T)| \quad (53)$$

$$\text{where } h(t) = \begin{cases} 0, & t < 0 \\ 1, & t \geq 0 \end{cases} \quad (54)$$

The leach time  $T$  of a species is obtained by solving the following mass balance equation

$$\frac{dM(t)}{dt} = -4\pi R^2 L(t) - \lambda M(t), \quad 0 < t \leq T \quad (55)$$

with side conditions

$$M(0) = M^0 \quad (56)$$

$$M(T) = 0 \quad (57)$$

where  $M(t)$  is the inventory of the species at time  $t$  in the waste form.

For very soluble species, for example cesium and iodine, one can only estimate the range of dissolution rates, since the solubilities of their usual compounds may be too large to limit their dissolution. A lower limit to the dissolution rate would be the dissolution rate of the waste matrix, if they dissolve congruently with the matrix.<sup>28</sup> The congruently dissolved species has the same fractional dissolution rate at any time  $t$  after beginning of dissolution as the waste matrix. Then the dissolution rate  $L(t)$  of the congruently dissolved species at time  $t$ , normalized to the instantaneous inventory  $M(t)$  of the species at time  $t$  in the undissolved waste is equal to the dissolution rate  $L_m(t)$  of the waste matrix at time  $t$ , normalized to the inventory  $M_m(t)$  of the waste matrix at time  $t$ :

$$\frac{L(t)}{M(t)} = \frac{L_m(t)}{M_m(t)}, \quad t < 0 \quad (58)$$

### 3. Discussion

Extrapolations based on laboratory leach data (eqs.(1),(2),(5), and (6)) may represent a conservative upper limit to the release rates in a repository

because the extrapolations give little credit for saturation effects. However, laboratory data cover a short exposure time so the extrapolations are necessarily of uncertain validity, even as upper-limit estimates. The time dependence of these correlations suggests physical processes that may control the leaching. In a geologic repository there will remain open-system pathways for diffusion and convection from the waste form's exterior surface into the pore water in the surrounding media. Therefore the validity of the proposed extrapolation of closed-system laboratory data, for example Macedo's extrapolation given in eq. (6), to a waste package in the open system of a repository is questionable. Various proposals have been made<sup>13,21,22,23</sup> to extrapolate the laboratory leach-rate data to repository conditions by adopting the laboratory data taken at the same S/V ratio that is presumed to exist for the waste package in a repository. It has been pointed out that there is no meaning to an equivalent volume of groundwater in contact with the surface area of each waste package.<sup>29</sup> Either the canister void water or the pore water, or both, isn't the appropriate analogue for the water volume in the closed-system experiment with well-mixed waste solid and water.

A chemical kinetics model<sup>21</sup> indicates that, only at short times, the surface processes dominate leaching rather than bulk diffusion, regardless of the leachant flow condition. Zavoshy *et al.*<sup>24</sup> reached the same conclusion that the solid-liquid reaction rate controls silica dissolution rates only during the first few days or months of exposure to groundwater, depending on the retardation coefficient of the dissolved silica. Eq.(36) shows that solid-liquid reaction rates may control dissolution of some small ore grains surrounded by nondissolving material and that exterior-field mass transfer can control for the same species in large solids similar to the repository waste forms. Since the expected groundwater velocity in any repository is so slow, the best estimate of the long-term mass-

transfer rate from the waste form can be obtained from the diffusion-controlled mass-transfer model with an assumed chemical equilibrium to allow equilibrium partitioning of the chemical species between the liquid and solid phases. The theory of dissolution rate controlled by mass transfer (eqs.(36) and (52)) is extended to predict the time-dependent mass transfer when a waste solid is exposed to groundwater when the repository is heated by radioactive decay(eq.(47)).

#### 4. Conclusion

Various source term models are reviewed, and as a result of this analysis the source term models are categorized as five groups: (1) measurement-based models, (2) diffusion models, (3) kinetics models, (4) diffusion and kinetics models, and (5) modified diffusion models. It is found that the chemical reaction controls the dissolution rates only at short times. The exterior-field mass transfer may control the dissolution rates from the waste solid in a geologic repository. The diffusion processes reviewed here includes the diffusion of species through surface layers of precipitates, the diffusion of water into a glass matrix, and the molecular diffusion of the dissolved species through the groundwater continuum in the tortuous pathways formed by pores and fractures. Mass-transfer analyses rely on detailed and careful application of the governing equations that describe the mechanistic processes of transport of material between and within phases. It is applicable to all situations in which transport occurs. The form of the mass-transfer model that is finally used for extrapolating waste-package performance into the future may not be the same as the simple equations presented in this paper. A point of this paper is that source term models based on mass-transfer theory are valuable and necessary tools for developing reliable predictions if used correctly. We will extend this study to include the experimental validation of the source-term models based on

mass-transfer theory and the uncertainty analysis of the parameter values.

### References

1. L. L. Hench *et al.* "Corrosion of glasses and glass-ceramics," Nucl. Chem. Waste Manag., 1, 59-75 (1980).
2. J. H. Westsik, Jr., and R. D. Peters, "Time and Temperature Dependence of the Leaching of a Simulated High-Level Waste Glass," Scientific Basis for Nuclear Waste Management III, J. G. Moore, ed., 355-362 (1981).
3. D. M. Strachan, "Results for a 1-Year Leach Test: Long-Term Use of MCC-1," PNL-SA-10036, Pacific Northwest Laboratory (1982).
4. F. K. Altenhein *et al.* "Long-Term Radioactivity Release from Solidified High-Level Waste -Part I: An Approach to Evaluating Experimental Data," Scientific Basis for Nuclear Waste Management V, W. Lutze, ed. (1982).
5. B. Grambow and D. M. Strachan, "Leach Testing of Waste Glasses under Near Saturation Conditions," Scientific Basis for Nuclear Waste Management VII, G. McVay, ed., 623-634 (1984).
6. B. P. McGrail *et al.* "Initial Results for the Experimental Evaluation of a Nuclear Waste Repository Source Term Model," Nucl. Tech., 69, 114-118 (1985).
7. N. Morcos *et al.* "Correlation of Cs-137 Release from Small-Scale to Large-Scale Cement Waste Forms," Scientific Basis for Nuclear Waste Management VI, D. G. Brookins, ed., 259-268 (1983).
8. P. L. Coté *et al.*, "An Evaluation of Cement-Based Waste forms Using the Results of Approximately Two Years of Dynamic Leaching," Nucl. chem. Waste Manag., 7, 129-139 (1987).
9. F. K. Altenhein *et al.*, "Long-Term Radioactivity Release from Solidified High-Level Waste Part II: Parametric Study of Waste Form Properties, Temperatures and Time," Scientific Basis for Nuclear Waste Management VI, D. G. Brookins, ed., 269-277 (1983).
10. W. L. Kuhn *et al.*, "Development of a Leach Model for a Commercial Nuclear Waste Gglass," Nucl. Chem. Waste Manag., 3, 13 (1982)
11. M. S. Chu *et al.*, "An Analysis of Waste Package Behavior for High-Level Waste," Scientific Basis for Nuclear Waste Management VI, D. G. Brookins, ed., 539-546 (1983).
12. R. W. Douglas and T. M. Shamy, "Reaction of Glasses with Aqueous Solutions," J. Am. Ceram. Soc., 50, 1 (1967).
13. P. B. Macedo, "Phenomenological Models of Nuclear Waste Glass Leaching," Chapter 6, Final Report of the Defence High-Level Waste Leaching Mechanisms Program, J. E. Medel, ed., PNL-5157, Pacific Northwest Laboratory (1982).
14. H. W. Godbee and D. S. Joy, "Assessment of the Loss of Radioactive Isotopes from Waste Solids to the Environment -Part I: Background and Theory," ORNL-TM-4333, Oak Ridge National Laboratory (1974).
15. H. W. Godbee *et al.*, "Applications of Mass Transport Theory to the Leaching of Radionclides from Waste Solids," Nucl. Chem. Waste Mang., 1, 29-35 (1980).
16. K. B. Harvey *et al.*, "The Dissolution of a Simple Glass -Part I: Initial Model and Application to an Open Glass/Water System," Phys. Chem. Glasses, 27, 15 (1986).
17. W. G. Mathers and K. B. Harvey, "The Dissolution of a Glass in an Infinite Volume of Water," Nucl. Chem. Waste Manag., 7, 163-166 (1987).
18. P. L. Chambré *et al.*, "Analytic Performance Models for Geologic Repositories," LBL-14842, Lawrence Berkeley Laboratory (1982).
19. P. L. Chambré and T. H. Pigford, "Prediction of Waste Performance in a Geologic Repository," Scientific Basis for Nuclear Waste Management VII, G. McVay, ed., 985-1008 (1984).
20. C. Pescatore *et al.* "Predictive Modeling of Long-Term Leaching Behaviors," Waste Management '82, R. G. Post, ed., 3, 323 (1982).
21. A. J. Machiels, and C. Pescatore, "The Functional Dependence of Leaching on the Surface Area-to-Solution Volume Ratio," Scientific Basis for Nuclear Waste Management VI, D. G. Brookins, ed., 209-216 (1983).
22. R. M. Wallace and G. G. Wicks, "Leaching Chemistry of Defense Borosilicate Glass," Scientific Basis for Nuclear Waste Management VI, D. G. Brookins, ed., 23-28 (1983).
23. W. L. Kuhn and R. D. Peters, "Leach Models for a Commercial Nuclear Waste Glass," Scientific Basis for Nuclear Waste Management VI, D. G. Brookins, ed., 167-174 (1983).
24. S. J. Zavoshy *et al.*, "Mass Transfer in a Geologic Environment," Scientific Basis for Nuclear Waste

- Management VIII, C. M. Jantzen *et al.*, ed., 311-322 (1985).
25. P. L. Chambré, W. Williams, C. L. Kim, and T. H. Pigford, "Time-Temperature Dissolution and Radionuclide Transport," *Trans. Am. Nucl. Soc.*, 46, 131-132 (1984).
26. P. L. Chambré *et al.*, "Mass Transfer and Transport in a Geologic Environment," LBL-19430, Lawrence Berkeley Laboratory (1985).
27. C. L. Kim *et al.*, "Near-Field and Far-Field Mass Transfer in a Geologic Repository," *Trans. Am. Nucl. Soc.*, 47, 87-89 (1984).
28. C. L. Kim, "Analyses of Mass Transfer from Solid Waste in a Geologic Environment," Ph. D. Dissertation, Department of Nuclear Engineering, University of California, Berkeley (1987).
29. T. H. Pigford *et al.*, "A Study of the Isolation System for Geologic Disposal of Radioactive Wastes," National Academy Press, Washington, D. C. (1983).