



## Modeling of nuclide release from low-level radioactive paraffin waste: a comparison of simulated and real waste

Ju Youl Kim<sup>a,\*</sup>, Chang Lak Kim<sup>b</sup>, Chang Hyun Chung<sup>a</sup>

<sup>a</sup> Department of Nuclear Engineering, Seoul National University, San 56-1 Shinrim-dong, Gwanak-gu, Seoul 151-742, South Korea

<sup>b</sup> Nuclear Environment Technology Institute, Korea Hydro & Nuclear Power Co. Ltd., 150 Dukjin-dong, Yuseung-gu, Daejeon 305-600, South Korea

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### Abstract

Nuclide leaching models based on mass transfer theory are reviewed and evaluated to analyze the leaching test results of simulated and real paraffin waste from Korean nuclear power plants (NPPs). An empirical model (EM), bulk diffusion model (BDM), coupled diffusion/dissolution model (CDDM), shrinking core model (SCM), modified SCM (MSCM), and uniform reaction model (URM) are selected for comparison. In case of simulated paraffin waste form, the experimental results are satisfactorily explained by the SCM which is based on a diffusion-controlled dissolution reaction. Leaching behavior of real paraffin waste form is well predicted by URM that considers inter-aggregated porous medium and intra-aggregated porous medium separately. If real paraffin waste forms are manufactured with relatively uniform composition, their leaching behaviors are expected to be similar to those of simulated paraffin waste forms.

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*Keywords:* Paraffin waste form; Nuclide release; Leaching model; Shrinking core model; Uniform reaction model

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### 1. Introduction

Low and intermediate level radioactive wastes (LILWs) generated from the operation of nuclear power plants (NPPs) need to be isolated from the human environment for at least few hundreds years. LILWs are solidified by mixing the waste with binder. The binder

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\* Corresponding author. Tel.: +82-2-880-8331; fax: +82-2-889-2688.

E-mail address: hispeace4u@hanmail.net (J.Y. Kim).

forms a monolithic solid by reacting chemically with the waste, by forming microscopic cells that encapsulate the waste, or by coating and binding the individual particles of waste together. The primary reason for solidifying waste is to satisfy regulatory requirements [1]. The widely used solidification agents are portland cements, blended cements (with flyash, slags, etc.), bitumen, polymers, and glass.

From the Korean radioactive waste management program, LILWs are scheduled to be disposed in an engineered near-surface disposal facility or in a mined cavity disposal facility by 2008. Radionuclides immobilized in waste forms could be released by the contact with infiltrating groundwater after the repository closure. The release mechanisms of radionuclides are related to various physico-chemical processes, such as diffusion, dissolution, adsorption, and chemical reaction. The modeling of radionuclide release from waste forms plays an important role in determining source term for the performance assessment of radioactive waste repository.

The liquid concentrates generated from Korean NPPs have been stabilized with paraffin wax since 1995 using the concentrate waste drying system (CWDS) [2]. The leaching mechanism of paraffin waste form is typically studied to develop its acceptance criteria and to obtain its source term for the performance assessment of radioactive waste repository. Previous studies [3–5] on leaching of simulated paraffin wastes show that about 55–65% of boric acid and 63–70% of cobalt, strontium, and cesium immobilized in the waste form are released during 90 days of leaching. The leaching behaviors of cobalt, strontium, and cesium also have been observed to be very similar. The leaching of these nuclides is expected to occur only on the surface contacted with leachant and along with the dissolution of boric acid which is the main ingredient of the dried liquid concentrate. The concentrations of cobalt, strontium, and cesium are quite low in comparison with their respective solubility. Thus, the leaching of cobalt, strontium, and cesium is not limited by the respective solubilities. The leaching rates of boric acid and these nuclides are controlled by the leached layer and reduced gradually.

Recently, a leaching test of real paraffin waste forms has been performed according to ANSI/ANS-16.1 test procedure [6–8]. The real paraffin waste forms show a leaching behavior of asymmetric breakthrough curves with high initial leaching rate followed by very low leaching rate. This behavior is quite different from that of the simulated paraffin waste form in view of distinct rate-controlling steps during the leaching process. The real waste forms have relatively unfavorable properties on homogeneity, compressive strength, and leaching resistance in comparison with the simulated waste forms elaborately made in laboratory for leaching tests. Paraffin binder may not be homogeneously mixed with dried concentrate waste, and the waste form has a complex entangled structure of aggregates. The enlarged surface of the simulated paraffin wastes taken by scanning electron microscope (SEM) is shown in Fig. 1. The structure of the real paraffin wastes is expected to be less dense than that of the simulated paraffin wastes. Therefore, the leaching characteristics are expected to be analogous to non-ideal transport of aggregated porous media as shown in Fig. 2 [9,10].

In the present study, mathematical models used to predict leaching behaviors of both simulated waste forms and real waste forms are presented, and their mechanisms and characteristics are compared. The suggested models are (1) empirical model (EM), such as orthogonal polynomial equation, power law of Freundlich type, hyperbola formula

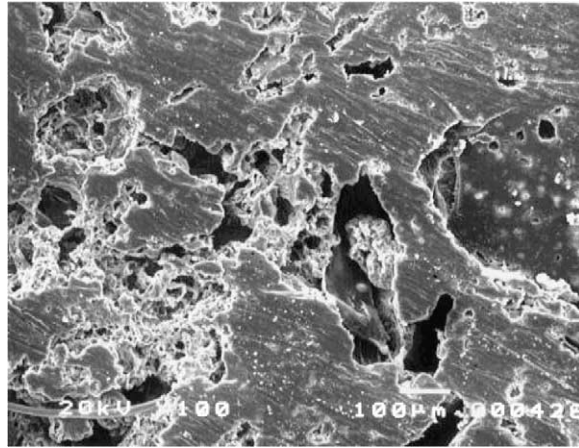


Fig. 1. Enlarged surface of simulated paraffin waste form taken by SEM.

of Langmuir type, Weibull model, and logarithmic relation; (2) bulk diffusion model (BDM) for a semi-infinite geometry, a finite cylinder and a sphere, respectively; (3) coupled diffusion/dissolution model (CDDM), such as diffusion model with concentration-dependent dissolution and diffusion model with surface dissolution; (4) shrinking core model (SCM) for a semi-infinite medium, an infinite cylinder and a sphere, respectively; (5) modified SCM (MSCM) considering wash-off effect; and finally (6) uniform reaction model (URM).

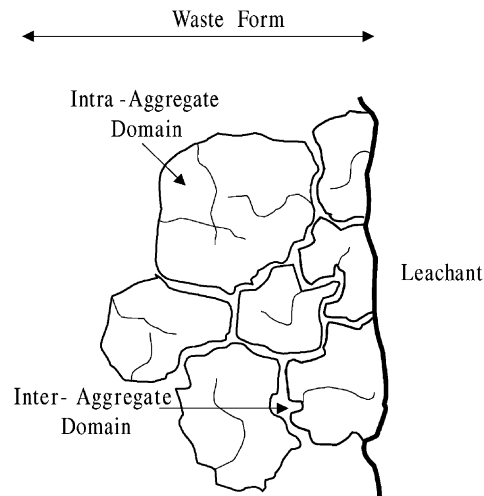


Fig. 2. Conceptual picture of real paraffin waste form with aggregate porous media.

## 2. Leaching models

### 2.1. Empirical model (EM)

The orthogonal polynomial is one of the most useful empirical equations [11]. Its general form is

$$y(x) = \sum_{i=0}^n A_i \phi_i(x) \quad (1)$$

where  $A_i$  is the parameter to be determined and  $\phi_i$  the function of  $x$ . In this study, the cumulative fraction leached (CFL) is given by

$$\text{CFL} = \sum_{i=0}^n A_i t^{i/2} \quad (2)$$

Then, the following third-degree polynomial is fitted to the leaching data of the simulated and the real waste forms:

$$\text{CFL} = A_0 + A_1 t^{1/2} + A_2 t \quad (3)$$

The three terms in the above expression represent three kinetic behaviors observed during leaching. The first term accounts for the loosely bound material that would be leached instantaneously and easily washed away. The second term represents the contribution of diffusive release. The final term is a first-order kinetic term and represents chemical reactions, such as dissolution, corrosion, or solubility control. If the leachate concentration is negligible and the pore solution within the waste form remains saturated, the driving force for diffusion is constant. Thus, the leaching rate will remain constant until the soluble portion of waste matrix was completely dissolved out.

A power law, such as the Freundlich type, which is one of the useful empirical equations, also can be applied as follows [12]:

$$\text{CFL} = at^b \quad (4)$$

The constants for this model must be estimated using a regression analysis. The CFL predicted by this equation does not approach to unit with time.

A hyperbola formula of the Langmuir type has the following form [12]:

$$\text{CFL} = \frac{at}{1 + bt} \quad (5)$$

The release is first-order at low values of  $t$  and decreases to zero-order as  $t$  increases. The following modified hyperbola formula with three parameters is used to analyze the leaching data of real paraffin waste form.

$$\text{CFL} = a + \frac{b}{t + c} \quad (6)$$

The Weibull equation can be successfully applied to almost all kinds of dissolution reactions [13]. When applied to nuclide release from paraffin waste form, the Weibull equation

expresses the CFL of nuclide by

$$\text{CFL} = 1 - \exp\left(-\frac{t^b}{a}\right) \quad (7)$$

where  $a$  is the scale parameter which represents time scale of the process and  $b$  the shape parameter of curve. If  $b = 1$ , the curve is characterized by exponential, whereas if  $b > 1$ , the curve is sigmoid and S-shaped with upward curvature followed by a turning point, and if  $b < 1$ , the curve is parabolic with a high initial slope followed by an exponential shape.

The following logarithmic relation, a modified form of Elovich equation, is also fitted to the leaching curves [14]. This relationship assumes that the rate of adsorption can be replaced by the rate of extraction [15,16].

$$\text{CFL} = a + b \ln t \quad (8)$$

The above EMs can be used to check for the predominant leaching mechanism.

## 2.2. Bulk diffusion model (BDM)

Generally, in conventional diffusion-controlled matrix systems, where the solute to be released is uniformly distributed in monolithic waste form, the release of a dissolved nuclide inherently follows first-order diffusion with an initially high release rate followed by a rapidly declining nuclide release rate. The basic assumption of BDM is that nuclide release is a result of the concentration gradient between the leachant and the bulk concentration within the waste form. Consider a semi-infinite medium with uniform initial concentration,  $C_0$ . If the surface concentration is maintained at zero for a  $t > 0$  (i.e. perfect sink condition), the solution of mass transport equation can be derived from the Fick's second law [17].

$$\begin{aligned} \frac{\partial C}{\partial t} &= D_e \frac{\partial^2 C}{\partial x^2}, & t = 0, x > 0, C = C_0; & \quad t > 0, x = \infty, C = C_0; \\ & & t > 0, x = 0, C = 0 & \end{aligned} \quad (9)$$

$$C(x, t) = C_0 \operatorname{erf}\left(\frac{x}{2\sqrt{D_e t}}\right) \quad (10)$$

where erf is the error function,  $D_e$  the effective diffusion coefficient ( $\text{cm}^2/\text{s}$ ) and  $t$  is time. CFL is obtained from the ratio of the amount of the nuclide released at time  $t$ ,  $M_t$ , to the total initial amount of the nuclide loaded in the waste form,  $M_\infty$

$$\text{CFL} = \frac{M_t}{M_\infty} = 2 \left(\frac{S}{V}\right) \left(\frac{D_e t}{\pi}\right)^{1/2} \quad (11)$$

where  $S$  is the surface area exposed to leachant,  $V$  the volume of the specimen. The fraction of nuclide released is proportional to the square root of time. Alternatively, the nuclide release rate is proportional to the reciprocal of the square root of time. A proportionality between the cumulative amount of nuclide released and the square root of time is commonly regarded as an indicator for diffusion-controlled nuclide release.

Nestor [18] described an analytical solution of Fick's second law for cylindrical geometry. For a finite cylindrical waste form of height  $H$  and radius  $R$ ,

$$\text{CFL} = 1 - \frac{32}{\pi^2} \sum_{n=1}^{\infty} \frac{\exp[-((2n-1)\pi/H)^2 D_e t]}{(2n-1)^2} \sum_{m=1}^{\infty} \frac{\exp[-(\beta_m/R)^2 D_e t]}{\beta_m^2} \quad (12)$$

where the parameter  $\beta_m$  represents the  $m$ th zero of the zero-order cylindrical Bessel function. This model is applicable to waste forms that range from the shape of a flat disk (radius > height) to that of a cylindrical rod (radius < height), the nuclide being homogeneously distributed with the waste form.

If the nuclide is molecularly dissolved in a spherical waste form with a radius of  $R_e$ , the release of nuclide by diffusion can be expressed by the following equation [17].

$$\text{CFL} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{\exp[-(n\pi/R_e)^2 D_e t]}{n^2} \quad (13)$$

### 2.3. Coupled diffusion/dissolution model (CDDM)

In some waste forms, such as borosilicate glasses, the released nuclides appear to be explained by diffusion and dissolution processes. For a semi-infinite medium, the solution for diffusion with concentration-dependent dissolution is given by the expression [19].

$$\frac{\partial C}{\partial t} = D_e \frac{\partial^2 C}{\partial x^2} + k(C_s - C) \quad (14)$$

with the initial and boundary conditions as follows:

$$\begin{aligned} \text{IC} : t = 0, x > 0, C = C_s; \quad \text{BC} : t > 0, x = \infty, C = C_s, \\ t > 0, x = 0, C = 0 \end{aligned} \quad (15)$$

$$\text{CFL} = \left(\frac{S}{V}\right) (D_e k)^{1/2} \left[ \left(t + \frac{1}{2k}\right) \text{erf}(kt)^{1/2} + \left(\frac{t}{\pi k}\right)^{1/2} \exp(-kt) \right] \quad (16)$$

where  $k$  is the dissolution constant (per day).

For diffusion with surface dissolution (i.e. moving boundary), the solution is given by the expression [19]:

$$\text{CFL} = \left(\frac{S}{V}\right) (D_e \gamma)^{1/2} \left[ \left(t + \frac{1}{2\gamma}\right) \text{erf}(\gamma t)^{1/2} + \left(\frac{t}{\pi \gamma}\right)^{1/2} \exp(-\gamma t) + t \right] \quad (17)$$

where  $\gamma = u^2/4D_e$  is the moving boundary constant (per day) and  $u$  the moving boundary velocity (cm per day).

### 2.4. Shrinking core model (SCM)

The initial nuclide concentration in the waste form may be above or below saturation. If above, the core concentration will be at the saturation until a sufficient amount of nuclide is released. If below, the core concentration will decrease continuously with time.

Theoretical models of monolithic (matrix-type) diffusion-controlled release devices assume that any amount of solute introduced into the waste form above the saturation limit (i.e. super-saturated) is in an immobile dispersed state [20–23]. In this system, the active agent (nuclide) is dispersed in the matrix and diffuses through the matrix continuum or inter-granular openings.

Most models describing the above processes are similar to those used for non-catalytic heterogeneous reactions, for example, SCM. The SCM considers that the leaching process is controlled either by the diffusion of reagent through a solid product layer, or through the liquid boundary layer, or by the rate of surface chemical reaction. In the BDM, nuclide leaching is considered as a result of diffusion from the monolithic waste form into the leachant, but in the SCM, nuclide leaching results from the diffusion of water into the solid matrix. As water penetrates into the matrix, a leached layer that is depleted of nuclide is formed and the sharp interface (dissolution front) between the inner core and the leached layer is moving inwardly. The inner core of the waste form is assumed to remain as a uniform concentration.

The simplified SCM for the leaching mechanism of simulated paraffin waste form is developed in the earlier study [3]. For a semi-infinite medium, the relation between CFL and time can be derived from the assumption that the dissolution rate at the dissolution front is equal to the diffusion rate through the leached layer, i.e. quasi-steady state condition:

$$\text{CFL} = \frac{1}{L} \sqrt{2D_e \frac{C_s}{C_0} t} \quad (18)$$

where  $L$  is the length of waste form (cm),  $C_s$  the solubility of nuclide in the waste form ( $\text{g}/\text{cm}^3$ ), and  $C_0$  is the initial nuclide concentration ( $\text{g}/\text{cm}^3$ ). Similar to the BDM, the fraction of nuclide released is proportional to the square root of time although both physical circumstances are substantially different, i.e. monolithic dissolved state versus monolithic dispersed state. The above equation is appropriate when  $C_0 > C_s$ , such as for boric acid. If  $C_0 < C_s$ , such as with cobalt and cesium,  $C_0/\varepsilon$  must be substituted for  $C_s$  as follows:

$$\text{CFL} = \frac{1}{L} \sqrt{2 \frac{D_e}{\varepsilon} t} \quad (19)$$

For an infinite cylindrical waste form of radius  $R$ ,

$$\text{CFL} + (1 - \text{CFL}) \ln(1 - \text{CFL}) = 4D_e \frac{C_s}{C_0} \frac{t}{R^2} \quad (20)$$

For a spherical waste form of equivalent radius  $R_e$ ,

$$1 - \frac{2}{3}\text{CFL} - (1 - \text{CFL})^{2/3} = 2D_e \frac{C_s}{C_0} \frac{t}{R_e^2} \quad (21)$$

where  $R_e$  is the radius of sphere having an equivalent external surface area to finite cylindrical waste form.

### 2.5. Modified shrinking core model (MSCM)

In the SCM for a simulated paraffin waste form, the conservative condition of zero surface concentration is assumed for  $t > 0$ , because the specimen is carefully manufactured and the leachant is periodically renewed. But this condition is not valid for a real paraffin waste form. If the instantaneous release fraction at the beginning of leaching test,  $CFL_{\text{wash-off}}$ , is considered, Eq. (21) can be rewritten as follows:

$$1 - \frac{2}{3}CFL_e - (1 - CFL_e)^{2/3} = 2D_e \frac{C_s}{C_0} \frac{t}{R_e^2} \quad (22)$$

where  $CFL_e = (1 - CFL_{\text{wash-off}}) \times (CFL - CFL_{\text{wash-off}})$

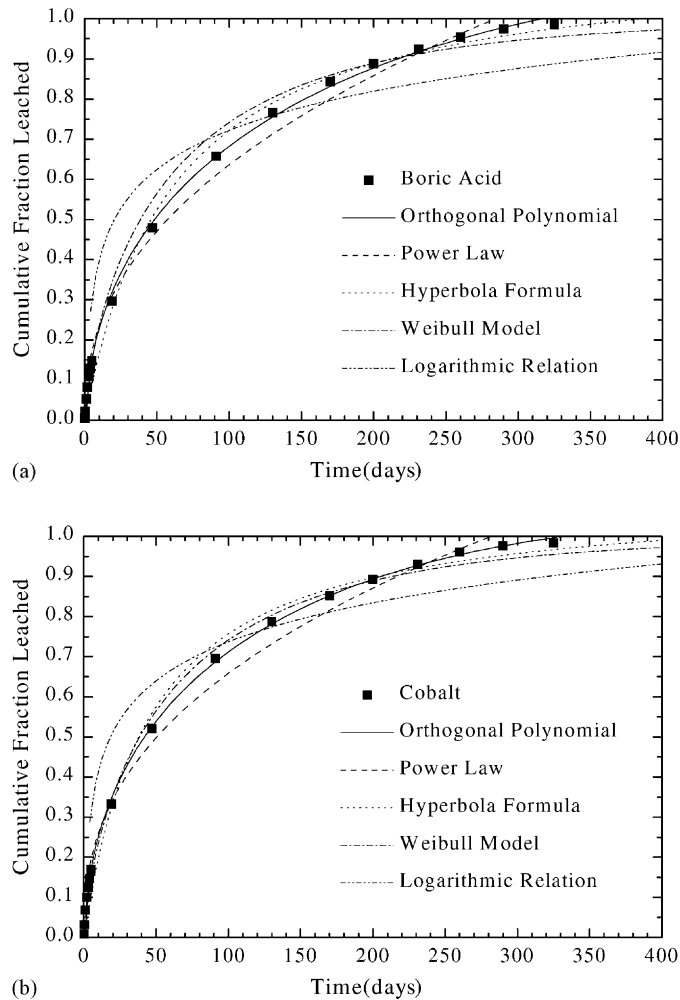


Fig. 3. Comparisons of the EMs to experimental results of boric acid (a) and cobalt (b) for simulated paraffin waste form.



Table 1  
Parameters of leaching models for simulated paraffin waste ( $\chi^2$  is the Chi-square value)

Models	Parameters	Boric acid	Cobalt
<b>EM</b>			
Orthogonal polynomial	$A_0$	-0.03712	-0.02836
	$A_1$	0.08942	0.09542
	$A_2$	-0.00175	-0.00214
	$\chi^2$	0.00015	0.00006
Power law	$a$	0.08657	0.10271
	$b$	0.43307	0.40345
	$\chi^2$	0.00142	0.00162
Hyperbola formula	$a$	0.01920	0.02186
	$b$	0.01661	0.00144
	$\chi^2$	0.00114	0.02411
Weibull model	$a$	18.72881	18.72881
	$b$	0.70195	0.70195
	$\chi^2$	0.00055	0.00044
Logarithmic relation	$a$	0.07536	0.09182
	$b$	0.14043	0.14011
	$\chi^2$	0.01742	0.01494
<b>BDM</b>			
Semi-infinite medium	$S$ (cm <sup>2</sup> )	196.34954	196.34954
	$V$ (cm <sup>3</sup> )	196.34954	196.34954
	$D_e$ (cm <sup>2</sup> /s)	$3.34491 \times 10^{-8}$	$3.44907 \times 10^{-8}$
	$\chi^2$	0.00347	0.00377
Finite cylinder	$H$ (cm)	10	10
	$R$ (cm)	2.5	2.5
	$D_e$ (cm <sup>2</sup> /s)	$7.75463 \times 10^{-8}$	$8.41435 \times 10^{-7}$
	$\chi^2$	0.0023	0.00234
Sphere	$R_e$ (cm)	3.95	3.95
	$D_e$ (cm <sup>2</sup> /s)	$1.33796 \times 10^{-7}$	$1.46065 \times 10^{-7}$
	$\chi^2$	0.0023	0.00234
<b>CDDM</b>			
Diffusion with concentration-dependent dissolution	$D_e$ (cm <sup>2</sup> /s)	$4.96528 \times 10^{-8}$	$4.96528 \times 10^{-8}$
	$k$ (per day)	$3.66260 \times 10^{-9}$	$5.98790 \times 10^{-9}$
	$\chi^2$	0.02354	0.02499
Diffusion with surface dissolution	$D_e$	$2.71991 \times 10^{-8}$	$2.71991 \times 10^{-8}$
	$k$ (per day)	$5.0 \times 10^{-5}$	$5.0 \times 10^{-5}$
	$\chi^2$	0.00406	0.00619
<b>SCM</b>			
Semi-infinite medium	$L$ (cm)	1	1
	$D_e$ (cm <sup>2</sup> /s)	$4.22801 \times 10^{-7}$	$1.53935 \times 10^{-8}$
	$C_s$ (g/cm <sup>3</sup> )	0.05	–
	$C_0$ (g/cm <sup>3</sup> )	0.9918	–
	$\varepsilon$	0.7	0.7
	$\chi^2$	0.0023	0.00377

Table 1 (Continued)

Models	Parameters	Boric acid	Cobalt
Infinite cylinder	$R$ (cm)	2.5	2.5
	$D_e$ (cm <sup>2</sup> /s)	$1.10197 \times 10^{-6}$	$3.96991 \times 10^{-8}$
	$C_s$ (g/cm <sup>3</sup> )	0.05	–
	$C_0$ (g/cm <sup>3</sup> )	0.9918	–
	$\varepsilon$	0.7	0.7
	$\chi^2$	0.00022	0.00049
Sphere	$R_e$ (cm)	3.95	3.95
	$D_e$ (cm <sup>2</sup> /s)	$1.61690 \times 10^{-6}$	$5.70602 \times 10^{-8}$
	$C_s$ (g/cm <sup>3</sup> )	0.05	–
	$C_0$ (g/cm <sup>3</sup> )	0.9918	–
	$\varepsilon$	0.7	0.7
	$\chi^2$	0.00002	0.00005

EM: empirical model; BDM: bulk diffusion model; CDDM: coupled diffusion/dissolution model; SCM: shrinking core model.

## 2.6. Uniform reaction model (URM)

URM assumes that all of the sub-particles in the system react uniformly. The dissolution rate in each aggregate is given by the following first-order rate equation:

$$\frac{dC}{dt} = -k(C - C_e) \quad (23)$$

where  $C$  is the nuclide concentration of the solid aggregate at time equal to  $t$ ,  $k$  the rate constant (per day), and  $C_e$  is the equilibrium concentration, i.e. nuclide concentration of the leach residue within the aggregate at the theoretically infinite time. By separating variables and integrating

$$\text{CFL} = \text{CFL}_e(1 - e^{-kt}) \quad (24)$$

where  $\text{CFL}_e$  is the ultimate leaching fraction of nuclide within the inter- or intra-aggregate. Thus, the final form of URM can be represented as

$$\text{CFL} = \text{CFL}_1(1 - e^{-k_1t}) + \text{CFL}_2(1 - e^{-k_2t}) + (1 - \text{CFL}_1 - \text{CFL}_2) \quad (25)$$

where  $\text{CFL}_1$  and  $\text{CFL}_2$  are ultimate extractions of nuclides within the inter- and intra-aggregate, respectively. The first and second term of the above equation explain time-dependent wash-out within the inter- and intra-aggregate, respectively. As expected, the leaching rate in the inter-aggregate domain represents a higher initial rate and that in the intra-aggregate domain represents a relatively lower rate in the latter period. The third term expresses the effect of time-independent instantaneous wash-off as previously stated. The URM is similar to the following volume reaction model (VRM) proposed by Wen [20].

$$-\ln(1 - \text{CFL}) = kt \quad (26)$$

### 3. Methods

The detailed explanations of experimental materials, specimen preparation, and leaching test are shown in the previous studies [3–5]. Only an outline is given here because the objective of this study is focused on the evaluation of leaching models for paraffin wastes. Boric acid and paraffin are two major constituents of the paraffin waste form. The properties of paraffin wax are a specific gravity of 0.933, melting temperature of 72 °C, insolubility in water, and thermoplastic material. Boric acid has a specific gravity of 1.44 and a melting temperature of 171 °C. The waste form is prepared under the mixing tem-

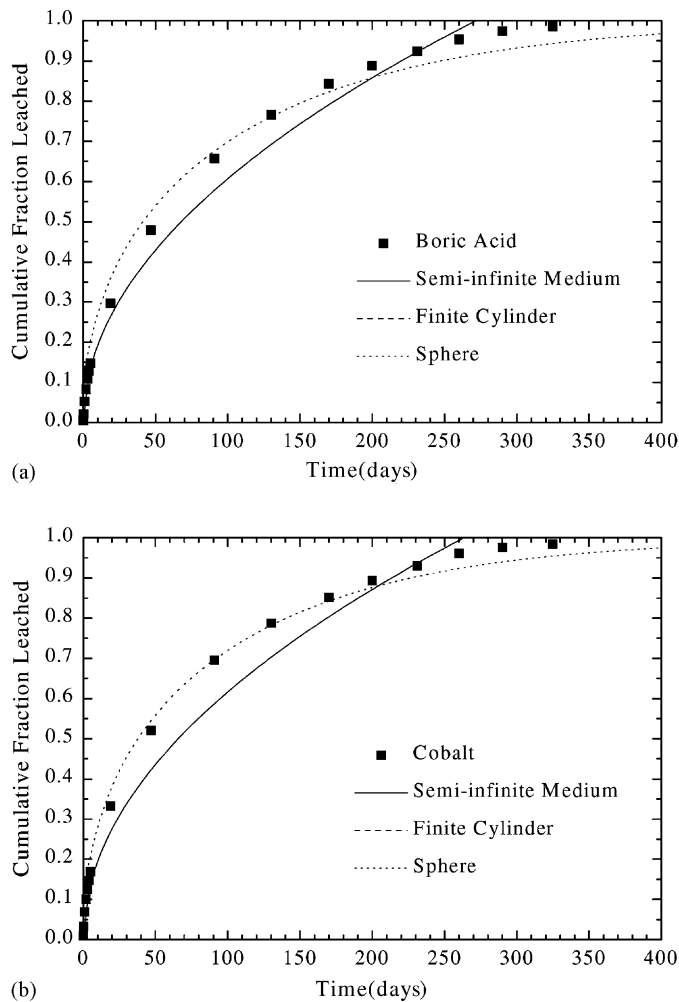


Fig. 4. Comparisons of the BDMs to experimental results of boric acid (a) and cobalt (b) for simulated paraffin waste form.

perature of 120–140 °C, stirrer speed of 600 rpm, and operation time of about 15 min. The mixture is poured into cylindrical PVC mold and hardened at a room temperature for a week. A cylindrical waste form with a diameter of 5 cm and a height of 10 cm is prepared. The mixing ratio of boric acid to paraffin is very important in order to make a homogeneous waste form. The leaching test is performed according to ANSI/ANS-16.1 standard procedure [8]. Demineralized water (0.03  $\mu\text{S}/\text{cm}$ ) is used as leachant and the temperature of leachant is maintained at 22.5 °C during the leaching test. Ratio of leachant volume to external surface of specimen is 10 cm. The leachant is replaced at the frequency of 2, 7 h; 1–5, 19, 47 and 90 days. The leachate including the released nuclide is analyzed by titration

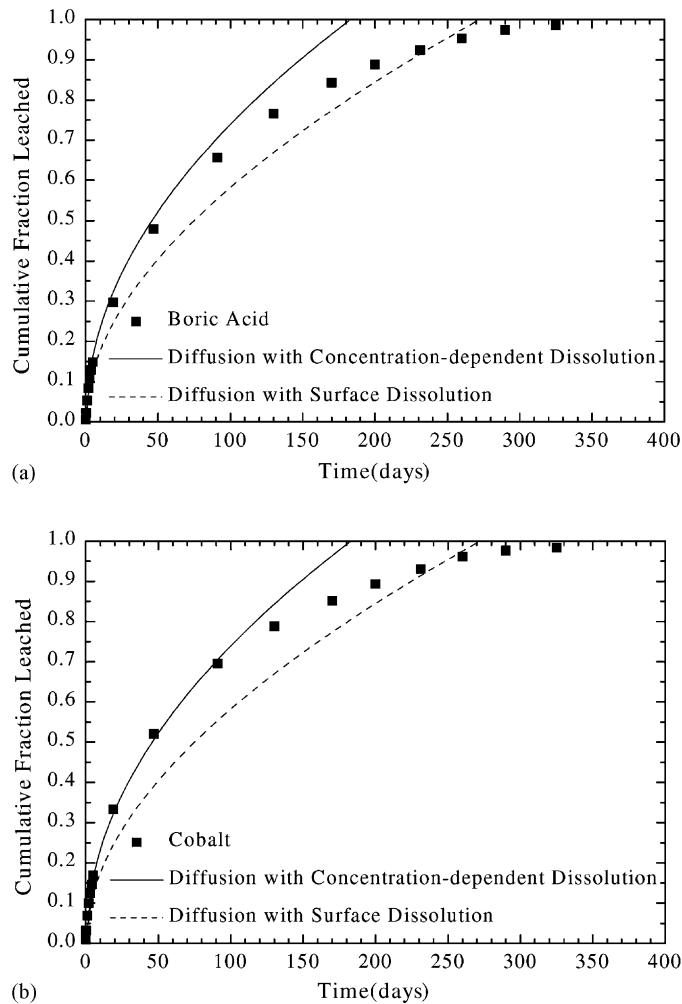


Fig. 5. Comparisons of the CDDMs to experimental results of boric acid (a) and cobalt (b) for simulated paraffin waste form.

for the concentration of boric acid, and by inductive coupled plasma–mass spectroscopy (ICP–MS) for the concentration of cobalt and cesium.

#### 4. Results and discussion

Fig. 3 shows the comparisons of the EMs to experimental results of boric acid and cobalt for the simulated paraffin waste form. The regular leaching test is extended to 325 days. The orthogonal polynomial model among the EMs appears to give the best fit to the test

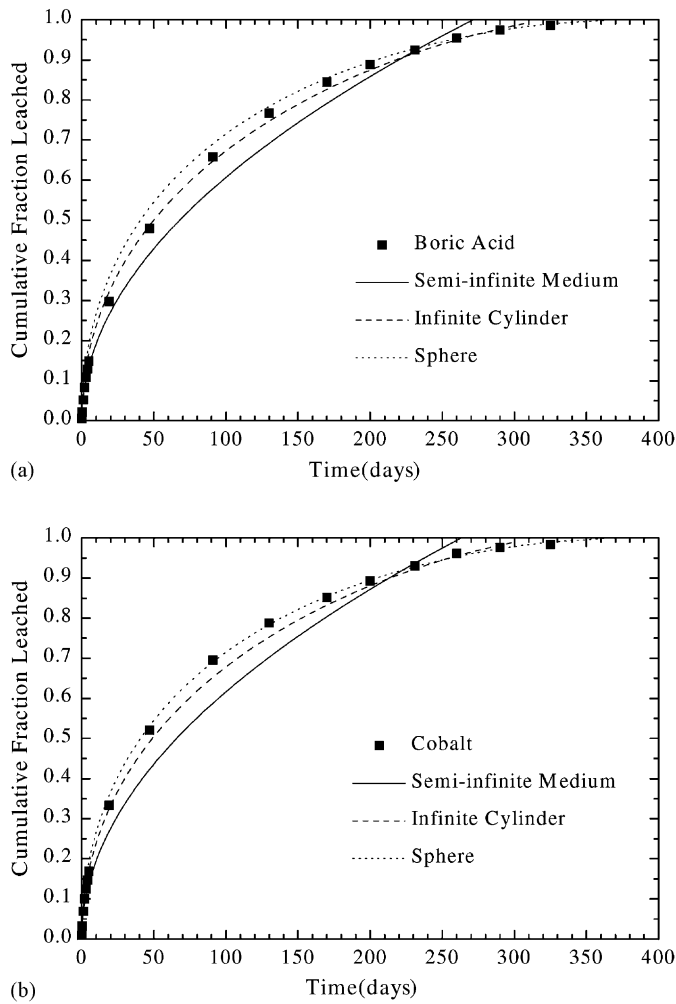


Fig. 6. Comparisons of the SCMs to experimental results of boric acid (a) and cobalt (b) for simulated paraffin waste form.

results. Various parameters of leaching models for simulated paraffin waste obtained from the non-linear least square fitting (NLSF) are shown in Table 1.

Because the second term of the orthogonal polynomial,  $A_1$ , is the largest value, diffusion is inferred to be the rate-controlling mechanism. Accordingly we apply the conventional diffusion model to the leaching data as shown in Fig. 4. BDMs for both finite cylinder and sphere agree well with the leaching behavior of paraffin waste form. The trends of these two models are very similar, so only one curve is shown in Fig. 4 due to overlapping. However, based on the observation of the internal section of the waste form [3–5], BDM cannot explain the leached layer and shrinking dissolution front formed during the reaction. The reaction initially occurs at the external surface of waste form and the dissolution front

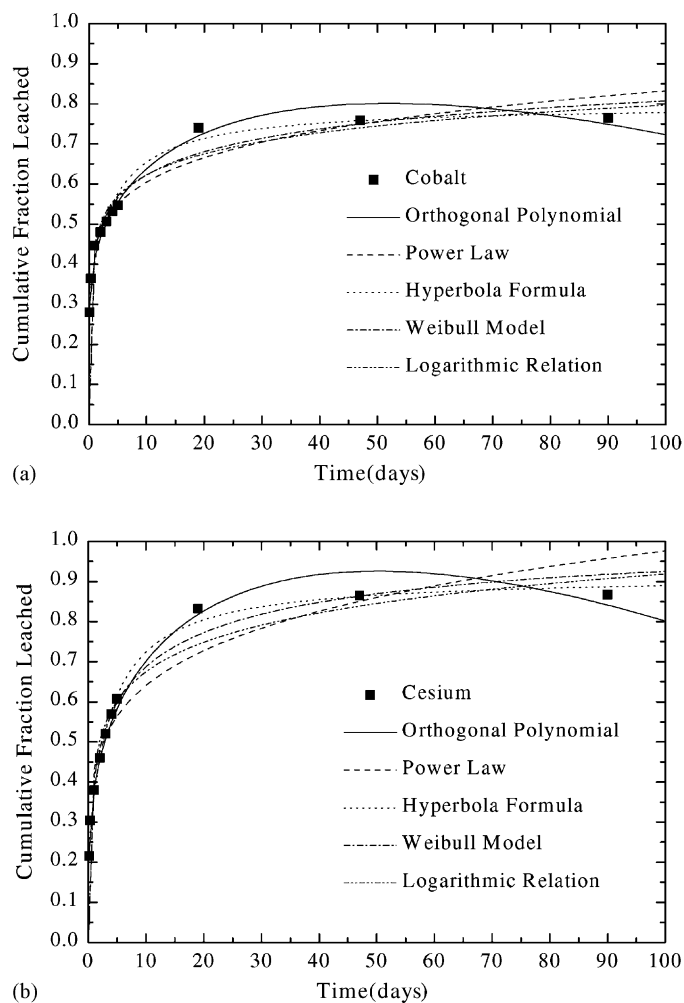


Fig. 7. Comparisons of the EMs to experimental results of cobalt (a) and cesium (b) for real paraffin waste form.

gradually moves inside, leaving a leached layer behind. The leaching rates of boric acid and cobalt are influenced by the leached layer depth as the reaction progresses. This leached layer decreases the diffusive fluxes of nuclides and controls the overall dissolution rates.

As a result of these observations, we first try to apply the CDDM to the test results as shown in Fig. 5. However, this model overestimates or underestimates the results because the model does not consider the diffusion of nuclide through a solid leached layer. Under these circumstances, we develop the SCM considering the leached layer and inwardly moving dissolution front. Although the waste form is a finite cylinder, SCM for a spherical waste form gives the best fit to the results in Fig. 6 because the leaching reaction uniformly occurs at the entire surface area.

Fig. 7 shows the comparisons of the EMs to experimental results of cobalt and cesium for a real paraffin waste form. Unlike the case for a simulated waste, the modified hyperbola formula agrees well with the test data. The release is nearly first-order initially and rapidly decreases to zero-order as the time increases. This leaching behavior is similar to the breakthrough curve whose characteristic is initially high release rate followed by a rapidly declining release rate. This implies that different rate-controlling steps exist around 5 days. This observation is also confirmed in comparison with MSCM as shown in Fig. 8.

The leaching behavior of real paraffin waste form is well predicted by MSCM up to 5 days. As shown in Table 1 and Table 2, the effective diffusion coefficient of cobalt for a real waste is the same value ( $5.71 \times 10^{-8} \text{ cm}^2/\text{s}$ ) as that for a simulated waste, predicted by the SCM. Although the SCM is modified to consider time-independent wash-off, the data after 19 days are not predicted. The reason is that the waste form is not homogeneously manufactured. Thus, we develop the URM with the assumption that the nuclide is macroscopically distributed into two aggregates (inter and intra).

Fig. 9 shows that the leaching behavior of real paraffin waste form can be well explained by the URM. From Table 2, ultimate leaching fractions of cobalt and cesium within the

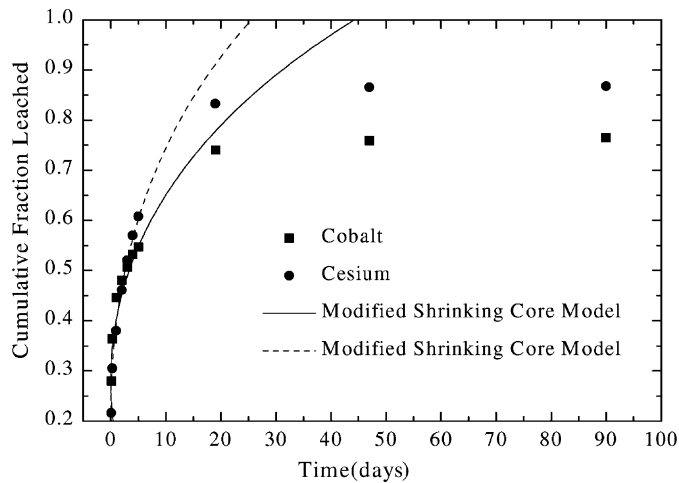


Fig. 8. Comparisons of the MSCMs to experimental results of cobalt (a) and cesium (b) for real paraffin waste form.

Table 2  
Parameters of leaching models for real paraffin waste

Models	Parameters	Cobalt	Cesium
EM			
Orthogonal polynomial	$A_0$	0.28343	0.19462
	$A_1$	0.14376	0.20649
	$A_2$	-0.00998	-0.01458
	$\chi^2$	0.00076	0.00101
Power law	$a$	0.43965	0.42073
	$b$	0.13856	0.18278
	$\chi^2$	0.00131	0.00362
Modified hyperbola formula	$a$	0.79744	0.91493
	$b$	-2.01921	-2.63647
	$c$	4.14950	3.83557
	$\chi^2$	0.00068	0.00047
Weibull model	$a$	1.73188	1.91267
	$b$	0.22756	0.34758
	$\chi^2$	0.00081	0.00114
Logarithmic relation	$a$	0.44886	0.43193
	$b$	0.07562	0.10563
	$c$	0.00103	0.00225
MSCM			
Sphere	$R_e$ (cm)	3.95	3.95
	$D_e$ (cm <sup>2</sup> /s)	$5.71 \times 10^{-8}$	$1.50 \times 10^{-7}$
	$\varepsilon$	0.70	0.70
	CFL <sub>wash-off</sub>	0.280	0.216
	$\chi^2$	0.06427	0.04419
URM			
	CFL <sub>1</sub>	0.410	0.588
	CFL <sub>2</sub>	0.261	0.164
	$k_1$ (per day)	0.184	0.203
	$k_2$ (per day)	0.001	0.003
	$\chi^2$	0.00121	0.00059

EM: empirical model; MSCM: modified shrinking core model; URM: uniform reaction model.

inter-aggregate are 0.410 and 0.588, respectively. Only small CFLs of 0.261 and 0.164 for cobalt and cesium, respectively, are strongly immobilized with paraffin binder.

If the real waste is uniformly manufactured, the waste form with only one aggregate is expected to act like a monolithic matrix and the leaching behavior of real waste will be similar to that of simulated waste. In this case, the URM is reduced to the following two-parameter model:

$$\text{CFL} = \text{CFL}_e(1 - e^{-kt}) + (1 - \text{CFL}_e) \quad (27)$$

where CFL<sub>e</sub> is ultimate leaching fraction of nuclide immobilized within the waste form and (1-CFL<sub>e</sub>) is the time-independent fraction at the earlier period of leaching test. Fig. 10 shows that the URM with two parameters can be successfully applicable to the test data of



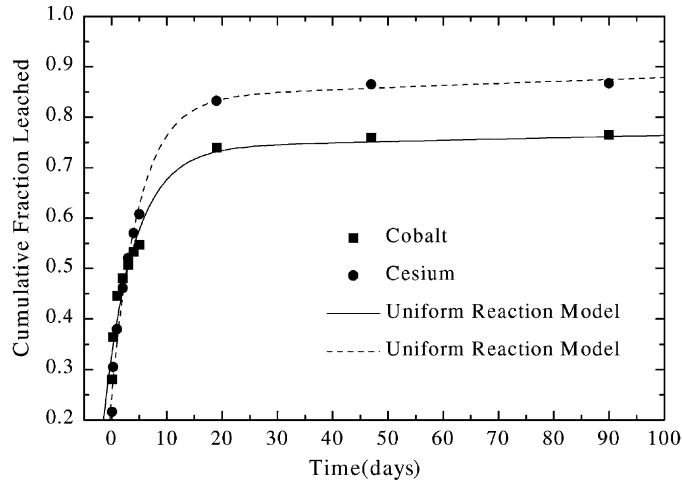


Fig. 9. Comparisons of the URMs to experimental results of cobalt (a) and cesium (b) for real paraffin waste form.

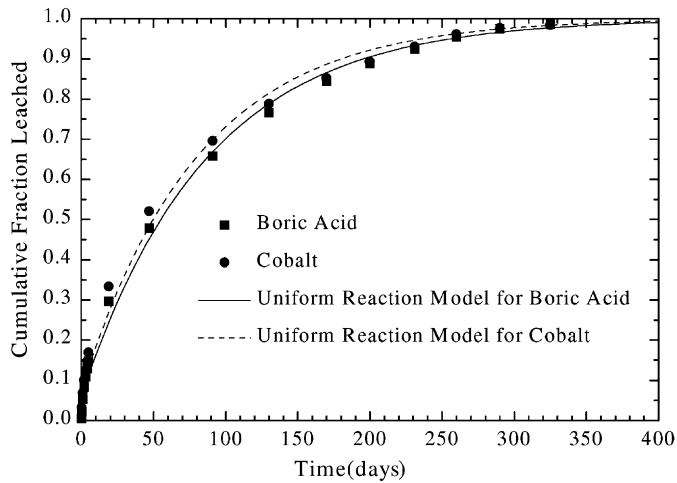


Fig. 10. Comparisons of the URMs to experimental results of boric acid and cobalt for simulated paraffin waste form.

simulated paraffin waste. The  $CFL_e$  of boric acid and cobalt are 0.93876 and 0.92377, respectively, and the rate constants,  $k$  (per day), for boric acid and cobalt are estimated to be 0.01145 and 0.01234, respectively.

## 5. Conclusion

For the analysis of the leaching mechanisms for simulated and real paraffin waste forms, several leaching models are evaluated using experimental results. The leaching behavior

of simulated paraffin waste form can be expressed well by the SCM based on diffusion-controlled dissolution reaction. The test result of real paraffin waste form shows asymmetric breakthrough curve in aggregated porous media. The URM gives the best fit for describing the leaching data of real waste. If the real paraffin wastes were more uniformly manufactured, their leaching behaviors also would be predicted by the SCM.

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