

MODELS FOR THE ESTIMATION OF THE LEACHING OF RADIONUCLIDES
FROM LOW-LEVEL WASTE DISPOSAL FACILITIES

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ABSTRACT

A model which describes the in-situ leaching of low-level waste has been developed. The basic idea of this model is the mass-transfer of radionuclides from a fixed bed into a percolating liquid phase. The model which is formulated in terms of fundamental waste, facility, and environmental parameters considers both the equilibrium aspects and the kinetic aspects of leaching. The model is both tractable and flexible and has been extended to include such phenomena as solubility-limited leaching, leaching with adsorption by backfill, leaching in the presence of a chelating agent, and leaching under dispersive flow conditions.

INTRODUCTION

An important step in modeling the groundwater transport of contaminants from any waste disposal facility is the determination of source terms. Depending on the groundwater transport model used, these source terms may be expressed as concentrations, fluxes or leach fractions. In low-level waste disposal facilities the wastes are varied in physical form and chemical content. This introduces a complexity and an uncertainty into the process of estimating source terms that will likely never be eliminated. None-the-less, when such estimates must be made, the use of systematic methodologies based on wasteform, environmental, and facility parameters is preferable. In this paper, a methodology which has its roots in the mass transfer phenomenology of the chemical process industry is presented. The basic system considered is that of a liquid phase percolating down through a fixed bed. Mass transfer of the leached radionuclide from the waste to the leachant is assumed to be driven by a concentration gradient in the liquid phase. This model incorporates important waste, facility, and environmental parameters and considers both the equilibrium or thermodynamic aspects and the kinetic aspects of leaching.

In the following section the leach model is developed. The assumptions are stated, the basic transport equation is derived, and its solution is obtained both in the form of a concentration and a leach fraction. Next, the essential parameters and the difficulties associated with their determination are briefly discussed. Extensions of the model which incorporate other physical and chemical processes are then developed in the final section. Processes considered include solubility-limited leaching, leaching with concurrent adsorption by backfill, leaching in the presence of a chelating agent, and leaching under dispersive flow conditions.

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SIMPLIFIED MASS TRANSFER MODEL

In this section the elements of a simplified mass transfer model for leaching from low-level waste are presented. This model has its origins in the chemical process industry where models for ion exchange, adsorption and heat transfer in packed beds have been extensively developed.^{1,2} The model is formulated in terms of a percolating liquid phase (infiltration) and a stationary, fixed-bed solid phase (the waste/backfill matrix). The waste/backfill matrix is assumed to be homogeneous and decay of the radionuclide is neglected. Mass transfer of the species of interest from the waste is assumed to be driven by a concentration gradient existing between the leachant at the waste surface and the bulk leachant solution. Two coupled partial differential equations completely describe the time-dependent behavior of the system.

The first equation is for the percolating liquid:

$$\left(\frac{\partial C_L^i}{\partial t}\right)_z = -\epsilon v \left(\frac{\partial C_L^i}{\partial z}\right)_t - ka(C_L^i - C_L^{i*}) \quad (1)$$

where

$C_L^i(z,t)$ = the bulk concentration of species i at a depth z from the surface at time t

v = the interstitial velocity of the liquid

ϵ = the fraction of fluid filled space in the bed external to the solid phase

ka = the product of the mass transfer coefficient and the solid phase's specific area (surface area/volume)

This equation states that the change of C_L^i in an incremental volume at depth z is result of a convective process and an interphase mass transfer process driven by the concentration gradient, $C_L^i - C_L^{i*}$. The C_L^{i*} is the leachant concentration at the surface of the waste and is assumed to be at equilibrium with the solid phase concentration C_S^i .

The second equation describes the time behavior of the stationary phase, i.e., the waste:

$$\left(\frac{\partial C_S^i}{\partial t}\right)_z = -ka(C_L^{i*} - C_L^i) \quad (2)$$

The solutions $C_L^i(z,t)$ and $C_S^i(z,t)$ resulting from the simultaneous solution of these two coupled partial differential equations describe the time and spatial aspects of the leaching problem. These equations have the same form as the equations describing fixed-bed ion exchange, fixed-bed adsorption and fixed-bed heat exchange. Such systems have been thoroughly studied and their solutions have been tabulated and documented.^{1,2} Those solutions are given in the Appendix.

If the concentration in the stationary phase, $C_S^i(z,t)$ remains constant over a period of time, then the description of the leaching during that time is greatly simplified. A leachant/waste system with a low leach rate is such a constant system, at least in the initial stages of leaching. In these circumstances Eq. 2 is not required and Eq. 1 may be cast into a simple "steady-state" form:

$$\epsilon v \frac{dC_L^i(z)}{dz} = ka(C_L^{i*} - C_L^i) \quad (3)$$

The appropriate boundary condition is $C_L^i(0) = 0$ at the top of the waste. Integrating Eq. 3 the concentration at depth z is:

$$C_L^i(z) = C_L^{i*} \left(1 - e^{-kaz/\epsilon v}\right) \quad (4)$$

In the case of linear equilibrium C_L^{i*} may be written as $M_0^i C_S^i$ where M_0^i is the partition coefficient for the i th species. This relation may be substituted into Eq. 4.

The leach fraction is defined as the ratio $\lambda_L = q/Q$, where q is the activity of the radionuclide leached during a year and Q is the total activity present in the stationary phase at the beginning of the year. It follows that the leach fraction can be written in terms of the parameters p , z_0 , M_0^i and ka :

$$\lambda_L = q/Q = \frac{C_L V_L}{C_S V_W} = \frac{p}{z_0} M_0^i \left(1 - e^{-kaz_0/\epsilon v}\right) \quad (5)$$

where $V_L = pA$ and $V_W = z_0 A$ are the leachant and waste bulk volume, respectively, p , is the annual infiltration, and z_0 is the waste thickness.

The leach fraction may be considered to be a product of three components: an equilibrium component, M_0^i ; a mass transfer component, $1 - e^{-kaz_0/\epsilon v}$ and a geometric component, p/z_0 . The partition coefficient

M_0^i denotes the distribution of the leached species i between the moving liquid phase and the stationary phase. The chemical nature of this stationary phase, and hence M_0^i , varies according to the waste being modeled.

The mass transfer component is an expression of the system's kinetic aspects. The overall mass transfer coefficient, ka , is a function of the species diffusivities in both phases, the liquid phase velocity distribution and extent of the waste's contacting surface. At the microscopic level, the mass transfer process occurs in repeated small segments as individual parcels of leachant are brought into and out of contact with the waste surface. Here, mass transfer and hence ka is characterized by a microscopic contact time, t^* . The term $z_0/\epsilon v$ also has units of time, and represents a macroscopic duration of contact between the leachant and the waste. Specifically, $z_0/\epsilon v$ is an approximation to the mean residence time of the percolating liquid as it flows through the waste. Since the contacting patterns within the waste are likely nonideal with both channeling and deadwater regions, a broad velocity distribution exhibiting dispersion and holdup is expected.

The geometric factor p/z_0 exerts a direct influence. As expected, the leach fraction depends on the infiltration. At high rates of mass transfer the concentration rapidly approaches the equilibrium value as the infiltrating water percolates through the waste. The driving force associated with the concentration gradient diminishes and relatively little additional mass transfer occurs in the middle and lower regions of the waste. Also, the ratio of waste volume to the volume of percolating water increases as the depth of the waste increases and the mathematics of equilibrium requires the leach fraction to decrease.

At low mass transfer rates the exponent in Eq. 5 becomes small and the leach fraction may be written:

$$\lambda_L = \frac{p}{\epsilon v} M_0^i ka \quad (6)$$

Substituting the Darcy velocity, $v_d = \epsilon v$, the low mass transfer expression may also be written in an alternative form:

$$\lambda_L = \frac{p}{v_d} M_0^i ka \quad (7)$$

Here, the leach fraction is directly proportional to the partition coefficient, the mass transfer coefficient, the waste's specific area and a contact time numerically equivalent to that defined in the 10CFR61 Draft EIS.³ When the wetting impulses arriving at the waste are not damped out the percolation is less than the Darcy velocity and the resulting contact time is less than unity. For deep percolation, however, the incoming wetting fronts have been damped out and the flow is more constant, the percolation is approximately equal to the Darcy velocity, and the contact time is closer to unity. Physically, impulses of water passing through the waste have less time in which to leach radionuclides than the same amount of water passing through slowly and continuously. However, it should be recognized that the mass transfer coefficient is also a function

of the velocity and so the overall rate of mass transfer exhibits a more complex dependence than described here. Still, within the context of the model considered it is evident that the degree to which a wetting front is dispersed in transit through the cover and the waste can significantly impact the leaching process.

PARAMETER VALUES

The model described in the preceding section identifies four parameters important in the leaching process. These are the partition coefficient, the percolation, the overall mass transfer coefficient including the specific area, and the interstitial water velocity or, alternatively, the Darcy velocity. The determination of appropriate values for these parameters is necessary for even a casual prediction of in-situ leaching of radionuclides from low-level wastes. Thus, some comments regarding the availability and estimation of these parameters is in order.

Prominent among the leaching parameters is the partition coefficient, M_o^i . It is specific to the radionuclide, the wasteform, and the soil backfill. The partition coefficient as used above represents an effective linear equilibrium distribution under trench conditions for a species i between the leachant and the composite, heterogeneous waste/soil matrix. This entity depends on the physical and chemical nature of the waste/soil matrix, the pH and Eh, the ionic strength of the leachant, the presence of chelating agents or ligands and the presence of other reactive species. The partition ratio is dimensionless and may be related to an effective distribution or sorption coefficient, K_d^i , via:

$$M_o^i = \frac{1}{\rho K_d^i} \quad (8)$$

where ρ is the density of the waste/soil matrix. Estimated M_o^i 's for a number of radionuclides have been tabulated in the 10CFR61 Draft EIS.³ The draft EIS does not explicitly state that these numbers represent equilibrium values but instead they represent "average upper bounds" of leachability under extreme leachability conditions.

The percolation, p , is a function of cover design, the drainage characteristics of the cover materials as installed, the type and extent of plant growth on the cover, the intensity and time distribution of precipitation, solar radiation, and the physical stability of the cover and wastes. These factors impact percolation in a collective manner. However, specific knowledge of all of these factors is often incomplete and simpler water balance techniques are used to estimate the infiltration.

The estimation of an overall mass transfer coefficient, k_a , follows methodologies used in the chemical process industry. The uncertainties in characterizing the waste/soil matrix, however, are much greater than the uncertainties encountered in industry. Estimates of mass transfer coefficients for well defined materials incorporate both fluid-side and particle-side effects and are based on the flow conditions, the dimensions of the materials, and nuclide diffusivities in the leachant and the wasteform. For example, the mass transfer coefficient for leaching from spent ion exchange resins can be estimated as:

$$k_{af} = 2.62 (D_f \epsilon_v)^{0.5} \sum_1^m \frac{n_i}{(d_i)^{1.5}} \quad (9)$$

where

i = particle size

D_f = diffusivity in the fluid

n_i = fraction of all particles of diameter d_i

for the fluid-side effect and

$$k_{ap} = 60 D_p \sum_1^m \frac{n_i}{(d_i)^2} \quad (10)$$

for the particle side effect.⁴ Additional effects such as mass-transfer resistance due to axial dispersion may be important. When more than one effect is operating, an overall mass transfer factor can be obtained in a manner analogous to the summing of resistances in series.

A mixture of compactible and noncompactible trash is much more heterogeneous and difficult to characterize than uniform ion exchange resins. If no internal resistance occurs the overall mass transfer is determined entirely by fluid-side resistance. As a first approximation k can be estimated by simple penetration theory⁵ as $(4D/t^*)^{0.5}$, where D is the diffusivity of the species in water and t^* is the microscopic contact time mentioned above. Diffusivities are typically on the order of 2×10^{-5} cm/sec. The determination of a representative t^* for a given waste stream is subject to great uncertainty. Two parameters which influence t^* are the interstitial velocity and the "size" of a representative piece of trash. For this work t^* is estimated to be equal to the size divided by the velocity. Estimates of the specific surface area "a" also depend on the size. In this study "a" is assumed to be equal to $1.0/d_p$ where d_p is interpreted as the length of one side of an open cube having ten exterior and interior surfaces exposed to the leachant. For values of d_p ranging from 0.5 cm to 100 cm "a" varies from 2.0 cm^{-1} to 0.01 cm^{-1} . Variation beyond these bounds is certain. In Table I estimates of k_a using three different models are listed. These models include penetration theory,⁵ packed bed,⁴ and axial dispersion limited mass transfer.⁴ As all three models are describing mass transfer processes on the same physical scale it is not surprising that their predictions tend to agree. This suggests a degree of flexibility in determining the fluid-side mass transfer coefficients.

In Table II exit concentrations calculated via Eq. 4 are listed for the preceding range of trash dimensions and for waste depths of 100 cm, 200 cm, and 500 cm. For the smaller "particle" size the exit concentration equals the equilibrium concentration. As d_p becomes larger the exit concentrations fall significantly below the equilibrium value. This is more pronounced for the shallow wastes.

Further study of mass transfer processes in waste may provide useful insights and suggest unique

TABLE I

ESTIMATION OF FLUID-SIDE MASS TRANSFER COEFFICIENT

d_p	ka		
	Penetration Theory ^a	Packed Bed ^b	Axial Dispersion ^c
0.5 cm	$3.6 \times 10^{-4} \text{sec}^{-1}$	$5.2 \times 10^{-4} \text{sec}^{-1}$	$2.0 \times 10^{-4} \text{sec}^{-1}$
1	1.3×10^{-4}	1.9×10^{-4}	1.0×10^{-4}
5	1.1×10^{-5}	1.7×10^{-5}	2.0×10^{-5}
10	4.0×10^{-6}	5.9×10^{-6}	1.0×10^{-5}
25	1.0×10^{-6}	1.5×10^{-6}	4.0×10^{-6}
50	3.6×10^{-7}	5.2×10^{-7}	2.0×10^{-6}
100	1.3×10^{-7}	1.9×10^{-7}	1.0×10^{-6}

a $ka = (1.0/d_p)(4Dv/\pi d_p)^{0.5}$, $D = 1.25 \times 10^{-5} \text{ cm}^2/\text{sec}$, $v = 1 \times 10^{-3} \text{ cm/sec}$.

b $ka = (2.62/d_p)(Dv/d_p)^{0.5}$, $\epsilon = 0.4$

c $ka = v/L$, $L = d_p/Pe = 10 d_p$

The Peclet number, Pe , is typically 0.5 for packed beds. Here, a value of 0.1 is assumed for the more heterogeneous waste.

solutions to problems that arise. For unprocessed trash, however, any description better than semiquantitative is unlikely to arise. Indeed the calculations in this study are intended merely to illustrate concepts. However, the prospects for describing the leach behavior of improved waste forms in the field is brighter since these waste forms are much better defined, though complexity in site and environmental parameters will continue to inject considerable uncertainty in any calculations.

It follows from the preceding discussions that the average interstitial water velocity, v , is a crucial leaching parameter. Unfortunately, its determination in an environmental unsaturated flow problem is not a simple task. In the upper regions of the soil the flow is a series of episodic wetting fronts with alternating wetting and drainage phases. As an added complication soil drainage curves generally exhibit hysteresis, i.e., the wetting curve and drainage curves do not coincide. One consequence of this is a gradual dispersion or flattening out of the impulse as it travels downward. In the deep percolation regime the incoming impulses have been almost completely damped and steady-state unsaturated flow ensues. Heterogeneities and layering in the soil and wastes will also induce dispersion or local variations in the interstitial velocity. The determination of an average interstitial water velocity through waste as a single number is a complex endeavor. Nevertheless, estimates can be made by using simplified descriptions of percolation.

For a situation where the waste is buried near the surface and "intact" impulses are reaching the waste, the flow is gravity driven and a shock front analogy⁶ is useful:

$$\frac{\Delta z}{\Delta t} = \frac{K(\theta_1) - K(\theta_2)}{\theta_1 - \theta_2} \leq \frac{K_{sat}}{n} \quad (11)$$

TABLE II

NORMALIZED EXIT CONCENTRATIONS AS A FUNCTION OF WASTE SIZE AND DEPTH OF WASTE

d_p	ka	C_L/C_L^*		
		$z_0 = 100 \text{ cm}$	200 cm	500 cm
0.5 cm	$3.6 \times 10^{-4} \text{sec}^{-1}$	1.00	1.00	1.00
5	1.1×10^{-5}	0.67	0.89	1.00
10	4.0×10^{-6}	0.33	0.55	0.87
25	1.0×10^{-6}	0.10	0.18	0.39
50	3.6×10^{-7}	0.04	0.07	0.17

Here Δz is the vertical distance of travel between points z_1 and z_2 in a homogeneous system, Δt is the time of travel, and $K(\theta_1)$ and $K(\theta_2)$ are the hydraulic conductivities corresponding to the volumetric moisture contents θ_1 and θ_2 at z_1 , and z_2 , respectively. The estimation of the hydraulic conductivities in the waste involves a high degree of uncertainty. Finally, a large effective "particle-size" and size irregularities for the waste would tend to induce significant dispersion of the impulses and degrade the shock front analogy.

For deep percolation where a steady flow is occurring, Darcy's Law permits an estimate of the interstitial water velocity:

$$v = p/\theta = p/nS \quad (12)$$

The variable θ is the volumetric water content of the waste under the existing flow conditions, n is the waste porosity and $S = \theta/n$ is the degree of saturation of the waste.

EXTENDING THE BASIC MODEL

A useful feature of the basic leach model described above is the ease with which the governing equation can be modified simulating additional physical/chemical aspects and the modified equation solved. In this section, four such extensions of the basic leach model are developed. The purpose is not to construct complete models for the various phenomena but instead to demonstrate the methodology while shedding some light on the underlying operative mechanisms. Considered here are solubility-limited leaching, adsorption by the backfill, reaction with a chelating agent and dispersive flow. The treatment of solubility-limited leaching requires only the redefinition of a single term and no modification of the governing equation. The remaining three phenomena require the definition of new parameters and the addition of new terms to the transport equation.

When the nuclide has a low solubility its maximum concentration in the leachant is independent of its concentration in the waste and the C_L^* in Eq. 3 and 4 is the solubility C_{S01} . The leach fraction λ_L is:

$$\lambda_L = \frac{C_{S01}}{C_s} \frac{p}{z_0} (1 - e^{-kaz_0/\epsilon v}) \quad (13)$$

In particular,

$$\lambda_L = \frac{C_{s01} p}{C_s \epsilon v} ka \quad (14)$$

at low rates of mass transfer. When the flow is constant the percolation equals the Darcy velocity. Estimating k via penetration theory:

$$\lambda_L = \frac{2C_{s01}}{C_s} \left(\frac{D_v}{\pi d_p} \right)^{0.5} \frac{1}{d_p} \quad (15)$$

This form of the leach fraction is interesting because of its similarity to the expression of Chambre' and Pigford' for the steady-state fractional release of a nondecaying species from a single cylindrical waste-form in a saturated deep-geologic repository:

$$\lambda_L = \frac{8\epsilon C_{s01}}{C_s} \left(\frac{D_v}{\pi d_p} \right)^{0.5} \left(\frac{1 + d_p/L}{d_p} \right) \quad (16)$$

The notation in Eq. 16 has been made consistent with this work. Here ϵ is the porosity of the media surrounding the wasteform, d_p is the diameter of the wasteform and L is its length.

The presence of backfill in the waste is expected to impact the radionuclide's exit concentration. The adsorption or ion exchange of the nuclide by the backfill acts as a sink which removes that species from solution. Thus the behavior of the system is determined by the source-sink interplay of the leaching and the adsorption. Characteristic parameters include the waste-to-leachant mass transfer coefficient $(ka)_1$, the leachant-to-backfill mass transfer coefficient $(ka)_2$, the nuclide's backfill-to-leachant distribution coefficient K_{dB}^1 , and the fractional amounts of waste and backfill, f_1 and f_2 , respectively.

Assuming an irreversible adsorption driven by the concentration gradient between C_L and the concentration at the surface of the backfill, $C_2^* = C_L / (1 + \rho_B K_{dB}^1)$, where ρ_B is the bulk density of the backfill divided by its moisture content, the transport equation for the system may be written:

$$v \frac{dC_L}{dz} = f_1(ka)_1(C_L^* - C_L) + f_2(ka)_2(C_2^* - C_L) \quad (17)$$

or

$$\epsilon v \frac{dC_L}{dz} = \kappa(\alpha - C_L) \quad (18)$$

where

$$\kappa = f_1(ka)_1 + f_2 \frac{\rho_B K_{dB}^1 (ka)_2}{1 + \rho_B K_{dB}^1}$$

$$\alpha = f_1(ka)_1 C_L^* / \kappa$$

Using $C_L(0) = 0$ as the boundary condition the solution to Eq. 18 is

$$C_L = \alpha(1 - e^{-\kappa z_0/\epsilon v}) \quad (19)$$

It is interesting to examine the effect on C_L of varying the backfill K_{dB}^1 . As K_{dB}^1 goes to zero Eq. 19 collapses to:

$$C_L = C_L^* (1 - e^{-f_1(ka)_1 z_0/\epsilon v}) \quad (20)$$

This expression is the same as the basic leaching model C_L except that the mass transfer factor is now reduced by f_1 . This reflects the dilution of the waste by the backfill.

As K_{dB}^1 becomes large

$$C_L = \frac{f_1(ka)_1 C_L^*}{f_1(ka)_1 + f_2(ka)_2} \times (1 - e^{-(f_1(ka)_1 + f_2(ka)_2) z_0/\epsilon v}) \quad (21)$$

and the distribution of the nuclide between the leachant and the backfill is determined solely by the waste-to-leachant and leachant-to-backfill mass transfer rates. When the former is greater than the latter, C_L is approximately equal to C_L^* - the maximum possible value. It is only when the leachant-to-backfill mass transfer rate is greater than the waste-to-leachant rate that C_L will become significantly less than C_L^* . Thus a high backfill K_{dB}^1 is a necessary but not sufficient condition for adsorption by the backfill to have a significant impact on the nuclide concentration. The kinetics of mass transfer must be taken into account.

Traditionally, there has been much interest in the effect of chelating agents on the leaching process and subsequent transportation in the environment. It is understood that chelating agents form chemically stable and highly mobile complexes with some of the radionuclides, but it may not be as universally appreciated that in certain circumstances the overall release rates of those radionuclides from the waste may be significantly increased. As an example, one may consider a leachant/waste system in which a chelating agent is present in the leachant at a constant concentration well in excess of chelation reaction stoichiometry and in which the reaction is pseudo first-order in the uncomplexed radionuclide's concentration:

$$\text{rate of chelation} = k_{app} C_L \quad (22)$$

Here, k_{app} is the apparent first-order rate constant. This is admittedly an oversimplification but it does illustrate the important roles played by mass transfer and reaction kinetics.

The addition of this sink term to Eq. 3 yields the transport equation:

$$\epsilon v \frac{dC_L}{dz} = (ka)_1(C_L^* - C_L) - k_{app} C_L \quad (23)$$

Assuming that $C_L(0) = 0$, the solution to Equation 23 is

$$C_L = \alpha (1 - e^{-\kappa z_0/\epsilon v}) \quad (24)$$

with

$$\alpha = M_0 k_a C_S / \kappa$$

$$\kappa = k_a + k_{app}$$

The concentration of the complexed species is governed by a second equation:

$$\epsilon v \frac{dC_{ML}}{dz} = k_{app} C_L \quad (25)$$

Assuming $C_{ML}(0) = 0$ it may be shown that

$$C_{ML} = \alpha k_{app} z_0 / \epsilon v - k_{app} C_L / \kappa \quad (26)$$

Though the chelated and unchelated species will move differently in the environment the total concentration of the radionuclide in its complexed and uncomplexed forms is of interest:

$$C_T = C_L + C_{ML} = (1 - k_{app}/\kappa)C_L + \alpha k_{app} z_0 / \epsilon v \quad (27)$$

The effects of chelation on leaching are illustrated in Table III where expressions are given for C_L , C_{ML} and C_T for the various high/low rate combinations of mass transfer and reaction. For all combinations the addition of the chelation reaction produces total concentrations C_T of the radionuclides in solution greater than or equal to that occurring in the absence of chelation (Eq. 4). The high mass transfer cases (a - c) result in total concentrations which exceed $M_0 C_S$ - the maximum possible concentration in the absence of chelation. Cases a and b with both high mass transfer and high reaction rates result in values of C_T several times as great as $M_0 C_S$. At low mass transfer rates the effect of the chelating agent is minimal.

The concurrent leaching of a chelating agent with the uncomplexed nuclide followed by reaction in the percolating liquid phase is a more difficult phenomenon to model. Extension of Eq. 4 results in a nonhomogeneous first order differential equation with variable coefficients. The problem may be circumvented by abandoning the steady-state plug-flow model, i.e., Eq. 3, for a simpler steady-state mixed tank formulation. The assumption of mixed flow imposes the constraint of uniform nuclide concentrations throughout the waste bed.⁸ As will be seen below, this may not be as inappropriate as it might first appear. Using a mixed tank model for the simple leach system the radionuclide concentration is:

$$C_L = \frac{k_a \tau C_L^*}{1 + k_a \tau} \quad (28)$$

TABLE III

EFFECT OF CHELATION ON LEACHING-LIMITING CASES

	C_L	C_{ML}	C_T	Equation 4
a. $k_{app}\tau \gg k_a\tau > 1$	$(k_a/k_{app})M_0C_S$	$k_a\tau M_0C_S$	$k_a\tau(1+1/k_{app}\tau)M_0C_S$	M_0C_S
b. $k_a\tau \gg k_{app}\tau > 1$	M_0C_S	$k_{app}\tau M_0C_S$	$(1+k_{app}\tau)M_0C_S$	M_0C_S
c. $k_a\tau > 1 > k_{app}\tau$	M_0C_S	$k_{app}\tau M_0C_S$	$(1+k_{app}\tau)M_0C_S$	M_0C_S
d. $k_a\tau \approx k_{app}\tau \ll 1$	$k_a\tau M_0C_S$	0	$k_a\tau M_0C_S$	$k_a\tau M_0C_S$
e. $k_{app}\tau > 1 > k_a\tau$	$(k_a/k_{app})M_0C_S$	$k_a\tau M_0C_S$	$k_a\tau(1+1/k_{app}\tau)M_0C_S$	$k_a\tau M_0C_S$

where τ is the residence time. For the concurrent leaching of a chelating agent,

$$C_L = \frac{k_a \tau C^*}{1 + k_{app}\tau + k_a\tau} \quad (29)$$

and

$$C_{ML} = \frac{k_a \tau k_{app}\tau C^*}{1 + k_{app}\tau + k_a\tau} \quad (30)$$

The apparent chelation rate constant k_{app} now reflects both the fundamental kinetics of the chelation reaction and the waste-to-leachant mass transfer of the chelating agent. The total exit concentration for the radionuclide is:

$$C_T = \frac{k_a \tau (1 + k_{app}\tau) M_0 C_S}{1 + k_{app}\tau + k_a\tau} \quad (31)$$

The limiting behavior of Eq. 31 closely parallels the behavior of Eq. 27 as given in Table III. Eq. 31 appears to be more tractable.

In the final example of this section, axial dispersion is introduced explicitly into the transport equation. The dispersion is assumed to be Fickian and as such is described by an expression analogous to Fick's Law for diffusion. Theoretically this description is appropriate only for small deviations from plug flow. Here, following tradition, the model will be pushed well beyond that bound as highly dispersive flow will be considered.

The transport equation with dispersion is:

$$D \frac{d^2 C_L}{dz^2} - \epsilon v \frac{dC_L}{dz} + k_a (C_L^* - C_L) = 0 \quad (32)$$

where D is the axial dispersion coefficient. Semi-infinite column boundary conditions are assumed:

$$C_L(0) = 0$$

$$\frac{dC_L}{dz} \rightarrow 0 \text{ as } z \rightarrow \infty$$

The solution to Eq. 32 subject to these boundary conditions is:

$$C_L = C_L^* (1 - e^{0.5(Pe - \Delta)}) \quad (33)$$

where

$$Pe = \text{the Peclet number } \epsilon v z_0 / D$$

$$\Delta = Pe (1 + 4 \text{kar} / Pe)^{0.5}$$

Equation 33 consolidates into a single parameter (Pe) the impact of dispersion regardless of its origin and is useful for examining the leach behavior over a wide spectrum of flow conditions. This is demonstrated in Table IV where the ratio of C_L to C_L^* is given for a range of Peclet numbers and kar's. Also included in this table are the corresponding C_L to C_L^* ratios for the plug flow and mixed flow leaching models. These serve as a gauge for evaluating the dispersive flow model.

When the Peclet number is large very little dispersion occurs and the leaching in the dispersive flow model should approach that found for plug flow. A comparison of the $Pe = 10$ and the plug flow results clearly reveals that trend. As the Peclet number is decreased more "backmixing" occurs and the leaching should at some point approximate mixed tank behavior. This point is reached in the vicinity of Pe equal to one (Table IV). It should be noted that the agreement between the mixed flow and dispersive flow models supports the current extension of the Fickian model beyond the low dispersion regime.

As the Peclet number is decreased further the leaching system enters the region of high dispersion. Physically this region is characterized by a low flow impedance in which a portion of the flow begins to bypass the bulk of the waste via channeling. As a consequence mass transfer should begin to fall off substantially. The entries in the $Pe = 0.1$ column of Table IV show this decrease.

From the preceding discussion it is evident that the dispersive flow model exhibits considerable flexibility in describing leaching in under a variety of flow conditions. The model is consistent with the plug flow and mixed flow models. From a practical perspective it should be noted that the extreme cases

TABLE IV

COMPARISON OF C_L/C_L^* FOR DIFFERENT FLOW MODELS

kar	Plug Flow	Mixed Flow	Dispersive Flow		
	Pe = ∞		Pe = 0.1	Pe = 1.0	Pe = 10
10	1.000	0.909	0.614	0.933	0.998
2.5	0.918	0.714	0.364	0.686	0.874
1.0	0.632	0.500	0.237	0.461	0.600
0.1	0.095	0.091	0.060	0.088	0.094
0.01	0.010	0.010	0.009	0.010	0.010

of plug flow and high dispersion ($Pe = 0.1$) differ in their predictions by no more than a factor of two to three over the entire range of kar's considered. The range of Peclet numbers and spacetimes (kar) investigated, while not exclusive, is certainly large. In real waste it is expected that heterogeneities in the waste and the transient nature of the infiltration will lead to nonideal flow conditions with dispersion, holdup, etc. The current results suggest that the dispersive aspects of leaching may not be behavior determining but, returning to the basic model, a quantitative understanding of the kinetic or mass transfer characteristics including holdup is essential.

It is evident from the results obtained in this section that the kinetic aspects cannot be ignored when one is seeking both quantitative and qualitative insights into leaching processes. Both in a simple leaching scenario and in a scenario compounded with other ongoing processes, kinetics determine how close the system approaches an equilibrium configuration. This conclusion certainly is not new and were this the only offering of the model developed in the present work that model would be without functional merit. It is felt, however, that the most important aspects of this model are: (1) it is based on established, fundamental principles; (2) it is formulated in terms of recognized wasteform, facility, and environmental parameters; (3) it treats the kinetic and equilibrium aspects on an equal footing; and (4) even though the model is based on certain simplifying assumptions, it retains more than enough sophistication to make meaningful predictions which can be tested. No more can be asked of a model other than the ability to make correct predictions.

APPENDIX

The formal solutions to Equations 1 and 2 are discussed in detail in the literature (1, 2, 4, 9, and 10). Only those results as apply to the leaching or desorption problem are given here. Translating the results given in the references above the concentrations in the leachant and the waste are:

$$C_L(z, t) = M_0 C_S^0 \int_0^{\text{kaz}/\epsilon v} e^{-M_0 \text{kat}'} e^{-(\text{kaz}/\epsilon v)'} J_0(21 \text{ka} \sqrt{M_0 z t' / \epsilon v}) d(\text{kaz}/\epsilon v)' \quad (A-1)$$

and

$$C_S(z, t) = C_S^0 (1 - e^{-\text{kaz}/\epsilon v}) \int_0^{M_0 \text{kat}'} e^{-(M_0 \text{kat}')'} J_0(21 \text{ka} \sqrt{M_0 z t' / \epsilon v}) d(M_0 \text{kat}')' \quad (A-2)$$

respectively, where $t' = t - z/\epsilon v$. Normally, t is the time elapsed after the initial entry of the leachant into the solid bed. Here, it is interpreted as the cumulative time of contact resulting from the passage of successive impulses of leachant. That is, the "clock runs" only when an impulse is present.

Approximating the leach fraction as $C_L/C_S z'$:

$$\lambda_L = (M_0 p/z') \frac{\int_0^{\text{kaz}/\epsilon v} e^{-(M_0 \text{kat}' + [\text{kaz}/\epsilon v]')} J_0(21 \text{ka} \sqrt{M_0 z t' / \epsilon v}) d[\text{kaz}/\epsilon v]'}{1 - \int_0^{M_0 \text{kat}'} e^{-([M_0 \text{kat}')' + \text{kaz}/\epsilon v)} J_0(21 \text{ka} \sqrt{M_0 z t' / \epsilon v}) d[M_0 \text{kat}')]} \quad (A-3)$$

where z' is the waste thickness. This is a general expression for the leach fraction as a function of time. Equation A-3 collapses to Equation 5 when $t' \ll 1$. The solutions for Equations 1 and 2 also have been presented in the form of graphs.¹ Though the solutions plotted are for the adsorption problem, a careful formulation of terms allows the direct application of these graphs to the leaching problem.

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