

LEACH MODELS: THEORY AND APPLICATION*

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Summary

Mechanistic leach models can be applied to describe performance of solidified wastes in the Toxicity Characteristic Leaching Procedure test. A simple model was modified to describe the effect of inward diffusion of acetic acid from the leaching solution. However, the model did not incorporate changes in the acetic acid concentration that would be observed over time as pH rises. Mechanistic leach models could also be applied to predict long-term leaching, to quantify the relative importance of chemical and physical immobilization mechanisms, to correlate and extrapolate leaching data for various contaminants and binders, and to predict ultimate performance from early characteristics of the solidified waste.

Introduction

Solidification is an important tool in management of hazardous wastes. Although waste reduction and waste recycle are preferable to treatment and disposal, they are not always possible. This is particularly true for many wastes contaminated by toxic inorganic compounds, which will continue to be land disposed.

The key characteristic of solidified wastes is the degree to which contaminants will leach from the waste form. A variety of tests have been developed to measure leaching under a variety of conditions [1-4]. Conditions such as size of the waste form, composition of the leaching solution, and mechanism of replenishment of leaching solution affect the leaching rates [1,5,6]. The Toxicity Characteristic Leaching Procedure (TCLP) [3] and its predecessor, the Extraction Procedure (EP) [4], are the most important leach tests.

Leach models are useful in predicting effects of process variables on performance of solidified wastes. They can be used to predict performance on the TCLP test, to predict long-term leaching behavior in the environment, to correlate experimental data, and to improve understanding of solidification-stabilization (S/S).

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Leach models

Assumptions

Two types of immobilization mechanisms are normally assumed to be important in leaching from solidified wastes. The first are physical processes that retard the movement of contaminants. It is generally assumed that a contaminant is partially immobilized by solidification because it is trapped in a tortuous solid. To some extent, it can move through the solid by diffusion, which can be described by Fick's law. This relationship is shown below for diffusion in one direction:

$$J = -D_m \frac{\partial C}{\partial X} \quad (1)$$

where: J = flux of component in x -direction [M/L^2T];

D_m = molecular diffusivity [L^2/T];

C = concentration of component, mass per of volume liquid, [M/L^3];

X = distance in x -direction, [L].

The key parameter in Fick's law is the molecular diffusivity. This coefficient has been measured for a number of compounds, and can be estimated for others [7].

Fick's law can be applied to diffusion through a solidified waste, but the proportionality factor is not the molecular diffusivity, but an effective diffusivity:

$$J = -D_e \frac{\partial C}{\partial X} \quad (2)$$

where: D_e = effective diffusivity, [L^2/T];

C = concentration of component, mass per volume of solid, [M/L^3].

It is important to recognize the differences between the application of Fick's law to free diffusion and diffusion within a porous solid. In a porous solid, the contaminant moves through pore water by molecular diffusion. However, the concentration is expressed in terms of the total volume of solid, rather than the volume of pore water. Furthermore, the flux is measured in a single direction, but the molecules would be following the path set out by the pores, which could be highly irregular. Because of these factors, the effective diffusivity is smaller than the molecular diffusivity. If all the pores in the solid are connected and parallel, the effective diffusivity can be simply related to the molecular diffusivity [8]:

$$D_e = \frac{\epsilon D_m}{\delta} \quad (3)$$

where ϵ denotes the porosity and δ the tortuosity factor.

Complete immobilization of a portion of a contaminant is another potential immobilization mechanism. "Complete" immobilization could occur by physical encapsulation or by a chemical reaction that irreversibly changes a contaminant into an immobile form.

Chemical immobilization mechanisms are also recognized as important processes in solidified wastes. Table 1 shows leaching indexes for a variety of compounds [9]. A large leaching index represents a higher degree of immobilization. It is clear from Table 1 that different contaminants are immobilized to different degrees in the same solidified waste. Those contaminants that should be relatively nonreactive, such as sodium, have the lowest leaching indexes, while contaminants that should be more reactive, such as lead, have the highest leaching indexes.

A variety of chemical reactions could result in immobilization of contaminants by changing the form of a contaminant from a mobile phase to an immobile one. Precipitation reactions could convert a mobile form of the contaminant into an immobile solid. Soluble contaminants could also be converted to immobile phases by sorption onto or into the internal matrix. Oxidation-reduction reactions could change a contaminant's form and result in a species which would be more or less susceptible to immobilization. An example would be conversion of trivalent chrome to the hexavalent form. Trivalent chrome would be susceptible to precipitation as a hydroxide, but hexavalent chrome would not. Acid-base reactions could also affect immobilization reactions, because many precipitation and sorption reactions are strongly affected by pH.

A number of assumptions about the environment in which leaching is occurring are required by leach models [10]. Typical assumptions are: the waste form has rectangular geometry, the concentration of contaminant at the solid-solution interface is zero (infinite bath assumption), the contaminant is distributed homogeneously before leaching begins, the concentration at the center of the solid does not change during the leaching period (infinite solid assumption).

TABLE 1

Reported values of the leachability index (*LI*) for various contaminants [9]

Contaminant	<i>LI</i>
Na	8.3
Phenol	9.5
Nitrate	10.7
As	11.9
Cr	13.2
Pb	15.4

Material balances

The heart of a mechanistic model of leaching is a material balance on the contaminant of interest in the solid. A general material balance equation can be expressed as in eqn. (4):

Accumulation of Material

- = Amount of material entering by physical transport (input)
- Amount of material leaving by physical transport (output)
- + Net amount of material formed by reactions (production)

When applied to a waste form with rectangular geometry in which Fickian diffusion is the physical transport mechanism, the material balance becomes:

$$\frac{\partial C}{\partial t} = D_e \frac{\partial^2 C}{\partial X^2} - R \quad (5)$$

where R denotes the net rate of production of mobile contaminant, $[M/TL^3]$. Solution of this partial differential equation depends on assumptions made (boundary conditions) about the environment of the leaching solid and about the types of reactions occurring within the solid.

Simple leach models

A number of simple leach models can be constructed that can be solved analytically. The simplest and most commonly used leach model assumes that no reactions occur, the slab is infinite, the bath is infinite, and the contaminant is distributed homogeneously at the start of the leaching period. This model is the basis for analyzing data from a standard dynamic leach test [2]. With these assumptions, the material balance equation can be solved to give a profile of the concentration within the solid (Fig. 1 and eqn. 6):

$$C(X,t) = C_0 \operatorname{erf} \left(\frac{X}{(4 D_e t)^{0.5}} \right) \quad (6)$$

where C_0 is the concentration of contaminant throughout slab when leaching starts, $[M/L^3]$; erf is the error function; and t is the time since leaching began, $[T]$. Equation (6) is not very useful in characterizing leaching from solidified wastes. It is much more useful to obtain the fraction of contaminant leached by integrating the concentration profile across the entire slab.

$$\frac{M_t}{M_0} = \frac{1}{L C_0} \int_0^L (C_0 - C) dX \quad (7)$$

where M_t/M_0 is the fraction of contaminant leached at time t . Equation (7) can be solved using the concentration distribution shown in eqn. (6).

CONCENTRATION PROFILES

Infinite Slab, Infinite Bath

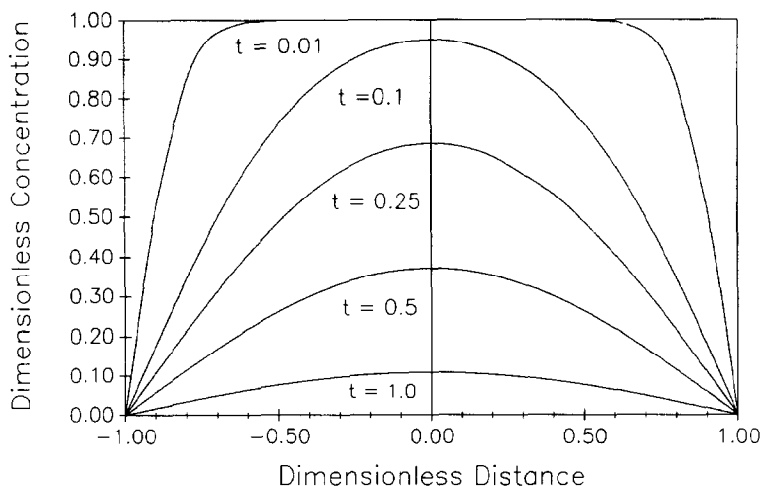


Fig. 1. Concentration profile in solidified waste containing mobile contaminant after various dimensionless leaching times (tD_e/L^2).

$$\frac{M_t}{M_0} = \left(\frac{4 D_e}{\pi L^2} \right)^{0.5} t^{0.5} \quad (8)$$

where L denotes the distance from the edge of the slab to its center. If the contaminant of interest is not undergoing any reactions in the solid, eqn. (8) can be used to calculate the effective diffusivity from measured data for the fraction leached as a function of time.

Most contaminants of interest are known to undergo reactions during solidification. The high pH observed in portland cement results in formation of precipitates of many metals. A simple model for precipitation and dissolution can be developed. Solution of this model results in concentration profiles as shown in Fig. 2, and a relationship for the fraction leached as shown in eqn. (9):

$$\frac{M_t}{M_0} = \left(\frac{2 D_e (F_m (1 - F_m) + 0.5 F_m^2)}{L^2} \right)^{0.5} t^{0.5} \quad (9)$$

where F_m is the fraction of contaminant that is mobile when leaching begins. Equation (9) has the same form as eqn. (8), i.e., a constant multiplied by the square root of time. The constant in eqn. (9) can be rearranged to be analogous

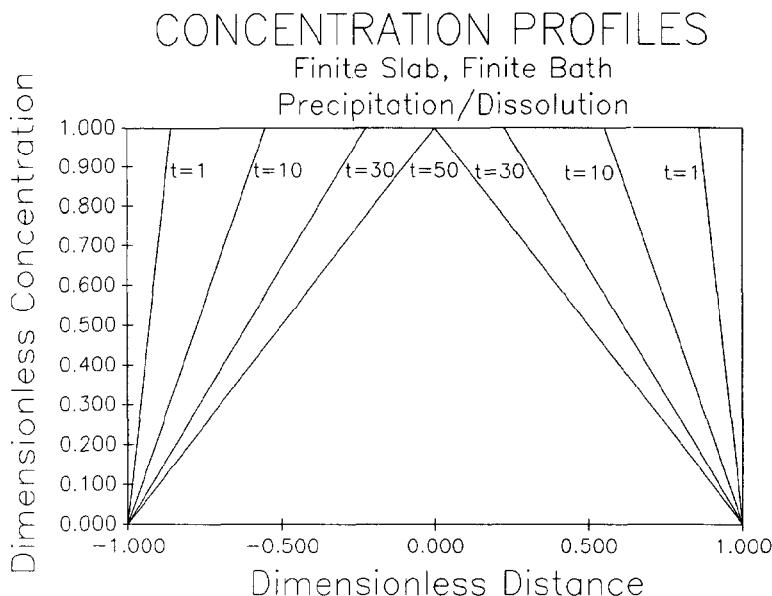


Fig. 2. Concentration profile in solidified waste containing mobile contaminant after various dimensionless leaching times (tD_e/L^2).

to eqn. (8):

$$\frac{M_t}{M_0} = \left(\frac{4 D_{\text{obs}}}{\pi L^2} \right)^{0.5} t^{0.5} \quad (10)$$

$$D_{\text{obs}} = \frac{\pi [F_m(1 - F_m) + 0.5 F_m^2] D_e}{2} \quad (11)$$

This result can be simplified for the case when the fraction of contaminant that is initially mobile is small. This would be a reasonable assumption for many contaminants:

$$\text{if } F_m \ll 1.0, \quad D_{\text{obs}} = \frac{\pi F_m D_e}{2} \quad (12)$$

The value of the observed diffusivity depends on the extent of physical immobilization, as represented by the effective diffusivity, and the extent of chemical immobilization, as represented by the mobile fraction. Since it is calculated from the results of a dynamic leach test, it is the parameter that quantifies the total extent of immobilization. Results of leaching tests should always be reported as observed diffusivities, rather than effective diffusivities, unless it is known that the contaminant of interest is not undergoing any reactions in the solid.

A similar result for the fraction leached occurs when it is assumed that a

contaminant reacts by linear sorption, i.e., an immobile sorbed contaminant is produced in proportion to the concentration of mobile contaminant:

$$C_i = K_p C \quad (13)$$

where C_i denotes the concentration of immobile, sorbed contaminant, $[M/L^3]$; and K_p the partition coefficient. The model again results in an equation for the fraction leached that is a constant multiplied by the square root of time. An observed diffusivity can be calculated that is again proportional to the effective diffusivity:

$$D_{\text{obs}} = \frac{D_e}{1 + K_p} = F_m D_e \quad (14)$$

The same form of model results when it is assumed that a portion of the contaminant is completely immobilized. This could result from physical encapsulation, or an irreversible chemical reaction. The observed diffusivity is again proportional to the effective diffusivity:

$$D_{\text{obs}} = F_m^2 D_e \quad (15)$$

All of these simple models have resulted in the same form of equation for the fraction leached. In each case, the observed diffusivity quantifies the overall extent of immobilization, and is proportional to the effective diffusivity. The proportionality constant is determined by the parameters that define the type of reaction. Because each model has the same form, leach tests by themselves are unable to differentiate between mechanisms of immobilization.

Parameter estimation

Although a model can provide insight into leaching processes by itself, it cannot be used as a predictive tool unless values are known for its parameters. The models presented here contain parameters to describe chemical processes, and a single parameter to describe physical processes (D_e).

The effective diffusivity could be calculated from results of leach test only when a set of restrictive assumptions are met. These conditions include: the compound being leached not reacting within the solid, being completely in a mobile form, and having its initial concentration known accurately. Although these conditions might be met by some waste forms, they could not be met in general. Furthermore, the time required for sufficient material to leach might be a matter of months for solids with low diffusivities. Therefore, leach tests are not good general methods for measuring effective diffusivities. The effective diffusivity could be calculated by measuring the transport of an unreactive compound through a slice of the solid [11,12]. This procedure suffers from many of the limitations of the leach test method and so would not be a good general method for determining effective diffusivities.

A more attractive approach for determining effective diffusivity is a proce-

ture based on measurements of electrical conductivity [13]. It is based on the analogy between transport of ions by diffusion to the transport of ions by electrical field. Transport by either mechanism is affected in the same way by the structure of a porous solid. Therefore, measurement of the conductivity of the solid and of the pore liquid can be used to calculate the effective diffusivity of a compound within the solid. The MacMullin number is defined as the ratio of the conductivity of the solid to the conductivity of the pore water, and is equal to the ratio of the molecular diffusivity of a contaminant to its effective diffusivity [14–17].

$$D_e = D_m / N_M \quad (16)$$

where N_M is the MacMullin number, equal to the ratio of the conductivity of the solid to the conductivity of the pore water.

Determination of the parameters that describe chemical immobilization depends on the type of chemical reaction occurring. In some cases, literature values of equilibrium constants could be used to estimate the needed parameters. However, a more reliable method would be to measure the distribution of contaminant between mobile and immobile forms in the solid itself.

Applications

One of the most useful applications of leaching models would be to predict performance of solidified wastes in the TCLP test. The simple models presented here could be applied to the conditions of the TCLP test by assuming that the length variable (L) can be approximated by the ratio of the particles' volume to their area (V/A).

$$C_{\text{TCLP}} = C'_0 \frac{M_t}{V_b} \frac{A}{V} \left(\frac{4 D_{\text{obs}}}{\pi} \right)^{0.5} t^{0.5} \quad (17)$$

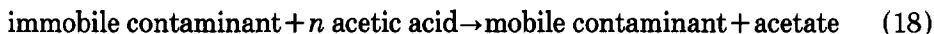
where C'_0 is the initial concentration of contaminant given in mass per mass of solid, [M/M].

This result could be used to correlate data for a number of contaminants to compare the importance of chemical and physical factors in their immobilization. Because the observed diffusivities are proportional to the molecular diffusivity, the ratio of observed diffusivity to molecular diffusivity for a given contaminant could be compared to the same ratio for another contaminant to determine the relative importance of chemical immobilization mechanisms.

A serious limitation to applying this model to the TCLP test is that this test procedure uses an acidic leach solution that increases the rate of leaching. The acidity of the leaching solution can result in anomalous leaching behavior.

The model presented for precipitation/dissolution can be adapted to consider the effect of acetic acid diffusing into the solid. The modified model assumes the same conditions as the initial model, but also assumes that acetic

acid diffuses into the solid by Fick's law and that it reacts with precipitated contaminant within the solid according to the following stoichiometry:



where n is the ratio of acetic acid reacting to contaminant dissolving. This model results in the same form of leach equation as before (eqn. 10), but the observed diffusivity depends on the concentration of acetic acid in the leach solution:

$$D_{\text{obs}} = \frac{\pi D_{e,\text{hac}} C_{b,\text{hac}}}{2 n C_{i,0}} \quad (19)$$

where $D_{e,\text{hac}}$ = effective diffusivity of acetic acid in solid, [L^2/T];
 $C_{b,\text{hac}}$ = concentration of acetic acid in leaching solution, [M/L^3];
 $C_{i,0}$ = concentration of immobile contaminant at start of leaching, [M/L^3].

This result describes leaching that depends both on characteristics of the leaching solution and characteristics of the solid. The observed diffusivity will increase in proportion to the concentration of acetic acid in the leaching solution. Data for leaching of cadmium, copper, chromium, lead, nickel, and zinc show that significantly larger fractions are leached when a buffer solution with a high concentration of acetic acid is used in place of the lower concentration used in the TCLP test [18]. These data provide a qualitative validation of the modified model.

Although this model is able to describe the effect of the acetic acid concentration on leaching, it is still limited by the assumption that the composition of the leaching solution remains constant during leaching. This would not be true in cases where the pH rises appreciably during leaching. The effect of changing concentrations in leach solution could be incorporated into the models, but the solutions could not be easily expressed in simple algebraic equations.

Leach models could find numerous other applications in solidification/stabilization. One application would be to predict long-term leaching of contaminants after the waste form has been placed in the environment. A key question to be answered before models can be applied to this problem concerns the structural integrity of the waste form. If the solid remains monolithic, leach rates will be much lower than if it disintegrates, producing greater external area from which contaminants would be leached. Changing conditions at the solid-solution interface would also have to be assumed, in order to make good predictions of contaminant leaching.

Leach models could also play an important role in delineating the relative importance of chemical and physical immobilization mechanisms. Although solidification has been determined to be a treatment process for regulatory purposes, the relative contributions of each immobilization process could be

determined for individual wastes. This could be useful in convincing the public of the relative safety of disposal of solidified wastes in landfills.

An important application of all types of models is in correlating data and using existing data to predict process performance under new conditions. If the effect on effective diffusivity and chemical immobilization parameters could be determined for a particular admixture, this data could be used to estimate the optimal amount of admixture to add to the binder for a specific waste. Although it is overly optimistic to assume that models could be developed that could make accurate predictions for all conditions. It is reasonable to expect that models could be developed that are suitable for guiding experimental work.

Another potential application of mechanistic leach models is in predicting ultimate performance of solidification technology based on measurements made during mixing of binder or shortly thereafter. This is a difficult problem, but mechanistic models based on describing the fundamental immobilization processes stand a better chance of being successful than total empiricism.

Conclusions

A variety of mechanistic leaching models can be developed to describe leaching from solidified wastes. The models are distinguished by the assumptions they make about the leaching environment and the chemical and physical immobilization mechanisms at work.

A number of simple leach models predict that the fraction of contaminant leached is proportional to the square root of leaching time. The different models assume that contaminants either do not react, or react by linear sorption, precipitation, or an undefined mechanism that results in complete immobilization of part of the contaminant. The observed diffusivity is the parameter in these models that describes the extent of immobilization, and it can be determined by conducting a leaching test. However, these leach tests cannot themselves describe the type of immobilization occurring. Each model results in a relationship that shows that the observed diffusivity is proportional to the effective diffusivity. The effective diffusivity is the parameter that describes diffusive transport by Fick's law, and therefore describes only physical immobilization. The proportionality coefficient depends on parameters that describe the particular chemical immobilization mechanisms assumed for that model.

Parameters needed by the leach models can be determined by independent tests. If parameters are chosen by other tests, the results of leach tests can be used to test the validity of the model.

Mechanistic leach models can be applied to describe performance of solidified wastes in the TCLP test. A simple model was modified to describe the effect of inward diffusion of acetic acid from the leaching solution. However, the model did not incorporate changes in the acetic acid concentration that

would be observed over time as pH rises. Mechanistic leach models could also be applied to predict long-term leaching, to quantify the relative importance of chemical and physical immobilization mechanisms, to correlate and extrapolate leaching data for various contaminants and binders, and to predict ultimate performance from early characteristics of the solidified waste.

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