

# MONOLITHIC WASTE FORMS-- AN UNDERRATED AND UNDER-UTILIZED TECHNOLOGY

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## ABSTRACT

It is widely known, but often forgotten, that the rate of release of a contaminant from a waste form is proportional to the available surface area. In addition, typical leach tests to determine rate of release are of relatively short duration and show disappointingly high release rates. By taking a novel approach to the modeling of leaching and using some available long-term leach data, we have been able to demonstrate a potential for obtaining the long-term leach rates from short-term data along with known or measurable properties of the waste form.

## INTRODUCTION

The ultimate purpose of proper waste disposal is to discard unwanted materials in a manner which protects the public health and the environment from undue harm. This objective is often obscured in the effort to meet the "Regs" and is sometimes not kept in focus in the writing of the "Regs". The major potential for harm from disposed waste, to either the public health or the environment, lies in the transport of harmful constituents in the waste to the accessible environment, primarily via water. Properly done, stabilization/solidification of wastes in large monoliths ( $> 1 \text{ m}^3$ ) can reduce the rate of the transport to the environment by many orders of magnitude. This pertains since release rate is proportional to accessible surface area and the surface to volume ratio for solids is inversely proportional to the characteristic length of the solid. For, example, the release rate of hazardous constituents from a  $1 \text{ m}^3$  monolith is 0.001 that of the same volume of waste in 1 mm cubes.

Furthermore, continuing long-term leaching experiments at CEA-Saclay(1) in France have shown leach rates of  $10^{-11}$  to  $10^{-12} \text{ cm}^2/\text{sec}$  for a very mobile species, cesium, from cement waste forms. Unfortunately, as can be seen in Fig. 1, these low leach rates were not observed until 30 to 60 days into the experiments. These low rates, which have persisted for more than 700 days, would not have been measured in standard short-term, leach tests. These tests such as, ANSI 16.1 (2) would have indicated that the leach rates were several factors of ten greater, a gross under-estimation of the retention capability of these waste forms. Similar results have been obtained in other long term leaching experiments(3).

Although earlier attempts at predicting long-term leachability from short-term tests have been partially successful, in this paper a modification to the effective diffusivity is introduced to correct for surface effects.

## GEOMETRIC ANALYSIS OF MONOLITH SURFACE

Cement-based waste forms generally consist of cement binder, water and an inert fill or aggregate. When radioactive waste is solidified with cement, the radionuclides primarily are contained in the cement matrix. When the radionuclides are leached, they must traverse a tortuous path through the cement matrix around the impervious aggregate. Although for the bulk of the waste form, this tortuosity can be considered uniform, at the surface the finite size of the aggregate results in less tortuosity than average.

To illustrate, it is assumed that the aggregate consists of uniformly sized spheres, in a hexagonal close packed arrangement with the first layer of spheres tangent to the surface of the monolith. It can be shown geometrically that the fraction of open area as a function of distance from the surface,  $x$ , is

$$F(x) = \frac{A_{\text{open}}}{A_{\text{total}}} = 1 - \frac{\pi}{2\sqrt{3}} \frac{2x'R - x^2}{R^2} + \frac{2x''R - x^2}{R^2} \quad (\text{Eq. 1})$$

where

$$x' = x - 2na; \quad 2na < x < 2na + 2R \quad x' = 0 \text{ otherwise}$$

$$x'' = x - (2n' + 1)a; \quad (2n' + 1)a < x < 2R + (2n' + 1)a \quad x'' = 0 \text{ otherwise}$$

$$a = \text{interplanar spacing} = 2R\sqrt{2/3} = 1.633 R$$

$n$  is the number of repeating sphere layers beginning with surface layer

$n'$  is the number of repeating offset layers of spheres

This function is plotted in Fig. 2.

If it is assumed that the free stream diffusivity is the diffusivity in the cement paste and that  $\sigma$  and  $\tau$  are constant, it is intuitively obvious that the porosity between the surface and depth  $d$ ,  $\epsilon(d)$  is equal to the average fractional area:

$$F(d) = \frac{1}{d} \int_0^d F(x) dx \quad (\text{Eq. 2})$$

and

$$D_e = D_w F(d) \frac{\sigma}{\tau} \quad (\text{Eq. 3})$$

the function  $F(d)$  is shown in Fig. 3.

## A FUNDAMENTAL MATHEMATICAL MODEL FOR THE LEACHING OF WASTE FROM A SOLID FORM

The migration of waste from a storage facility to the groundwater supply is a complex process that has been extensively studied for the past twenty five years (4). It involves, in the large, a number of independent or coupled processes, each of which is rather complex itself. Included are water penetration into the facility (5), leaching from the waste form ((6), (7), (8)) deterioration of the container and/or solid phase (9), migration through backfill materials (5), structural integrity of the facility, and migration external to the facility to the ground water supply (10).

In this study we focus on one aspect, the leaching of a waste material from a solid phase immersed in water; specifically, the leaching of cesium from a dense concrete. The usual mechanisms for leaching are diffusion, convection, sorption,

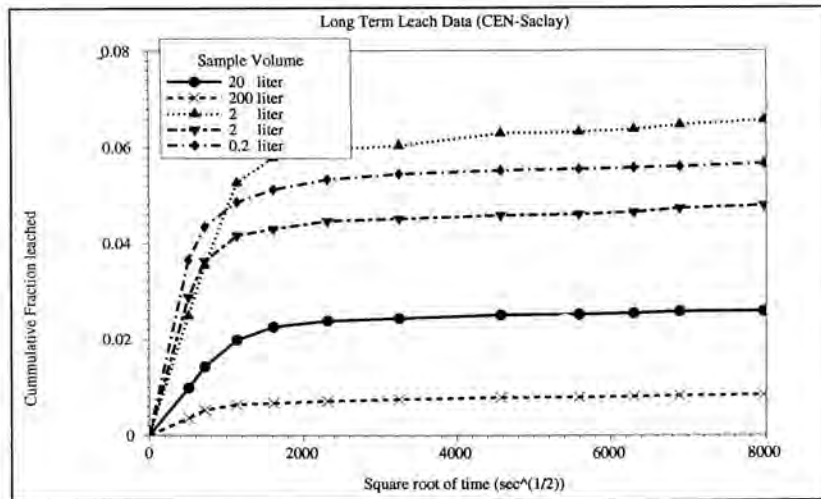


Fig. 1. Leaching of cesium from various sizes of low porosity cement waste forms.

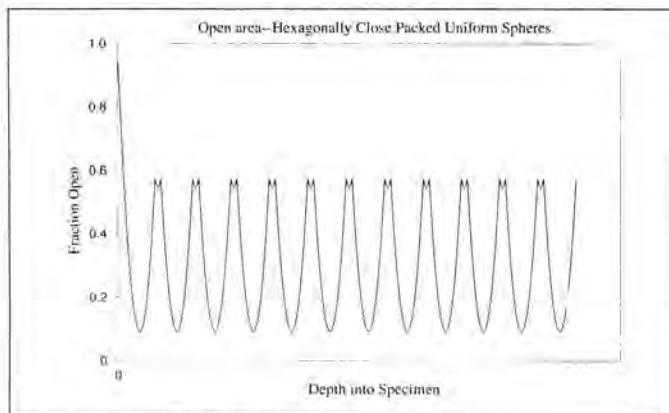


Fig. 2. Variation of the fractional open cross-section with distance from the surface of hexagonally close packed arrangement of uniform spheres.

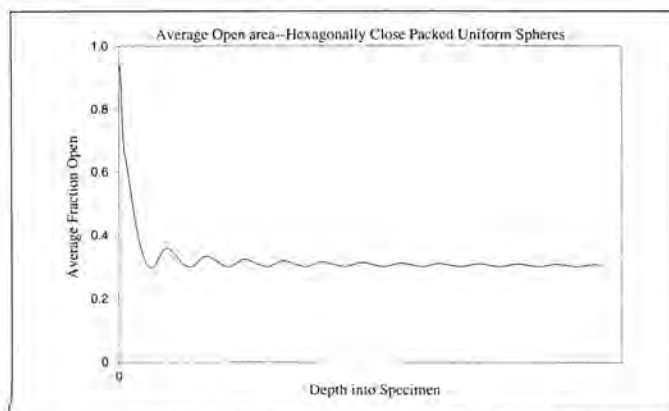


Fig. 3. The average fractional open area between the surface and depth, *d*.

and chemical reaction. Since we assume here that the solid phase is immersed in pure water, we have effectively eliminated convection and reaction from consideration. Even so, extensive work has been carried out for this reduced form of leaching. Matsuzuru (9) presents a theoretical analysis of some of the processes involved. Spence, et al (11) and Cheng

(12) compare several empirical models on the basis of tabular data.

Our principle thrust in this paper is to construct a dimensional model of the diffusion process in which we account for the presence of the inert filler material. To accomplish this we assume a slab geometry and allow the diffusion coefficient to be a function of depth, *x*. Thus the proposed model, based on Fick's Law is

$$u_t = (D(x)u_x)_x \tag{Eq. 4}$$

where *u(x,t)* denotes the concentration of the leachant at depth, *x* and time, *t*. The initial condition is taken to be constant

$$u(x,0) = C_0 \tag{Eq. 5}$$

and we assume a non-dimensional length *x* to range between 0 and 1. The boundary conditions

$$u(0, t) + u(1, t) = 0 \tag{Eq. 6}$$

are taken to mean that mass transfer external to the cylinder is rapid relative to the mass transfer internal to the cylinder. This assumption is consistent with the experimental data which will be used for comparison.

Thus the initial boundary value problem considered is

$$u_t = (d(x)u_x)_x \tag{Eq. 7}$$

$$u(x,0) = C_0, 0 \leq x \leq 1 \tag{Eq. 8}$$

$$u(0, t) = u(1, t) = 0, t \geq 0 \tag{Eq. 9}$$

To accommodate the experimental data which was obtained for cylindrical specimens, we make the usual surface/volume correction.

The fact that *D(x)* is not constant implies that the solution to this boundary value problem cannot be determined in a computable integral or series form as in other treatments (5), (13), (9), and (7). Thus the solution must be obtained numerically. A numerical Partial Differential Equation (PDE) solver in the International Mathematics and Statistical Library (IMSL) was used on the Texas A & M University Cray YMP (1 CPU) to obtain the results presented here.

In most treatments heretofore an effective but constant diffusion coefficient *D<sub>e</sub>* based on the formula

$$D_e = D_w e^{\frac{\sigma}{\tau}} \tag{Eq. 10}$$

where  $D_w$  is the free stream diffusion coefficient,  $\epsilon$  is the porosity (volume fraction of pores),  $\sigma$  is the constrictivity coefficient, and  $\tau$  is the tortuosity (8). Our numerical results illustrate that with our model for  $D(x)$ , normalized so that

$$D_e = \int_0^1 D(x) dx \tag{Eq. 11}$$

the results, in the short term, vary considerably from those for the fixed  $D_e$  unless  $D'(x)$  is small. Although long term results do compare more favorably (though not exactly in practice or theory), the application of a constant effective diffusion coefficient is therefore not entirely valid. This accounts for the development of several empirical models such as NEWBOX (11). This observation alone gives merit to any model that accounts for "real position" tortuosity constrictivity and porosity. In effect our model can be interpreted in the form

$$D(x) = D_w \frac{\epsilon(x)\sigma(x)}{\tau(x)} \tag{Eq. 12}$$

At time,  $t$ , the quantity

$$\int_0^1 u(x, t) dx \tag{Eq. 13}$$

is the amount of material remaining in the solid phase at time,  $t$ .

Thus

$$u(t) = \frac{C_0 - \int_0^1 u(x, t) dx}{C_0} \tag{Eq. 14}$$

is the cumulative fraction leached (CFL). Assume that  $D(x)$  is continuously differentiable. We have observed experimentally (but have not proven) that

$$\lim_{t \rightarrow 0} \frac{u(t)}{\sqrt{t}} = c \frac{D(0) + D(1)}{2} \tag{Eq. 15}$$

where  $c$  is a fixed constant, independent of  $D(x)$ . In a practical sense this should not be surprising for two reasons. First, this limit has been established for  $D(x)$  constant (14), and second, the CFL for diminishing time is dependent on the diffusion rate increasingly near the surface.

Again assuming that the solid phase is a matrix packed by inert spheres of radius,  $R$ , in a hexagonal arrangement; as shown earlier, at depths greater than one radius,  $R$ , the frac-

tion of area parallel to the surface that is not occluded by the filler is a periodic function of period  $1.633 R$  as given by Eq. (1) and shown in Fig. 1. Thus, the effective diffusion rate should also be a periodic function of depth. In non-dimensional terms, this function should oscillate at least 50 times in the range 0,1 ( $R = 100$  microns,  $0,1 = 1$  cm.).

The geometric model, equation (1) has a couple of obvious defects. The fact that it was derived for a packed matrix implies a filler volume fraction of about 0.6. A more reasonable fraction would be 0.4. This model can be adjusted for this aspect by using the centers of the packed model as centers of filler particles of a smaller radius. Thus Eq.(1) must be adjusted as follows: the variable  $R$  in the numerator is replaced by  $R' < R$  and when either  $(2x'R' - x'^2)$  or  $(2x''R' - x''^2)$  become negative they are replaced by zero.

Another exception is that filler particles are not in general spheres of uniform radius, but are polyhedra of various diameters and shapes. Thus the model  $F(x)$  only serves to yield intuition about the functional nature of cross sectional occlusion by filler material. Therefore we idealize the situation by an diffusion rate that is more or less tractable numerically. We select the normalized model

$$D(x) = \frac{(1 + b \cos(f\pi x)) (1 + x^{50} + (1-x)^{50})}{1.04} \tag{Eq. 16}$$

where  $f$  is an even positive integer representing the number of layers of inert fill particles per unit of length, and  $b$  is a factor chosen to represent the magnitude of relative occlusion by the inert fill. Both of these factors can be estimated from physical properties of the original mixture;  $f$  from the average inert particle diameter, and  $b$  from the inert volume fraction. In the examples below,  $f = 50$  and  $b = 0.5$ . The expression containing the exponentials is an attempt to empirically account for the "wash off". Note also that Eq.16 is divided by 1.04 such that

$$\int_0^1 D(x) dx = 1 \tag{Eq. 17}$$

### RESULTS

Comparison of Fig. 4 with Fig. 1 shows that the computed results are a better fit for the experimental results with the larger (200 l and 20 l) specimens than the smaller ones. This is apparently a result of the use of the surface to volume ratio

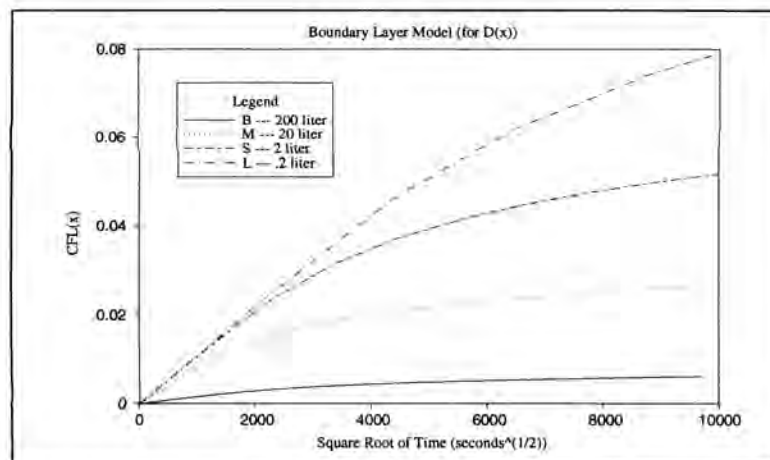


Fig. 4. Cumulative fraction leached calculated by model.

as a means of converting the dimensionless model to the cylindrical specimen data. This is not unexpected as the use of the one-dimensional model for a three dimensional object is only valid very near the surface and for the smaller specimens, the data represents a significant penetration. A 2-d or 3-d PDE Solver would perhaps yield better results.

Our ultimate goal remains to be able to predict the long term leaching behavior based on very short term data. The results described here are encouraging in that the nature of the near surface(short-term) data can be described by geometric(physical) correction to the long-term effective diffusivity.

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