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OPTIMIZING CONDITIONS FOR AN ACCELERATED LEACH TEST*

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ABSTRACT

An accelerated leach test for low-level radioactive waste forms is being developed to provide, in a short time, data that can be extrapolated to long time periods. The approach is to provide experimental conditions that will accelerate leaching without changing the dominant release mechanism. Experimental efforts have focused on combining individual factors that have been observed to accelerate leaching. These include elevated temperature, increased leachant volume, and reduced specimen size. The response of diffusion coefficients to various acceleration factors have been evaluated and provide information on experimental parameters that need to be optimized to increase leach rates. For example, these data show that large volumes of leachant are required when leaching portland cement waste forms at elevated temperatures because of high concentrations of dissolved species. Sr-85 leaching is particularly susceptible to suppression due to concentration effects while Cs-137 leaching is less so.

Preliminary modeling using a diffusion mechanism (allowing for depletion) of a finite cylinder geometry indicates that during early portions of experiments (daily sampling intervals), leaching is diffusion controlled and more rapid than later in the same experiments (weekly or greater sampling intervals). For cement waste forms, this reduction in rate may be partially controlled by changes in physical structure and chemistry (sometimes related to environmental influences such as CO_2), but it is more likely associated with the duration of the sampling interval. By using a combination of mathematical modeling and by experimentally investigating various leach rate controlling factors, a more complete understanding of leaching processes is being developed. This, in turn, is leading to optimized accelerating conditions for a leach test.

INTRODUCTION

The objective of this work is to develop an accelerated leach test that can be used to predict the long-term leaching behavior of solidified low-level waste forms. Data from leach tests are important input parameters for disposal site performance assessments. Because predictions over long times are required for this use, leaching mechanisms must be known. Mechanistically sound mathematical models can then be used with the leaching results to make reasonable long-term projections.

The effect of many individual accelerating test conditions and their combinations have been experimentally measured [Dougherty et al., 1987].

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Determination of the optimum conditions for the design of an accelerated test is the subject of this paper. To this end, the applicability of specific models to predict radionuclide releases from specific waste form materials and leaching conditions has been examined. While work in this program involved several types of solidification agents (specifically, portland cement, vinyl ester-styrene, and bitumen), only portland cement containing sodium sulfate as a simulated waste will be discussed in this paper.

If diffusion is the operating release mechanism for cement waste forms, then elevated temperatures, small specimen size, and larger volumes of leachant will increase leach rates in a systematic way [Dougherty, 1985]. However, to develop a useful accelerated leach test, certain practical considerations are necessary. For example, temperature should be as high as possible but it must not alter the leaching mechanism, the chemistry or physical structure of the specimen. Also, the temperatures used should not require special equipment such as autoclaves or teflon containers. Leachant volumes should be as large as possible but small enough to be easily handled. Specimens should be small but not so small that they are not representative of full-scale waste forms. When several requirements are combined, for example, a small specimen in a large leachant volume, the potential of being below analytical limits also exists for good waste forms. These problems must be addressed in a way that optimizes leach rates yet provides a workable test protocol.

REVIEW OF LEACHING MODELS

Models based on mass transport theory that have been validated with experimental data are regarded as an excellent means of estimating the amounts of material released by solidified waste.

Bulk Diffusion

The mathematical theory of transport by diffusion from solids is based on Fick's hypothesis that the diffusion rate is proportional to the concentration gradient [Crank, 1975; and Carslaw and Jaeger, 1959]. The fundamental partial differential equation for diffusion is

$$\frac{\partial C}{\partial t} = D_e \nabla^2 C \qquad (1)$$

where C = concentration of species

t = time

D_e = effective diffusion coefficient in porous media.

Mathematical solutions to the transport equation for diffusion have been described in the literature and applied to the leaching of radionuclides from waste solids [Godbee, 1980]. The exact form of the solution the mass transport equation of diffusion depends on the initial and boundary conditions of the problem. A simple case is that of a semi-infinite solid with a constant diffusion coefficient where ideally the cumulative fraction released from a porous medium is predicted as

$$\frac{\Sigma a_n}{A_o} = 2 \frac{S}{V} \left[\frac{D_e t}{\pi} \right]^{1/2} \tag{2}$$

where Σa_n = the total amount of radioactive material released in all leaching periods up to time, t,

A_o = the initial amount of radioactive material,

V = waste form volume,

S = waste form surface area,

D_e = effective diffusion coefficient.

Finite samples which release radioactive materials by the diffusion mechanism to aqueous solutions have a plot of cumulative fraction leached (CFL) versus $\sqrt{\text{time}}$ that is linear to CFL = 0.2 (20% release).

The exact solution for diffusion from a finite cylinder has been described by Nestor, 1980. The solution of the mass transport equation for a constant diffusion coefficient, a uniform and homogeneous solid and zero surface concentration during leaching is

$$\frac{\Sigma a_n}{A_o} = 1 - \frac{32}{\pi^2 r^2} \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} \frac{e^{-tD_e[\beta_m^2 + (2n-1)^2 \pi^2/4\ell^2]}}{(2n-1)^2 (\beta_m)^2}, \tag{3}$$

where D_e = effective diffusivity (cm^2/s),

ℓ = half length of cylinder (cm)

r = radius of cylinder (cm)

a_n = cumulative leached activity (Ci)

A_o = initial total activity in case (Ci)

β_m = positive roots of Bessel function where $J_o(r \beta_m) = 0$.

The convergence of equation (3) is slow but computer programs were developed to determine the cumulative fraction leached.

Diffusion and Reaction

Mass transport of the diffusing radionuclides from solidified waste can be limited by local instantaneous equilibrium. The simplest case is where the adsorbed species (S) is proportional to the mobile species (C).

$$S = KdC$$

The solutions for the semi-infinite media and the finite cylinder are identical to equations (2) and (3) respectively, where

$$D_e = D_f \, (\delta/\tau^2) \, (1/(1+\rho_a \, Kd/\epsilon) \; .$$

where δ = constrictivity,

τ = tortuosity,

ρ_a = apparent density,

ϵ = porosity,

D_f = diffusion coefficient in free liquid.

Models for diffusion and kinetically controlled reactions, interface resistance, irreversible reactions, dissolution, desorption, and moving boundaries have been reported for numerous practical applications. Several such models were reviewed in an earlier report [Dougherty, 1985].

Anomalous Non-Fickian Diffusion

The diffusion of radionuclides from several types of solidified waste forms cannot be described adequately by the concentration-dependent form of the diffusion equation with a constant boundary. Penetration of water into the waste form eventually causes swelling and the characteristic leach curve shows two stages that are dependent on time and waste loading. This type of behavior has been observed with bitumen specimens in this program and will be reported elsewhere. No entirely satisfactory model for this type of diffusion has been reported.

RESULTS AND DISCUSSION OF ACCELERATED LEACH TESTING

Several kinds of leach tests are used in this program. One is a semi-dynamic test in which specimens are placed in the leachant, allowed to stand for a defined amount of time and then placed in fresh leachant. Several sampling schedules are used with this type of test: daily leachant replacements and an ANS 16.1 [American Nuclear Society, 1986] type of schedule. The latter requires leachant replacements to take place twice on the first day, once per day for five days, and then longer intervals of one, two, or three weeks. Another kind of leach test that has been explored in this study is a static test in which the leachant is not changed at all during the course of the experiment.

Experimental results for an extensive series of tests to investigate the effects of leach test factors were reported by Doughtery (1987). Some of the significant observations and efforts to quantify these experimental observations lead to the use of the semi-infinite and the finite cylinder diffusion models for leaching.

Results for Sr-85 and Cs-137 leached from cement containing 5 wt% sodium sulfate at 20°C are shown in Figure 1. The solid line is the result of the finite cylinder model for cumulative fraction leached (CFL) using diffusion coefficients of $D_e = 6.4 \times 10^{-10}$ cm^2/s for Sr-85 and $D_e = 4.2 \times 10^{-8}$ cm^2/s for Cs-137. Bulk diffusion accounts for the entire leaching curve in both cases. With this being true, a variety of means to accelerate leaching are possible. The first choice is to elevate temperature. The results of that work have been discussed previously [Fuhrmann et al., 1987]. Other choices include decreasing the specimen size and increasing the leachant volume. Currently, the experimental work in this program is focusing on combinations of these accelerating factors.

Temperature

To summarize the effects of elevated temperatures, at 50°C leaching of Cs-137 from plain cement is increased by a factor of 11 when compared to leaching at 20°C. When cement containing 5 wt% sodium sulfate is leached at 50°C, the increase is only a factor of 3 over leaching at 20°C. These experiments were conducted with a leachant volume to waste form surface area ratio of 10 (1.3 ℓ). Leaching of plain cement at 70°C shows anomalous behavior which may be caused by changes in the physical structure of the material.

Leachant Volume

At 20°C leachant volume or replacement frequency has little effect on Cs-137 leaching but there is a distinct change in Sr-85 leaching. Figure 2 shows experimental data for Sr-85 releases from cement with 5 wt% sodium sulfate. One experiment had daily leachant replacements while the other used a modified ANS sampling schedule. The finite cylinder model accurately described the entire data set for the daily replacement experiment as it did for the beginning of the ANS data. Once the ANS experiment shifted to a weekly leachant replacement schedule, the model overestimated releases. Leaching of Sr-85 was suppressed by some factor related to replacement frequency such as concentration increases or back reactions.

Since the frequency of leachant renewal influences the diffusion of radionuclides from waste forms, the effect of the ratio of leachant volume to specimen surface area was investigated. The ANS 16.1 test recommends a ratio of 10:1. The results of experiments using increased leachant ratios of 30:1 and 50:1 show that increased leachant volumes enhance the leaching of Sr-85 although not as much as simply changing the leachant on a daily schedule. Again, there is little change in Cs-137 leaching.

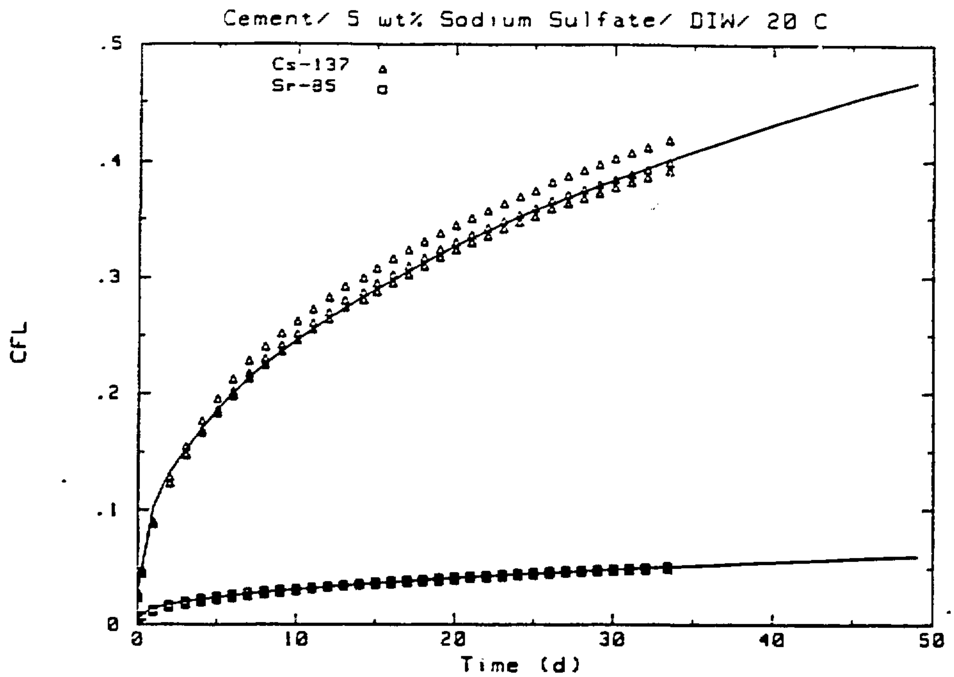

Figure 1. Cumulative Fraction Leached (CFL) of Cs-137 and Sr-85 plotted against time for experiments in which the leachant was replaced daily. The solid lines are calculated from the finite cylinder model for diffusion.

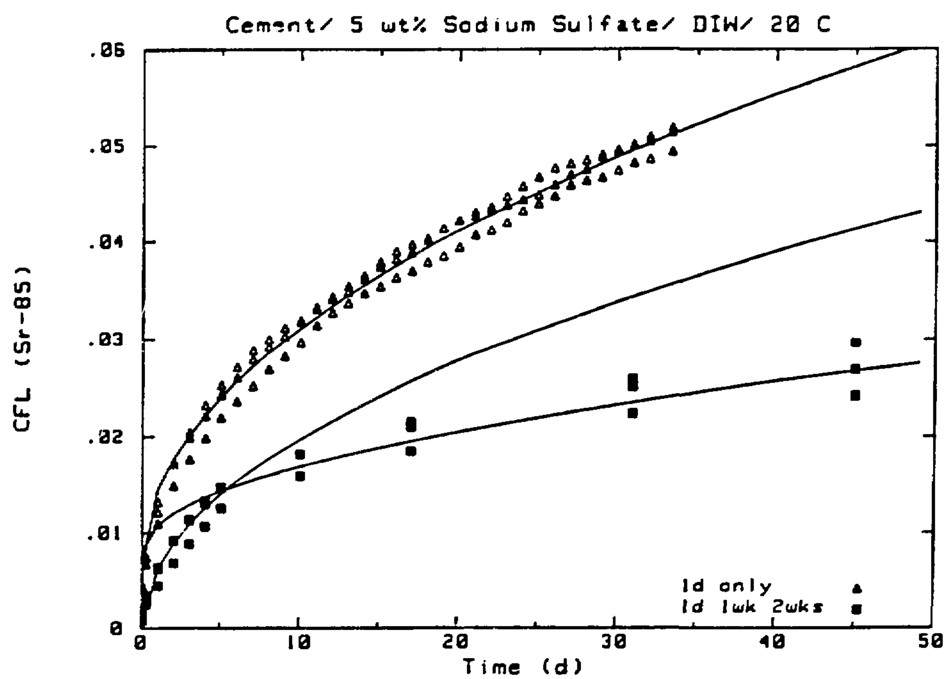

Figure 2. Cumulative Fraction Leached (CFL) of Sr-85 comparing releases from experiments with daily and variable leachant replacement schedules. The solid lines are calculated from the finite cylinder model.

Size

The ability to correct for size is critical to the development of a leach test that is meant to be extrapolated to full-scale specimens. As shown in equation (2), by normalizing CFL data with the ratio of waste form volume to waste form surface area (V/S), data from small-scale specimens can be used to predict releases from large-scale waste forms. This assumes that diffusion is the leaching mechanism. Data in the form of CFL x V/S are plotted in Figure 3 for triplicate specimens of three different size cylinders. They should only be compared up to about 25% release. The points for the two smallest sizes fall on top of each other indicating the V/S size correction works. The larger size (10.1 x 12.7 cm) had lower values. This is probably caused by the inherent variability among batches of waste forms. As an example of what this variation can be, leaching data was taken from the literature [Arora, 1987] and plotted in Figure 4. This set of curves is for Cs-137 leached from portland cement containing ion-exchange resin. Six different-sized specimens are compared and show a band with a width of about a factor of 2, very similar to the data generated in this program.

Combined Effect of Temperature and Leachant Volume

In leaching experiments with cement specimens, as temperature increases so do concentrations of dissolved species in the leachate for any given time interval. Experiments run at elevated temperatures therefore require increased volumes of leachant, either with frequent leachant replacement or with larger volumes in each interval. Figure 5 shows leaching data for Cs-137 from several experiments illustrating the effect of elevated temperature (50° and 60°C) and larger volumes (6.5 ℓ) of leachant for static and ANS-type tests. At each temperature there is little difference between Cs-137 releases under static or semi-dynamic leaching conditions, although the static test does have a slightly lower average release. At 50°C releases are significantly greater than at 60°C. This apparently anomalous behavior was confirmed with other experiments and may be the result of temperature-induced structural or surface changes. Earlier data also indicate that at this temperature the behavior of cement waste forms containing sodium sulfate changes.

By using a larger leachant volume (6.5 ℓ), releases of Cs-137 at 50°C give an acceleration of about 9 times over the baseline experiment at 20° (1.3 ℓ). Without the larger volume of leachant the acceleration factor is about 3.

Figure 6 shows leaching data for Sr-85 from static and ANS-type experiments at 60°C. These experiments were run with 6.5 ℓ of water. Also included is a data set for the baseline, an ANS-type experiment using 1.3 ℓ of water at 20°C. The behavior of Sr-85 is quite different than that of Cs-137. The static test reaches a maximum Sr-85 activity at 18 days which then begins to drop. This type of behavior requires adsorption or precipitation to remove Sr-85 from solution. Given the very high alkalinity of the water and the high Ca concentration, it is likely that $CaCO_3$ precipitation is proceeding very quickly as CO_2 is drawn into the leachate from the air.

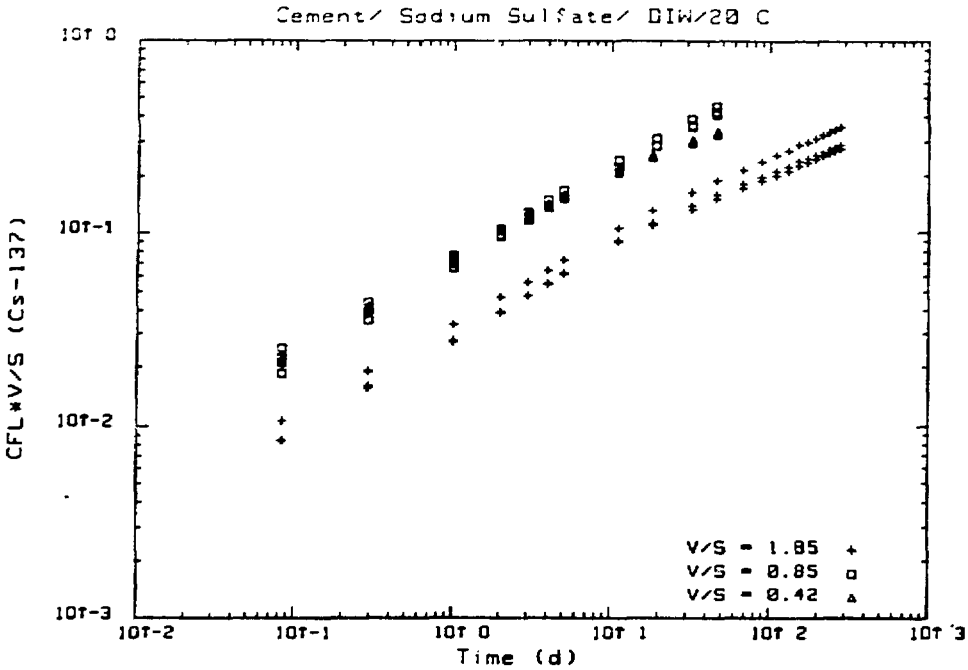

Figure 3. Cumulative Fraction Leached (CFL) corrected for size by using the volume to surface area ratio (V/S). Results are shown for three sets of specimens with different sizes.

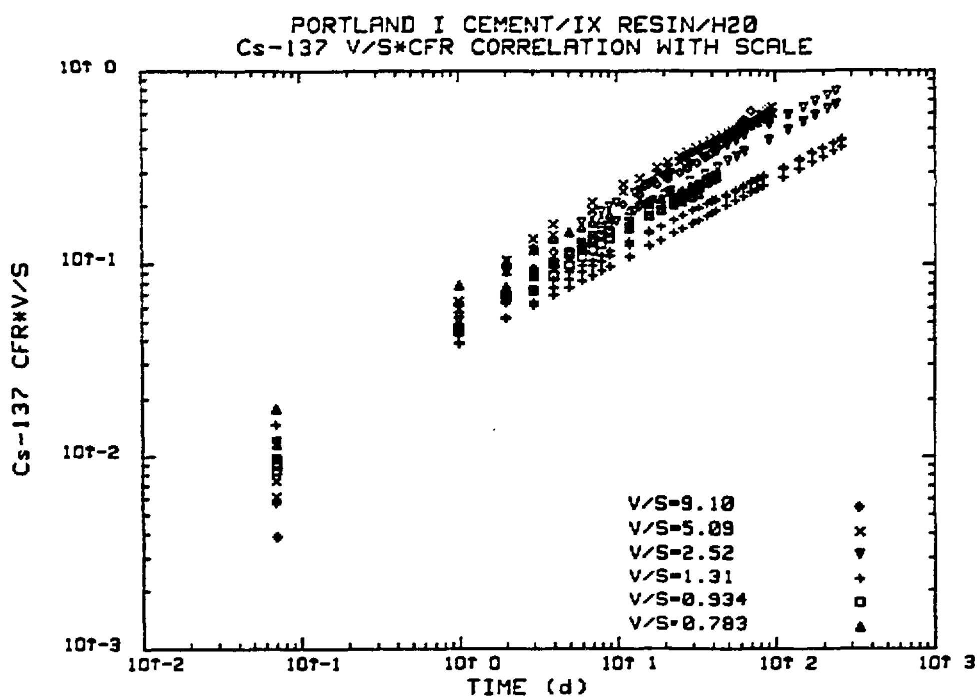

Figure 4. Cumulative Fraction Leached (CFL) corrected for size by using the volume to surface area (V/S). Results are taken from Arora (1984) and illustrate the band of error typical for V/S corrections.

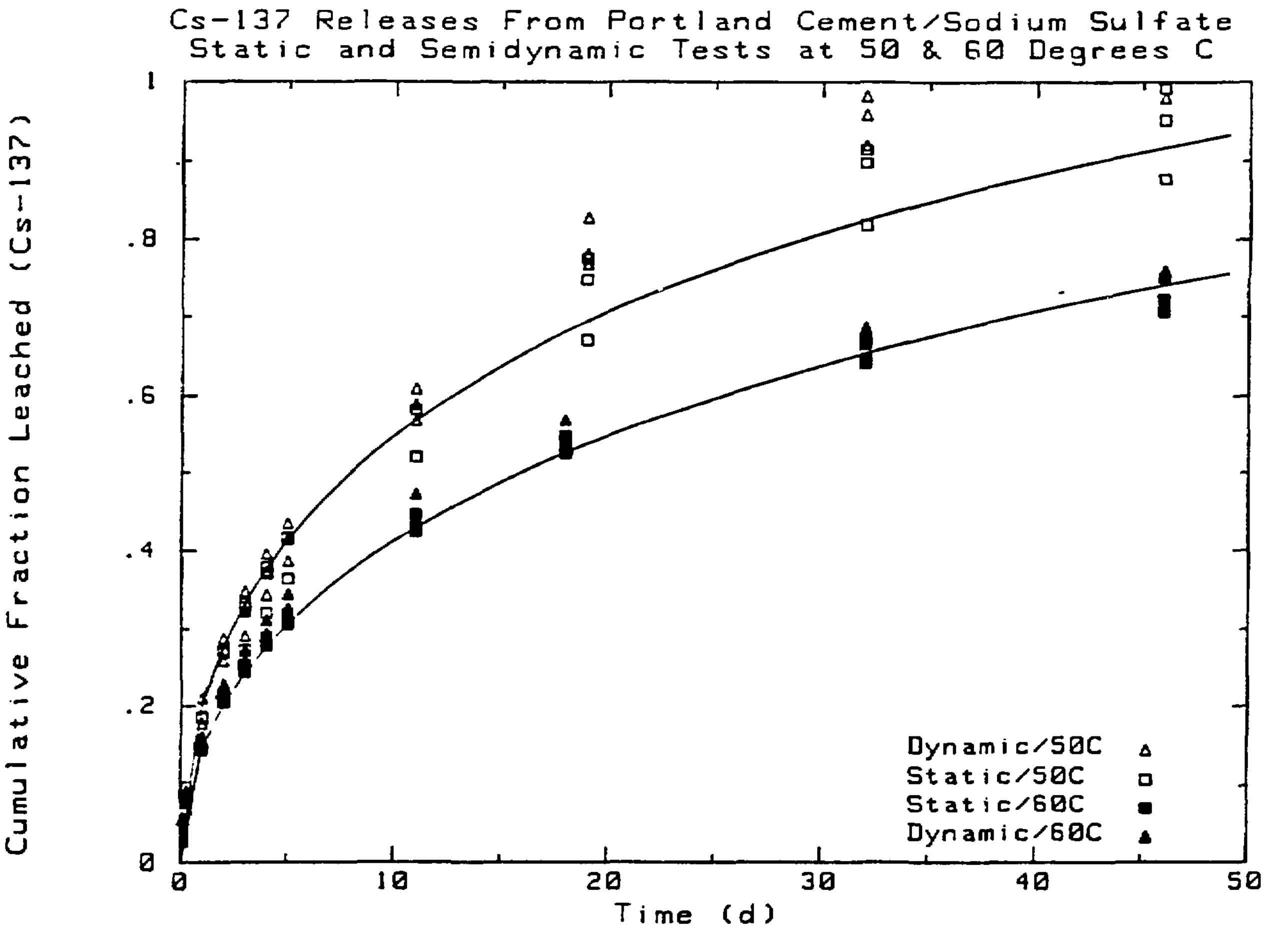

Figure 5. Releases of Cs-137 are shown for waste forms leached at 50°C and 60°C in static leach tests and in tests with varying leachant replacement schedules.

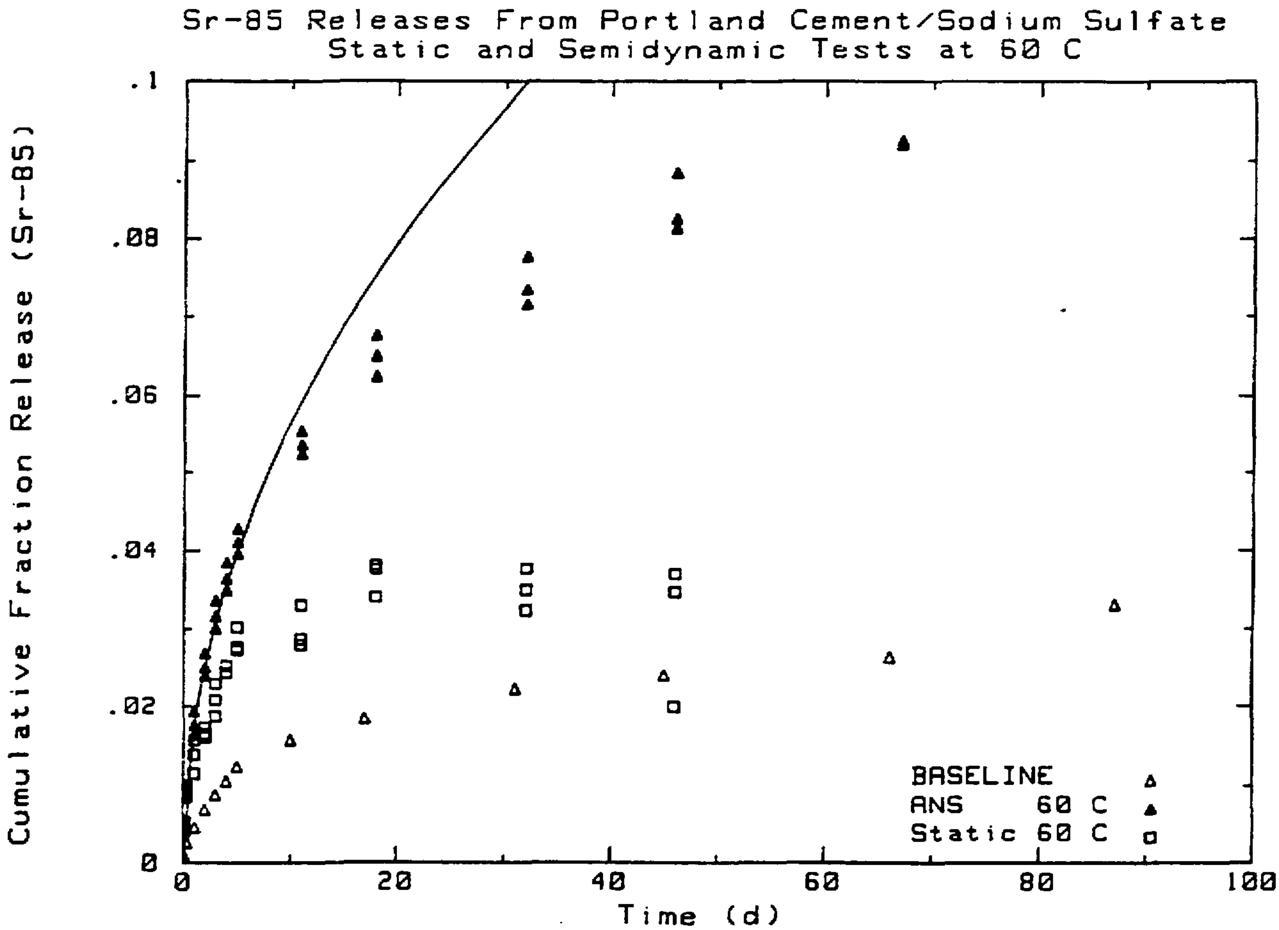

Figure 6. Releases of Sr-85 are shown for a static test and an ANS-type test run at 60°C in 6.5 ℓ of water. Also shown is a "baseline" data set run at 20°C in 1.3 ℓ.

Sr-85 from the 60°C ANS test leaches at a much greater rate than the static or baseline tests. Nevertheless, it is also suppressed when the weekly leachant replacements are reached. The solid curve on Figure 6 is the finite cylinder calculation for $D_e = 2.2 \times 10^{-9}$ cm^2/s. It shows that data from the daily sampling fit the model. However, the weekly volume change of 6.5 ℓ is not adequate to provide uninhibited leaching. Experiments are currently underway that combine the three factors of: small specimen size, large leachant volume (and daily leachant replacement), and elevated temperature.

CONCLUSIONS

Releases of Cs-137 and Sr-85 from portland cement waste forms containing 5-wt% sodium sulfate as a simulated waste can be modeled by a finite cylinder diffusion equation. However, for the purposes of developing an accelerated leach test, several experimental parameters must be optimized.

Particular attention must be paid to the volume of water used as well as to the leachant replacement frequency. While a smaller volume is adequate for Cs-137, much more water is required for Sr-85. This is evident from the different behavior of the two radionuclides when comparing static and semi-dynamic leach tests. Size can be normalized by V/S, as expected from the diffusion equations, but there appears to be a range of a factor of two within which the corrected values fall. This is true for cement containing sodium sulfate as well as cement with ion exchange resin.

By combining elevated temperatures with increased volumes of water and more frequent leachant replacements, leaching can be accelerated significantly. Moreover, with the proper experimental conditions, accelerated leaching can be accurately modeled.

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