DEVELOPMENT OF AN ACCELERATED LEACH TEST*

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ABSTRACT

An accelerated leach test is being developed for low-level radioactive waste forms that will provide data that can be extrapolated to estimate long-term releases. This paper describes the methods that are being used to provide a sound physical basis for this test. The approach has been to determine the experimental conditions that will give the maximum leach rate without disturbing the mechanisms of leaching. This requires that the leaching mechanism can be identified and that a mechanistically defensible model is available. Results of accelerated tests are compared to results from long-term standard tests to obtain the acceleration factor. Data curves are also compared to model results to ascertain that no change in mechanisms has occurred. For many applications, a diffusion model for a finite cylinder was used successfully.

Leaching studies were conducted on portland cement, asphalt and thermosetting polymers used as solidification agents containing various types of simulated wastes and the radioactive tracers ^{57}Co, ^{85}Sr and ^{137}Cs. These materials were leached under experimental conditions (i.e., elevated temperature, increased leachant volume, reduced specimen size and leachant solutions containing complexing agents) that were expected to increase release rates. Initially, only one condition was altered in each experiment, but successful accelerating factors were combined later to provide a more effective leach test. Preliminary results of these studies are described.

INTRODUCTION

An accelerated leach test is being developed for low-level radioactive waste forms that will provide data that can be used to estimate long-term releases. This paper describes the general approach we have taken to provide a sound physical basis for this test.

Leach tests for low-level radioactive waste have served two purposes: (1) to provide data for comparison among solidification agents or additives for waste forms and (2) to meet licensing requirements of the Nuclear Regulatory Commission for shallow land burial disposal (10 CFR 61). In both cases, short-term (90-days) tests typically are considered adequate. A third use of leaching data, which has only recently been applied, is for source term determinations and performance assessment of disposal sites (1,2).

The need for an accelerated leach test has arisen because projections over long times are necessary for performance assessments and the leaching data used in these assessments also should be applicable over long times. In addition, leaching from advanced waste forms that are effectively solidified is so slow that prolonged leach tests are required before the long-term leaching behaviour can be determined. Time limitations and the high cost of these tests have limited data *acquisition* to the early stages of leaching. This does not necessarily provide useful information about releases over the life of the waste form. Moreover, it is rare that a mechanistic study of leaching behaviour is conducted for low-level waste forms, even though such a study is required to understand and predict long-term leaching behaviour. The accelerated leach test methodology that is being developed attempts to address these problems.

ACCELERATED LEACH TESTING

A general approach to developing accelerated leach tests is given in ASTM Standard Practice E632-82 (3). It outlines a systematic approach that should be followed in developing tests for predicting the service life of building materials. Problems associated with accelerated tests for building materials, as discussed in the ASTM document, also are true for accelerated leach tests. These include:

- degradation mechanisms (taken to be distinct from leaching mechanisms) are seldom well-understood
- external factors can lead to test artifacts
- accelerated tests seldom relate quantitatively to expected service conditions
- test configurations are different than those in actual use

Leach tests have the additional problem that the leaching mechanism itself is seldom understood. After all, most tests that are performed on low-level radioactive waste are done to show that waste forms do not exceed a maximum leach rate as defined by the Nuclear Regulatory Commission (NRC) (4). Leach tests required by the Environmental Protection Agency for hazardous wastes provide even less information, giving a concentration at a single point in time, leading to a pass/fail decision (5).

The question of waste form degradation is a particularly important one when predicting leaching from low-level waste. Predictions depend, in part, on waste form geometry

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(on a micro-scale as well as on a large scale) being maintained over time. They also are sensitive to changes in chemistry that can take place within an aging material. Unfortunately, little research has been done to determine the long-term durability of waste/solidification agent composites or the failure mechanisms of those that are not durable. The relationship of short-term tests, accelerated or not, to the durability of waste forms is open to question if no mechanistic foundation is available as a basis for the tests.

In the case of leach tests, the last two problems noted above question the relationship of the test to actual disposal conditions. This point exists for standard tests as well as for accelerated tests. Complex experiments (such as lysimeter studies) that duplicate the disposal environment contain too many variables to effectively supply data for determinations of waste form release mechanisms. For this reason simple leach tests are required that can then be used to provide input to groundwater transport and geochemical codes.

MATERIALS USED

Four types of waste forms are being used in this study of accelerated leaching:

- portland type I cement containing 5 wt% sodium sulfate
- portland type I cement containing 15 wt% incinerator ash
- vinyl ester-styrene containing 40 wt% sodium sulfate
- bitumen containing 40 wt% sodium tetraborate

These materials were chosen because they are wastes that are currently generated or are expected to be generated in the future. In addition, these solidification agents represent materials (hydraulic cement, thermosetting polymer and a thermoplastic) having dissimilar properties that behave differently under accelerating conditions. Simulated wastes and the radioactive tracers, ^{137}Cs, ^{85}Sr and ^{57}Co, are added to the specimens which are typically run in triplicate.

APPROACH

The general approach of this study is to generate experimental evidence that allows us to select a set of optimized parameters for leaching experiments. In this case, the leach rate should be as great as possible without having to resort to methods that make the test cumbersome. For example, elevated pressures and temperatures greater than 100°C were not considered.

The first stage of the work was to leach specimens at room temperature with long-term (greater than 500 days) tests. These serve as a baseline or reference against which accelerated leach tests are judged. At the same time, a wide ranging survey of individual potential accelerating conditions was conducted, consisting of short-term leach tests. Effects of the following were examined:

- leachant pH of 4, 6 and 8
- temperatures of 20, 30, 40, 50 and 70°C
- ratio of leachant volume to specimen surface area of 10, 20, 30 and 50
- anoxic and oxic groundwater and distilled water
- leachant containing humic acid or EDTA
- specimen size
- leachant replacement frequency

Results of these studies are given in a topical report along with information from solid phase studies that were used to observe pre- and post-leaching structure (6).

Based on the survey of single accelerating conditions, a more detailed study was carried out in which successful accelerating conditions were combined to provide even faster leaching. Results of these studies are reviewed later in this paper and also are contained in another topical report (7). Ultimately, this information will lead to an accelerated test method that provides the greatest leach rate without altering the controlling leaching mechanism.

Data from the accelerated leach test must be calibrated so the acceleration is known. This is done by plotting the accelerated leach test data and the reference leach test data on the same graph in the form of cumulative fraction leached (CFL) versus time (Fig. 1). A value of cumulative fraction leached is then selected (for example, 0.70) and the times to obtain that amount of release for both sets of data are determined as illustrated in the figure. The acceleration factor is the ratio of the two.

Data from the accelerated leach test must reflect the same processes that occur during the reference leach test. This can be demonstrated in several ways. The most satisfactory approach is to use a computer model that describes a theoretically sound leaching mechanism. If the fit between the reference data and the modeled curve is good and the same model can be used to describe the accelerated data, then the rate controlling leaching mechanism is defined and does not change during the accelerated leach test.

For this study, emphasis has been placed on using a model that describes diffusion from a finite cylinder. Mathematical solutions to the transport equation for diffusion have been described in the literature and applied to the leaching of radionuclides from waste forms (8). Solutions for the finite cylinder were given by Nestor (9) and by Pescatore (10). A computer program using these equations was used to analyze the data.

An example is shown in Fig. 2 for ^{137}Cs and ^{85}Sr releases from portland cement containing 5 wt% sodium sulfate. The model fits both sets of data when leachant is replaced daily. A computer program containing this model as well as other necessary calculations and plotting routines will be supplied with the final test method.

Another approach is more empirical and is used when no mechanistic model is available to describe the leaching process. The CFL data from the reference experiment is plotted against the CFL data from the accelerated experiment. The data points are matched in chronological order: the first reference sampling versus the first accelerated sampling, etc. The resulting plot is linear if the leaching mechanism has not changed. A change in leachant

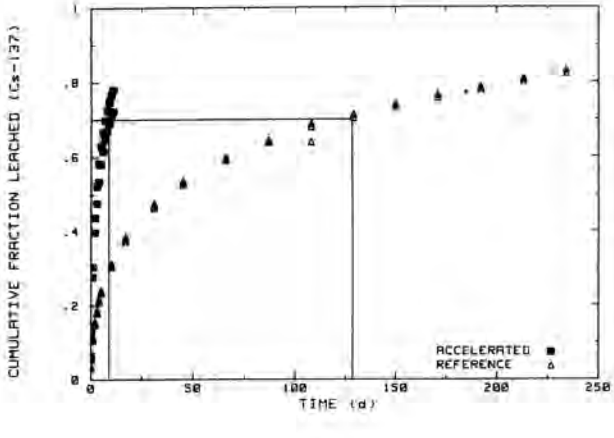

Fig. 1. ^{137}Cs Results From Optimized Accelerated Leach Test for Cement/Sulfate Specimens are Compared to Results From the Baseline Test. The

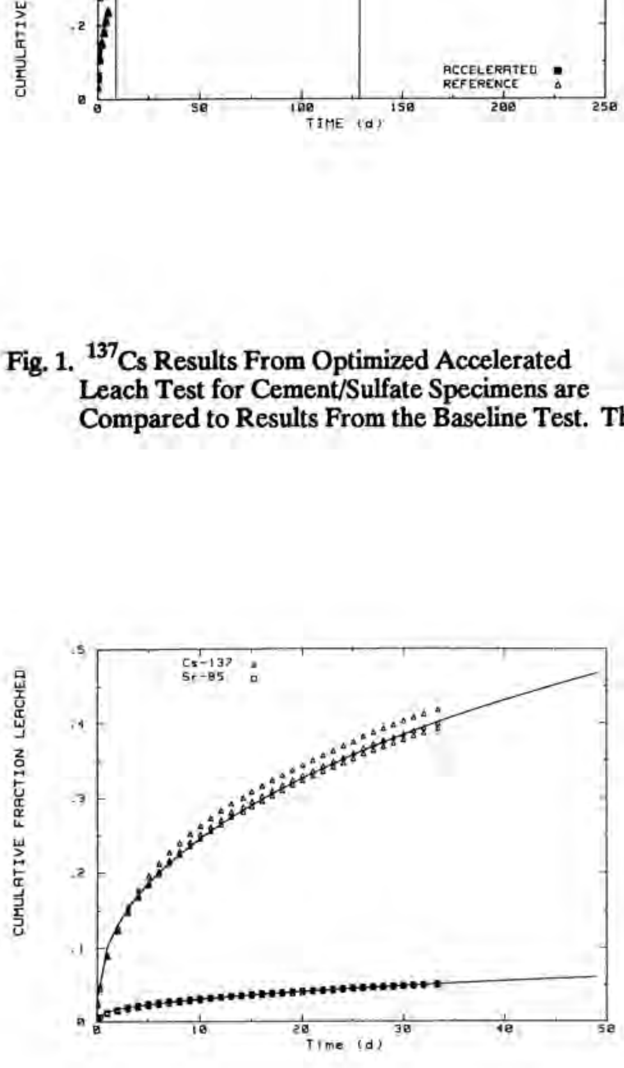

Fig. 2. Cumulative Fraction Leached (CEL) of ^{137}Cs and ^{85}Sr Plotted Against Time for Experiments in Which the Leachant was Replaced Daily. The Solid Lines are Calculated From the Finite Cylinder Model for Diffusion.

replacement intervals for one of the two tests will cause a break in the plot and a change in the slope, but the two segments will be linear. This is shown in Fig. 3 for portland cement containing incinerator ash. In this figure, the change in slope occurred when the daily leachant replacement of the reference experiment was extended to weekly or greater. Both segments, however, are linear, indicating that no change in leaching mechanism took place during the accelerated test.

A third method is to look at the relationship of leaching to temperature. This is of particular concern because elevated temperature, which is the primary accelerating condition being used, could alter the leaching mechanism in several ways. These include changes in physical structure of the material, such as microcracking, as well as chemical changes resulting in shifts in the balance of mineral composition of the cement.

Theoretically, the temperature dependence of leaching depends on the Arrhenius equation:

$$De = A \exp -Ea/RT \tag{1}$$

where,

De = effective diffusion coefficient at T

A = constant

Ea = the activation energy, kcal/mole

R = the gas constant

T = temperature, K

From this, diffusion coefficients determined from experiments run at varying temperatures are plotted against 1/T in degrees kelvin. If a linear plot results, the leaching mechanism remains constant with changing temperature. The rate increase is indicated by the slope of the line. An Arrhenius plot is shown in Fig. 4 for ^{85}Sr leached from portland cement containing sodium sulfate. Between 50 and 60°C a change in leaching mechanism is indicated by the low value for specimens leached at 60°C (a value of 3 calculated as 1/T x 1000 on the figure). This is attributed to a physical or chemical change in the structure of the cement and means that an accelerated test cannot use temperatures greater than 50°C. Data for much more detailed Arrhenius plots are currently being generated for ^{137}CS, ^{85}Sr, Na, K and Ca.

RESULTS OF STUDIES TO ACCELERATE LEACHING

Elevated temperature is the most effective means of accelerating leaching, but other conditions must be optimized to obtain the maximum leach rate. Comparisons of data with modeling results provided a good way of judging the effects of various accelerating conditions to determine if they are providing the greatest possible leach rate. In general, the greater release of elements at elevated temperatures requires larger volumes of leachant and more frequent leachant replacement. Preliminary results for each

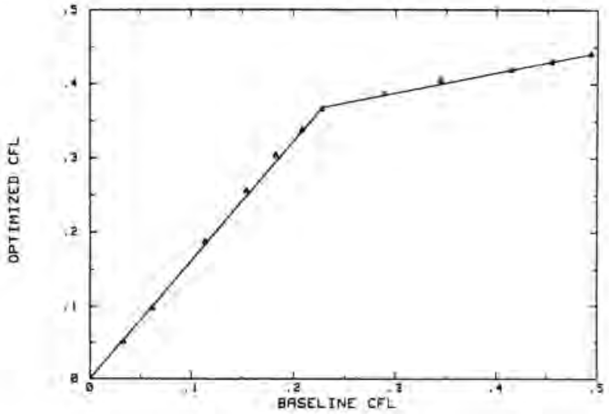

Fig. 3. Releases of 137Cs Leaching from Accelerated Tests are Plotted Against Releases from the Baseline (or Reference) Test. The Results Produce a Linear Plot in two Segments. The Break is Caused by the Change in Sampling Interval During the Baseline Test.

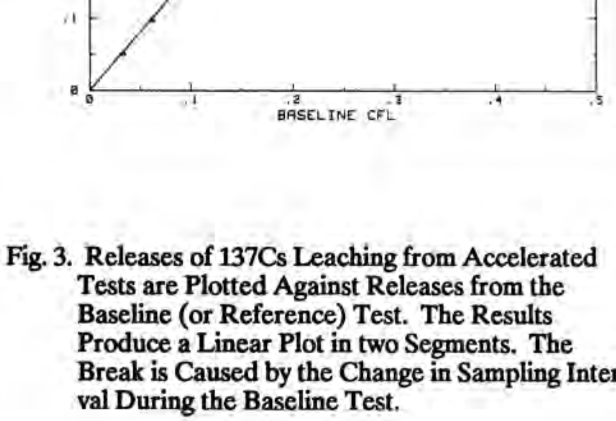

Fig. 4. Logarithm of the effective diffusion coefficient, De, for ^{85}Sr is plotted against the reciprocal of the absolute temperature T, for cement containing 5 wt% sodium sulfate leached in deionized water.

Elevated temperature is the most effective means of accelerating leaching, but other conditions must be optimized to obtain the maximum leach rate. Comparisons of data with modeling results provided a good way of judging the effects of various accelerating conditions to determine if they are providing the greatest possible leach rate. In general, the greater release of elements at elevated temperatures requires larger volumes of leachant and more frequent leachant replacement. Preliminary results for each material are briefly described below.

Releases of both ^{137}Cs and ^{85}Sr from portland cement containing sodium sulfate can be increased to an acceleration factor of approximately 18. In an 11-day accelerated leach test, the equivalent of almost 200 days of baseline leaching takes place. Optimum conditions require a maximum temperature of 50°C and 3 liters of water replaced daily for 2.5 cm diameter by 2.5 cm high cylinders. Releases of both radionuclides can be modeled by diffusion from the finite cylinder.

Similar conditions can be used for portland cement containing incinerator ash but the acceleration factor for ^{137}Cs is 5 while it is 17 for ^{85}Sr. Leaching of neither radionuclide can be modeled by the finite cylinder model. Additional experimental evidence indicates that adsorption is an important leach rate controlling factor for this material [7].

Releases from thermosetting polymers can also be accelerated by elevated temperature and increased leachant volume. However, for this material, the upper limit for temperature appears to be greater than 50°C. Although leaching conditions can be further optimized, acceleration factors of 17 have been achieved.

Leaching from asphalt waste forms cannot be accelerated under the conditions used for cement and polymers. In fact, lower leach rates were observed at elevated temperatures, presumably due to the self-sealing characteristics of bitumen. Several modeling approaches are being examined for this material.

CONCLUSIONS

The general approach described in this paper will provide a sound physical basis for an accelerated leach test. Preliminary results, as indicated by modeling using diffusion from a finite cylinder and by Arrhenius plots, show that for portland cement waste forms the leaching mechanism remains intact up to 50°C. At 60°C the mechanism changes. For thermosetting polymers, higher temperatures can be used successfully. In both cases, an acceleration factor of 17 or 18 is typical. This means that an 11-day experiment can provide the equivalent of almost 200 days leaching in a standard test.

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