

ACCELERATED LEACH TEST DEVELOPMENT PROGRAM

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ABSTRACT

In FY 1989, a draft accelerated leach test for solidified waste was written. Combined test conditions that accelerate leaching were validated through experimental and modeling efforts. A computer program was developed that calculates test results and models leaching mechanisms. This program allows the user to determine if diffusion controls leaching and, if this is the case, to make projections of releases. Leaching mechanisms other than diffusion (diffusion plus source term partitioning and solubility limited leaching) are included in the program as indicators of other processes that may control leaching. Leach test data are presented and modeling results are discussed for laboratory scale waste forms composed of portland cement containing sodium sulfate salt, portland cement containing incinerator ash, and vinyl ester-styrene containing sodium sulfate.

EXECUTIVE SUMMARY

This annual report presents an overview of work done in Fiscal Year 1989 for the accelerated leach test development program. The work covered three major topics:

- 1) Development and submission of draft procedures for an accelerated leach test for solidified waste to the DOE National Low-Level Waste Management Program and to the American Society for Testing and Materials.
- 2) Development of a computer program to be used with the leach test to calculate and model results.
- 3) Experimental validation of the test method and model.

The test method was designed to minimize the effects of increased ionic concentrations in the leachate that can give erroneous results, especially in waste forms with relatively high leach rates (i.e., many low-level radioactive waste forms). This year, the work focused on selection, fine tuning, and validation of the combined test conditions that were surveyed during the previous year. The test conditions that were found to accelerate leaching were used as standard parameters for experiments this year. They are:

- 1) specimen size of 2.5 cm diameter by 2.5 cm height
- 2) ratio of leachant volume to specimen surface area of 100
- 3) daily leachate changes (twice the first day)
- 4) test duration of 11 days.

A major goal of these experiments was to determine what temperatures are optimum for leaching and if the controls on leaching change above any temperature. One topic of particular interest was the magnitude of the acceleration induced by elevated temperature under the new test conditions. Experiments were conducted at 20°, 35°, 45°, 50°, 55°, and 65°C. Temperatures greater than 65°C were too warm for easy handling.

Data was analyzed in two ways to determine the mechanistic effects of elevated temperature. One method was with Arrhenius plots, and the second method was using the diffusion model discussed earlier. Analysis of the data by modeling is an integral component of the test development process. Consequently, experimental results and modeling results are discussed together.

A computer program, that calculates test results and models leaching mechanisms, was developed to accompany the accelerated leach test. This program determines if diffusion controls leaching and, if this is the case, makes projections of releases. Other leaching mechanisms are included (diffusion plus source term partitioning and solubility limited leaching) as indicators of other processes that may control leaching. With these tools (the test method and the computer program) we can begin to understand the mechanisms that control leaching from waste forms.

The following conclusions are drawn from the FY 1989 work.

- Releases of some elements from certain waste forms (notably sodium from cement/sodium sulfate waste form), are controlled by diffusion under the conditions of the proposed test.
- Leaching of other elements from various waste forms is not controlled by diffusion alone. Other mechanisms, especially adsorption are important.
- Elevated temperature is a useful means of increasing leach rates even though the release mechanisms are not necessarily diffusion alone. This is true for all elements investigated for cement/sodium sulfate waste forms. For cement/ash samples, temperature effectively increases the releases of potassium and sodium. The effect of increased temperature on the leaching of calcium, cesium-137, and strontium-85 is less clear and can be interpreted in two ways:
 - 1) There is no acceleration of leaching after an initial increase in leach rate at temperatures above 20°C.
 - 2) There is a systematic increase in leach rate to about 55°C followed by a change in release mechanism as indicated by a drop in D_e at high temperatures.
- The mechanism of leaching of sodium from VES waste forms changes at temperatures of 50°C or greater, with diffusion operating at the higher temperatures. Release mechanisms of cesium-137 and strontium-85 show no clear pattern.

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1. INTRODUCTION

This annual report presents an overview of work done in Fiscal Year 1989 for the accelerated leach test development program. The work covered three major topics:

- 1) Development and submission of draft procedures for the accelerated leach test to the DOE National Low-Level Waste Management Program and to the American Society for Testing and Materials.**
- 2) Development of a computer program to be used with the leach test to calculate and model results.**
- 3) Experimental validation of the test method and model.**

The work undertaken this year is the culmination of several years worth of extensive experimental investigations that were reported earlier [1,2], in which the ability of several factors to accelerate leaching (such as temperature, leachant volume and frequency of leachant changes) were examined. Initially, these factors were studied individually; later, the most useful factors were combined to obtain greater acceleration of leaching. The experimental work performed this year validated the optimized test conditions.

The accelerated leach test will be a useful tool in performance assessment work because leaching of waste forms is the first event in mobilization of radionuclides in a disposal site. Consequently, it is most important to know leach rates and understand the leaching mechanisms, especially if any predictions are to be made. The test method was designed to minimize the effects of increased ionic concentrations in the leachate that can give erroneous results, especially in waste forms with relatively high leach rates (i.e., many low-level waste forms). The computer program for the test allows the user to test experimental results against a basic mechanistic model for diffusion from a finite cylinder. If the model and the data agree, then projections can be made using the model. This test method will lead to a better ability to provide long-term predictions of leach rates for performance assessments.

2. MATERIALS AND METHODS

This section summarizes the materials used for fabricating waste forms, and the methods used to analyze the leachates and the solid phase. The solidification agents used this year, portland type I cement and vinyl ester-styrene copolymer, were selected primarily to represent a cross-section of material properties. The simulated waste streams chosen were sodium sulfate waste, such as that generated at Boiling Water Reactors (BWRs), and incinerator ash, which is becoming a major waste stream as advanced volume-reduction processes become common. In earlier studies, bitumen with sodium tetraborate was used as a simulated waste; Reference 1 discusses the leaching mechanism of this material.

The choice of solidification agents was based on two criteria: (i) that they were either in use or being considered for use in low-level waste management, and (ii) that they cover a range of materials properties. By providing a detailed knowledge of the leaching behavior of several types of materials, e.g., hydraulic cement, thermoplastic binders, and thermosetting polymers, it is anticipated that the results would apply generally to solidification agents that may be developed in the future.

Over the course of this program, the following test specimens were investigated:

- Solidification agents.
- Solidification agent with radioactive tracers.
- Solidification agents containing simulated waste.
- Solidification agents containing simulated waste with radioactive tracers.

The samples containing radioactive tracers were used to investigate the leaching behavior of radionuclides of cesium, strontium, and cobalt from the matrices. The other samples were used to study the leaching of the components of the solidification agent and nonradioactive elements from the waste. For this year's work, specimens containing simulated waste with and without radioactive tracers were used. Table 2.1 lists the compositions of the waste forms containing simulated wastes that were studied.

Table 2.1

Composition (weight %) of the Waste Forms
Containing Simulated Waste

Portland Type I Cement/Sodium Sulfate

<u>Component</u>	<u>Weight %</u>	<u>Activity (μCi)</u>
Cement Powder	65	-
Sodium Sulfate (anhydrous)	5	-
Water	30	-
Co-57	-	6.3
Cs-137	-	6.3
Sr-85	-	12.5

Portland I Cement/Incinerator Ash

<u>Component</u>	<u>Weight %</u>	<u>Activity (μCi)</u>
Cement Powder	60	-
Incinerator Ash	15	-
Water	25	-
Co-57	-	100
Cs-137	-	100
Sr-85	-	200

Vinyl Ester-Styrene/Sodium Sulfate

<u>Component</u>	<u>Weight %</u>	<u>Activity (μCi)</u>
Vinyl Ester- Styrene Monomer	54.7	-
Sodium Sulfate (anhydrous)	39.3	-
Water	1.8	-
Catalyst	1.5	-
Promoter	0.06	-
Co-57	-	100
Cs-137	-	100
Sr-85	-	200

2.1 Waste Form Types

Studies were made to select the composites of solidification agent/waste material that are chemically compatible. Formulations were optimized to maintain the physical integrity of waste forms when immersed in water during the leaching experiments.

2.1.1 Portland I Cement Containing Sodium Sulfate as Simulated Waste. Sodium sulfate waste is a product of ion exchange resin regeneration at BWR power stations. It is usually concentrated by evaporation to approximately 22 wt% solids content. Further, evaporation of this concentrate to dryness results in the formation of sodium sulfate decahydrate (Glauber's salt), that dehydrates to anhydrous sodium sulfate at 32°C.

Loadings up to approximately 45 wt% sodium sulfate can be solidified with cement. However, waste forms containing more than approximately 8 wt% sodium sulfate were unstable when immersed in deionized water, disintegrating before 90 days. A formulation of 5 wt% sodium sulfate, 30 wt% water, and 65 wt% cement was selected for testing, corresponding to a waste-to-binder ratio, i.e., evaporator concentrate to cement, of 0.54.

2.1.2 Portland I Cement Containing Incinerator Ash as Simulated Waste. Up to 50 wt% incinerator ash can be solidified by portland I cement without free-standing water being present. However, on curing specimens swell, developing large voids. A formulation of 15 wt% ash, 25 wt% water, and 60 wt% cement was selected for leach testing because this composition produced waste forms with few voids.

Incinerator ash was obtained from the waste incinerator of the Tennessee Valley Authority. The major components of incinerator ash typically are uncombusted carbon, aluminum oxide (Al_2O_3), ferric oxide (Fe_2O_3), and silicon dioxide (SiO_2). The ash was passed through a 2.38mm sieve size to produce a uniform powder, free of large clinkers and metal objects.

2.1.3 Vinyl Ester-Styrene Containing Sodium Sulfate as Simulated Waste. Mixtures of up to 60 wt% dry sodium sulfate with vinyl ester-styrene monomer polymerized satisfactorily to produce waste forms with hard surfaces. The leaching of sodium sulfate from solidified waste forms was used to select a composition which maximized the amount of incorporated waste while minimizing leaching. The amount of sodium that was leached increased rapidly at waste loadings above 40 wt%; therefore, this was the maximum loading used.

2.2 Preparation of Samples

Cylindrical samples were prepared with approximate dimensions of 2.5 cm diameter and 2.5 cm length ($V/S=0.42$). Based on past experience, this size is convenient for laboratory studies.

Radioactive samples had the radioactive tracers Co-57, Cs-137, and Sr-85 incorporated into the simulated waste. The low-energy gamma ray emitted by Co-57 ($T_{1/2}=270$ days) is better suited to the automated NaI counting system than is Co-60, and also works well with the intrinsic Ge counting system.

2.3 Leaching Tests

The draft accelerated leach test method developed in this project is being published separately [3]. It is a semi-dynamic test, in which the leachate is replaced periodically after intervals of static leaching. Specimens are placed into the leachant solution in such a way that the entire external surface area is exposed to the solution. Specimens are leached in individual containers containing a ratio of 100 cm between the volume of the leachant and the external geometric surface area of the specimen. The leachant is distilled water, with a conductance of less than $5\mu\text{mhos/cm}$. Specimens are tested in triplicate to determine the variation in leaching. Experiments run at elevated temperatures are conducted in an environmental chamber (Forma Scientific) with strict temperature controls. The results of the leach tests are expressed as the incremental fraction leached, the cumulative fraction leached, or as the diffusion coefficient, to compare alternative methods of treating the data.

2.4 Analytical Methods

Leachates are analyzed for a variety of materials, depending on the composition of the solidification agent and the simulated waste. Cement leachates are subjected to the most analysis because reactions within the matrix cause significant differences in leaching among different elements. Specific analytical methods are given below.

2.4.1 Radiochemical Analysis. The radiochemical component of the leachate, such as Cs-137, Sr-85, and Co-60 (or Co-57) is analyzed by gamma-ray spectroscopy using an intrinsic germanium detector or a sodium iodide detector in accordance with the methods described in ASTM D3648-78 [4] and ASTM D3649-78 [5].

2.4.2 Elemental Leachate Analysis. Analysis of leachates for non-radioactive elements is conducted with standard methods such as ASTM E663 [6] and those in Analytical Methods for Atomic Absorption Spectrophotometry, revised January 1982, Perkin-Elmer Corporation, Norwalk, CT [7].

3. THEORY

3.1 Introduction

Short-term leach tests on laboratory-scale specimens can be used to predict long-term releases of full-scale waste forms only if 1) extensive studies of empirical correlations are performed consisting of size-scaling effects and long-term leach tests, or 2) the leaching mechanism can be identified and modeled with a suitable mechanistic mathematical model. The latter approach used in this study lends itself to incorporation into the accelerated leach test method. The inherent assumptions made when using models for prediction are:

- 1) the model accurately describes the leaching process of the material over the entire period of interest.
- 2) the geometric form of the material remains essentially unchanged over the period of interest.
- 3) the data used in the model is taken from an experiment that approximates the boundary conditions required by the model.

Each of these assumptions are discussed in more detail below as they relate to low-level waste and the accelerated leach test. Judging how effectively the model describes the data is a statistical problem, the approach to which will be described later.

To use assumption #1, it must be demonstrated that the model describes the leaching process over the period of interest. To do this, short-term tests need to be correlated to longer-term tests experimentally, as was done in References 1 and 2 where data from 11-day accelerated tests were compared to data from long-term reference tests for several types of waste forms. The assumption will fail if changes in mechanism take place over time. An example is the formation of carbonated surface coatings on cement which cause adsorption of radionuclides. Such a process may selectively alter leaching for particular elements (e.g., Sr), while having no effect on others.

To successfully model leaching from short-term data, the geometry of the waste form must be consistent. The gross physical dimensions of the specimen, as well as its smaller-scale structure, cannot change significantly over time. Perhaps the most difficult problem in modeling to long times is embodied in this question, "Can the waste form be expected to maintain its integrity over the periods required?" Processes that cause a change in porosity or surface area (something that is expected with any portland cement-based material) cause a change in rate of leaching but do not alter the mechanism.

The third assumption is often overlooked. Mechanistic interpretations of data have frequently faltered due to attempts to model experimental results that are governed by experimental conditions and not by an intrinsic property of the material. In experiments, the boundary conditions of the models are not absolute but they must be maintained to as practical an extent as possible. For example, ideally there should be zero concentration of the species of interest in the leachate at all times to provide the greatest concentration gradient between the porewater in the specimen and the leachate. However, zero concentration in the leachate is clearly not practical, since it is necessary to have a measurable quantity to model. Fortunately, a compromise can generally be reached (especially when using radionuclides because of their ease of detection) where measurable quantities of the species of interest can be obtained in the leachate without having a noticeable effect on the leaching process. Providing low concentrations in the leachate has been the point where other leach tests have demonstrated serious inadequacies. Saturation effects (e.g. during the longer intervals of the ANS 16.1 Leach Test) suppress the release rate, so that data, taken with the ANS 16.1 Test cannot be modeled. This effect is particularly pronounced with materials with the high rates of release that are typical of low-level wastes.

With a standard leach test method, such as that being developed in this program, the most generally applicable model should be used. Therefore, a model describing diffusion from a finite cylinder was selected. While this model is not appropriate for all elements or for every type of waste form, it is suitable for many cases.

3.2 Theory

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. Critical to the evaluation of observed leaching results is a comparison with the theoretical models for releases by diffusion. The models used in this program are for simple bulk diffusion. The amounts of radioactive species were corrected for decay to a single reference time, namely, the starting time of a leaching test.

3.2.1 **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 [8,9]. The fundamental partial differential equation for diffusion is:

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

where C is the concentration of the species, t is time, and D_e is the effective diffusion coefficient in porous media.

Mathematical solutions to the transport equation for diffusion have been applied to the leaching of radionuclides from waste solids [10,11]. The exact form of the solution to the mass transport equation of diffusion depends on the initial and boundary conditions of the problem. The semi-infinite media and the finite shape models are the most direct and generally used.

3.2.2 **Diffusion from Semi-Infinite Media.** 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:

$$\frac{\sum a_n}{A_0} = \frac{2S}{V} \left[\frac{D_e t}{\pi} \right]^{1/2} \quad (2)$$

where a_n is the total amount of radioactive material released in all leaching periods up to time, t, A_0 is the initial amount of radioactive material, V is the volume of the waste form, S is the surface area of the waste form, and D_e is the effective diffusion coefficient. The semi-infinite model has been used to model leaching behavior when the cumulative fraction leached ($CFL = \sum a_n / A_0$) is less than 0.20 (20% release).

3.2.3 **Diffusion from Finite Media.** Laboratory samples are often leached well beyond the 20% maximum limit for the semi-infinite model. Consequently, the analytical solution for diffusion from a finite shape must be used to account for depletion of the source term. Cylindrical shaped waste forms are commonly used. Hence, the exact solution for diffusion from a finite cylinder using a constant diffusion coefficient, described by Nestor, is appropriate [11]. The solution of the mass transport equation for a constant diffusion coefficient, a uniform and homogeneous solid, and zero surface concentration during

leaching is:

$$\frac{\sum a_n}{A_o} = 1 - \frac{32}{\pi^2} \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} \frac{e^{-D_e[\beta_m^2 + (2n-1)^2\pi^2/4\ell^2]t}}{(2n-1)^2(\beta_m)^2} \quad (3)$$

where D_e = effective diffusion coefficient (cm^2/s), ℓ is the half height of the cylinder (cm), r is the radius of the cylinder (cm), a_n is the cumulative amount of species leached, A_o is the initial amount of species, and β_m is the positive roots of the Bessel function where $J_0(\beta_m)=0$.

The finite cylinder model provides a guideline to determine if diffusion consistently operates as the release mechanism during leaching. However, the use of equation (3) has been frustrated by the slow convergence of the double infinite series. Consequently, several investigators presented alternative methods of using the difficult-to-evaluate solution of the double infinite series for diffusion from a finite cylinder [11,12,13,14]. Pescatore's technique transformed the double series into a rapidly converging form for which the error associated with the truncation of each series can be evaluated [12].

For finite cylinder waste forms of height H and radius R , the double series expressions used instead:

$$CFL = \sum a_n/A_o = (1-b)[1 - 32/\pi^2 S_p(t)S_c(t)] + b \quad (4)$$

with:

$$S_p(t) = \sum_{n=1}^{\infty} \frac{\exp\{-[(2n-1)\pi/H]^2 D_e t\}}{(2n-1)^2}$$

and:

$$S_c(t) = \sum_{m=1}^{\infty} \frac{\exp[-(\beta_m/R)^2 D_e t]}{\beta_m^2}$$

For the $S_p(t)$ series:

$$S_p(t) = S_{p,N}(t) + E_{p,N}(t) \quad (5)$$

with:

$$S_{P,N}(t) = \sum_{n=1}^{N-1} \frac{\exp[-(2n-1)^2 \gamma^2(t)]}{(2n-1)^2} + \frac{N}{(2N-1)^2} \exp[-(2N-1)^2 \gamma^2(t)]$$

$$- (\sqrt{\pi}/2) \gamma(t) \operatorname{erfc}[(2N-1)\gamma(t)]$$

$$\gamma(t) = \frac{\pi(D_e t)^{1/2}}{H}$$

and:

$$0 < E_{P,N}(t) < \frac{1}{6(2N-1)} [\gamma^2(t) + 2/(2N-1)^2] \exp[-(2N-1)^2 \gamma^2(t)]$$

and for the $S_c(t)$ series:

$$S_c(t) = S_{c,M}(t) + E_{c,M}(t) \quad (6)$$

with:

$$S_{c,M}(t) = \sum_{m=1}^{M-1} \frac{\exp[-\beta_m^2 \theta^2(t)]}{\beta_m^2} + \frac{1}{\beta_M f_M} + \frac{1}{2\beta_M^2} \exp[-\beta_M^2 \theta^2(t)]$$

$$- \frac{\sqrt{\pi \theta(t)}}{f_M} \operatorname{erfc}[\beta_M \theta(t)],$$

$$f_M = \pi - 1/(8\pi M^2), \quad M \gg 1$$

$$\theta(t) = \frac{(Dt)^{1/2}}{R}$$

and:

$$E_{c,M}(t) < \frac{\pi}{6\beta_M} \left[\theta^2(t) + \frac{1}{\beta_M^2} \right] \exp [-\beta_M^2 \theta^2(t)]$$

In practice an intercept term, b, must be added to equations (2), (3) and (4) since extrapolation of observed results to t=0 does not pass through CFL=0. For low-level waste forms, this intercept, b, is often small (<0.5% A₀) and has been referred to as the instantaneous wash-off term for extraneous surface material [6].

3.2.4 Temperature. Theoretically, the temperature dependence of the effective diffusion coefficient, D_e, depends on the activation energy, E_a, for diffusion according to the Arrhenius equation:

$$D_e = A \exp(-E_a/RT) \quad (7)$$

where D_e is the effective diffusion coefficient at absolute temperature, T (°K), A is a constant, E_a is the activation energy (kcal/mole), and R is the gas constant. Log D_e plotted versus 1/T was used to evaluate the temperature effect on leaching, the activation energy, E_a, and the constant A. The concepts discussed in this section are put into practice in the computer program developed for the accelerated leach test. That program is discussed in more detail in section 4.

4. ACCELERATED LEACH TEST METHOD AND COMPUTER PROGRAM

4.1 Introduction

The final product of this project is an accelerated leach test that can be used to predict leach rates from low-level radioactive waste forms over long periods. This fiscal year a draft accelerated leach test method was prepared and submitted to the National Low-Level Waste Management Program [3]. In addition the test method was revised to conform to the format required by the American Society for Testing and Material (ASTM) and was submitted for consideration as a standard test method. It is being reviewed by members of ASTM committee C26.07.

4.2 The Accelerated Leach Test Method

The test method is a semi-dynamic leach test, that is the leachant is changed at predefined intervals. The test requires a volume of distilled water that is 100 times the surface area of the sample, for example, a sample with a dimensional surface area of 30 cm² would be leached in 3000 ml of water. The leachant is changed twice on the first day and then daily for 11 more days. Elevated temperatures may be used to accelerate leaching if it can be demonstrated that the leaching mechanism is not changed.

After the two draft test methods were submitted, the method and the associated computer program were revised. The change is in the statistical method used to determine the "goodness of fit" of the model to the experimental data. The DOE revision of the test method is being published separately [3].

A computer program was developed with the accelerated leach test method to calculate the effective diffusion coefficient that best fits the experimental data. The program also analyses the "goodness of fit" of the model results to the data. The computer program is an integral part of the accelerated leach test in that it provides a means of determining if diffusion controls the rate of leaching. If so, then projections can be made to long times. The computer program is described in detail below.

4.3 The Computer Program

The program is a compiled version and runs on IBM or IBM-compatible personal computers. A math co-processor is recommended to reduce computation time to a few seconds. A graphics board is required to perform the plotting routines, although without it the calculations will be made and the results displayed.

A flow chart of the essential functions of the program is shown in Figure 4.1. Each block on the flow chart is described briefly below:

4.3.1 Data Input. Data can be input as "raw" data, either as "counts per minute" for radionuclides or as concentration. Data can also be imported from other files. In addition to the leachate analysis data, values for the source terms of the species of interest, and the diameter and height of the specimen are required.

4.3.2 Estimate the Diffusion Coefficient. As a starting point, the effective diffusion coefficient is estimated based on the semi-infinite medium by plotting CFL against the square root of time and calculating the D_e from the linear (less than $CFL = 0.20$) portion of the plot.

4.3.3 Calculate the Effective Diffusion Coefficient. Using the value of D_e estimated previously, the program then uses the method described in Section 4.2.2 to calculate a more exact value for D_e . This takes place only when $CFL \geq 0.014$. Below this value, the semi-infinite method provides a better value of D_e and is used by the program.

4.3.4 Determine Residuals. The differences in CFL between individual data points and the results calculated by the model for the same times are determined and summed. The program then runs through a series of iterations to determine the value of D_e that provides the smallest sum of the residuals for the entire curve. This is the optimized effective diffusion coefficient.

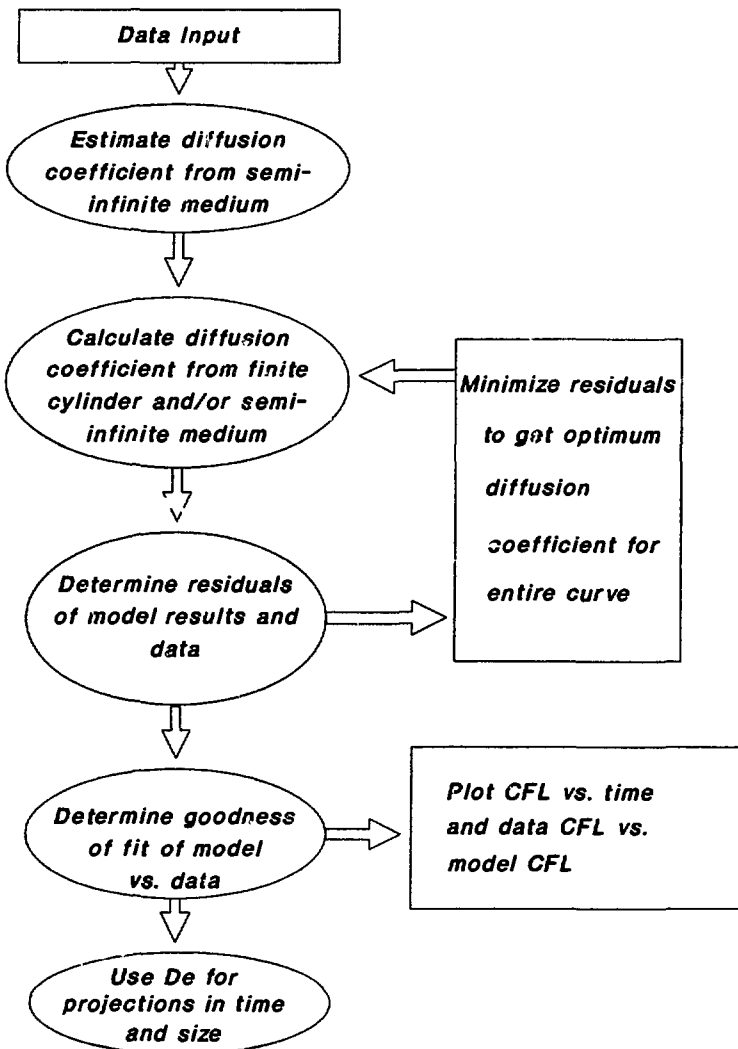


Figure 4.1 The flow chart illustrates the general concepts in the ALT program.

4.3.5 Determine Goodness of Fit. By calculating the sum of the residuals between the optimized model curve and the data, "the goodness of fit" can be evaluated. The program displays the sum of the residuals expressed as a percentage of the experimental CFL as a value called E_R . With a perfect fit of the model to the data, E_R should be zero. Any value of E_R less than 0.5% is taken to mean that the diffusion model accurately represents the data.

4.3.6 Projections. If the diffusion model is shown to represent the data, then projections to long times can be made using the calculated value for D_e and the model. Also, leaching from full-scale waste forms can be projected with the same model.

4.3.7 Temperature. To use elevated temperature to accelerate leaching, it must be shown that increased temperature does not alter the leaching mechanism. The computer program contains a subroutine that will calculate activation energies from diffusion coefficients determined at 3 or more temperatures and interpolate D_e for any other temperature.

4.3.8 Graphics. The current version of the program only produces graphics on the screen. Hard copies can be obtained with a "screen grab" program, but they are not high quality. Three types of plots are generated by the accelerated leach test program. One is a plot of CFL as a function of time on which the experimental data points and the model results appear. Some plots of this type are included in Section 5. The second type is the linear regression plot illustrating the "goodness of fit" of the model to the experimental data. The third type of plot illustrates the calculated projections of CFL plotted as a function of time. Any value of time (in days) can be input as a target for the projection. The value for D_e derived earlier can be used or a new value can be input.

5. LEACHING MECHANISMS AND ACCELERATED LEACHING

This section presents the results of experimental investigations of accelerated leaching and leaching mechanisms. This year, the work focused on selection, fine tuning, and validation of the combined test conditions that were surveyed during the previous year [1]. The test conditions that were found to accelerate leaching were used as standard parameters for experiments this year. They are:

- 1) specimen size of 2.5 cm diameter by 2.5 cm height
- 2) ratio of leachant volume to specimen surface area of 100
- 3) daily leachate changes (twice the first day)
- 4) test duration of 11 days.

A major goal of these experiments was to determine what temperatures are optimum for leaching and if the controls on leaching change above any temperature. One topic of particular interest was the magnitude of the acceleration induced by elevated temperature under the new test conditions. Experiments were conducted at 20°, 35°, 45°, 50°, 55°, and 65°C. Temperatures greater than 65°C were too warm for easy handling.

Data was analyzed in two ways to determine the mechanistic effects of elevated temperature. One method was with Arrhenius plots, and the second method was using the diffusion model discussed earlier. Analysis of the data by modeling is an integral component of the test development process. Consequently, experimental results and modeling results will be discussed together.

The data is typically expressed as an effective diffusion coefficient (D_e) which is the form most useful as input for site performance assessments. The "goodness of fit," as discussed previously, is determined by calculating the sum of the differences between individual CFL values for the experimental data and the CFL values calculated by the model for the same time intervals as the experimental data points. It is converted to a percentage by dividing by the maximum experimental CFR and multiplying by 100, giving a value for E_R . An E_R value $\leq 0.5\%$ indicates that the model and the data fit closely enough that the model can be taken to represent the data.

5.1 Portland Cement/Sodium Sulfate Specimens

Table 5.1 shows the results of leach tests for sodium, potassium, calcium, cesium-137, and strontium-85 as effective diffusion coefficients (D_e) and relative errors (E_R). The experiments were run in triplicate and results are given for each sample. The values of D_e and E_R were calculated with the ALT program and represent values that were optimized for the smallest sum of residuals over the entire set of data for that experiment. A value of $E_R \leq 0.5\%$ is required to indicate that diffusion is the rate controlling leaching mechanism.

5.1.1 Sodium. The release of sodium is controlled by diffusion. For most experiments, the E_R value is less than 0.5%. Two samples at 45°C and one at 65°C had E_R values that are greater than the cut off, but all other samples at each temperature had lower E_R values. Examples of the fit of the data to the diffusion model are illustrated in Figures 5.1a and b for two of the three specimens leached at 20°C, showing the small amount of scatter at that temperature. There is no change in leaching mechanism with increasing temperature.

The diffusion coefficient increased by an average factor of 13 (actual factors are 15.1, 11.6 and 12.2) as the temperature increased from 20°C to 65°C. The effect of temperature is illustrated on Figure 5.2, showing model results using the 20°C and 65°C diffusion coefficients from Sample A. The sample leached at 20°C would require 450 days to become completely depleted, while at 65°C, the sample would be depleted in about 30 days. The Arrhenius plot (Figure 5.3) indicates that the response of the leaching of sodium to increasing temperature is linear within the range studied. The correlation coefficient (r) is 0.974 and the activation energy of sodium release from cement/sodium sulfate is 11.1 kcal/mole.

TABLE 5.1
Cement Containing Sodium Sulfate

	Sample A		Sample B		Sample C	
	$D_e(\text{cm}^2/\text{s})$	$E_R(\%)$	$D_e(\text{cm}^2/\text{s})$	$E_R(\%)$	$D_e(\text{cm}^2/\text{s})$	$E_R(\%)$
Sodium						
20°C	2.17×10^{-8}	0.10	3.04×10^{-8}	0.16	2.92×10^{-8}	0.01
35°C	7.99×10^{-8}	0.02	4.88×10^{-8}	0.30	7.43×10^{-8}	0.07
45°C	1.47×10^{-7}	1.26	1.72×10^{-7}	1.26	9.58×10^{-8}	0.01
50°C	1.26×10^{-7}	0.04	1.47×10^{-7}	0.19	1.56×10^{-7}	0.06
55°C	1.72×10^{-7}	0.08	2.00×10^{-7}	0.53	1.74×10^{-7}	0.02
65°C	3.34×10^{-7}	0.55	3.51×10^{-7}	0.24	3.51×10^{-7}	0.07
Potassium						
20°C	3.35×10^{-8}	0.04	3.95×10^{-8}	0.03	3.34×10^{-8}	0.11
35°C	7.90×10^{-8}	1.07	4.98×10^{-8}	0.02	7.48×10^{-8}	1.00
45°C	1.02×10^{-7}	5.94	1.22×10^{-7}	6.82	7.78×10^{-8}	1.20
50°C	1.31×10^{-7}	0.30	1.63×10^{-7}	0.60	1.57×10^{-7}	0.35
55°C	2.12×10^{-7}	0.05	2.05×10^{-7}	0.04	2.11×10^{-7}	0.06
65°C	2.22×10^{-7}	0.97	2.36×10^{-7}	0.87	2.91×10^{-7}	1.18
Calcium						
20°C	5.56×10^{-11}	4.41	5.89×10^{-11}	3.86	5.62×10^{-11}	3.17
35°C	3.83×10^{-10}	0.74	2.62×10^{-10}	1.10	3.49×10^{-10}	0.55
45°C	3.73×10^{-10}	1.97	3.95×10^{-10}	1.16	2.91×10^{-10}	2.30
50°C	4.92×10^{-10}	0.76	5.66×10^{-10}	0.67	5.29×10^{-10}	0.88
55°C	3.65×10^{-10}	3.67	3.16×10^{-10}	3.44	3.45×10^{-10}	3.91
65°C	8.86×10^{-10}	0.53	8.89×10^{-10}	0.39	8.65×10^{-10}	0.19
Cesium-137						
20°C	1.33×10^{-7}	0.55	1.24×10^{-7}	0.52	1.22×10^{-7}	1.08
45°C	1.53×10^{-7}	0.85	1.84×10^{-7}	1.16	3.38×10^{-7}	2.52
50°C	1.72×10^{-7}	0.51	2.16×10^{-7}	0.38		
55°C	2.94×10^{-7}	1.07	3.06×10^{-7}	2.17	2.47×10^{-7}	1.76
65°C	5.26×10^{-7}	0.88	3.79×10^{-7}	2.55	2.94×10^{-7}	1.32
Strontium-85						
20°C	4.41×10^{-10}	0.05	4.80×10^{-10}	0.14	4.88×10^{-10}	0.29
45°C	1.40×10^{-9}	0.06	1.51×10^{-9}	0.10	1.84×10^{-9}	0.20
50°C	1.01×10^{-9}	0.02	1.31×10^{-9}	0.14		
55°C	1.03×10^{-8}	0.69	1.02×10^{-8}	0.66	7.76×10^{-9}	0.45
65°C	4.00×10^{-9}	1.44	3.44×10^{-9}	1.46	2.98×10^{-9}	1.57

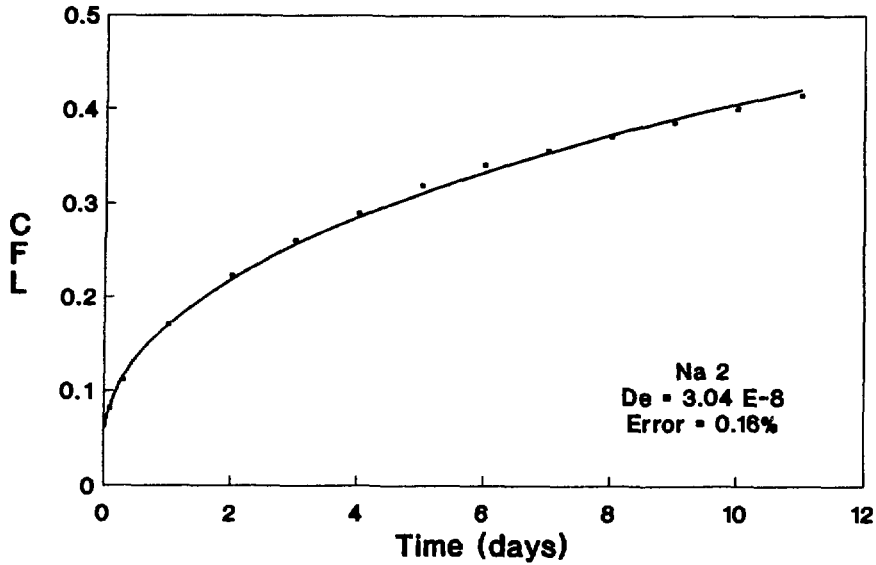


Figure 5.1a Cumulative fraction leached of sodium is plotted against time for a cement/sodium sulfate sample leached at 20°C. The diffusion model fits the sodium leaching data with a 0.16% error. This is the worst fit of the triplicate specimens.

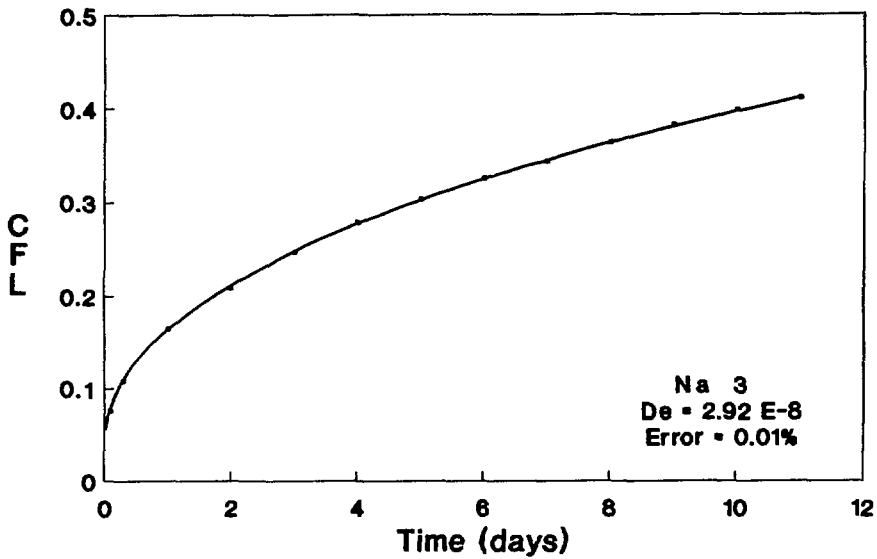


Figure 5.1b Cumulative fraction leached of sodium is plotted against time for a cement/sodium sulfate sample leached at 20°C. The diffusion model fits the sodium leaching data very closely, with an error of only 0.01%. This is the best fit of the triplicate specimens.

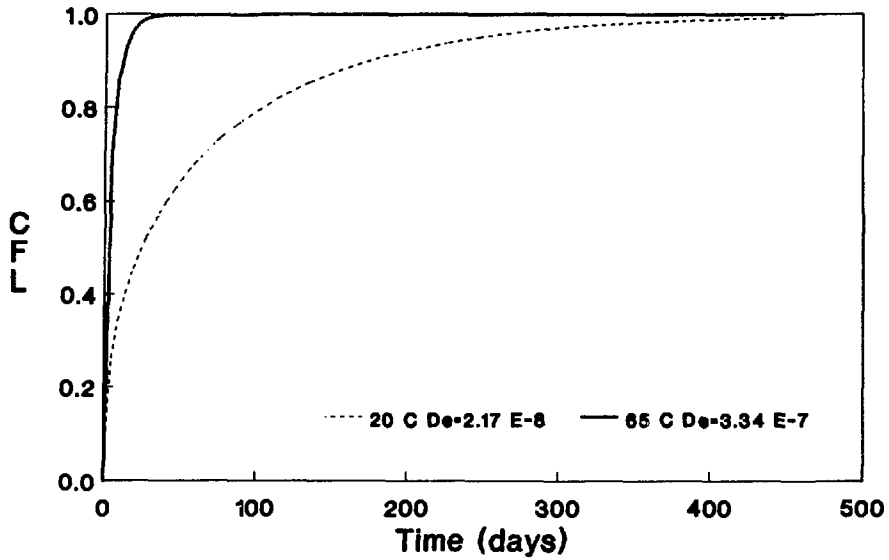


Figure 5.2 Model results using diffusion coefficients obtained at 20°C and at 65°C for sodium leached from cement/sodium sulfate samples show the amount of time required to reach complete depletion of 2.5 x 2.5 cm samples at those temperatures.

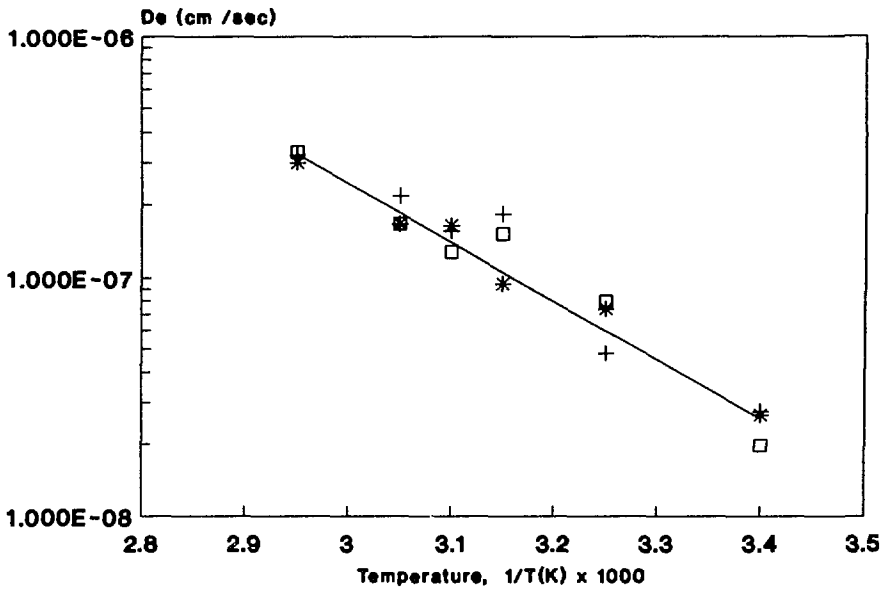


Figure 5.3 The Arrhenius plot for sodium releases from cement/sodium sulfate waste forms shows good correlation between D_e and temperature. The correlation coefficient is 0.974.

5.1.2 Potassium. Leaching of potassium from cement/sodium sulfate specimens is very similar in rate to the release of sodium, but, the "goodness of fit" of the model to the experimental data is scattered (see Table 5.1). The E_R values for the data taken at 45°C are anomalously high, indicating a very poor fit. The reason for this is unknown but may be caused by some structural defects in the samples. A similar anomaly was observed for sodium releases from the same samples. Two samples at 35°C had E_R values of about 1.0%. At 65°C, the fit was also poor, with E_R values of about 1.0% which are not reflected in the sodium data. While some data are represented very well by the diffusion model, other data are not, with no discernible trend. In all cases where the model fails, it does so by overestimating the data from the later part of the experiment. This implies one of two possibilities:

- 1) The source term was incorrect.
- 2) Leaching by diffusion is modified by some other process.

Since the source term was checked repeatedly, the only alternative is that leaching was influenced by another mechanism that reduced the leach rate toward the end of the experiments. It is likely that adsorption of potassium takes place onto freshly forming calcium carbonate, a process that was observed in earlier studies [15]. Increasing the temperature increases the effective diffusion coefficient but does not influence the "goodness of fit" in any systematic way. The Arrhenius plot (Figure 5.4) shows a strong linear relationship among all temperatures tested, with a correlation coefficient of 0.972. Between 20°C and 65°C, D_e increased by an average factor of 6.9. The activation energy is 9.37 kcal/mole.

5.1.3 Calcium. Releases of calcium are not controlled by diffusion. In all but two cases, the E_R value is greater than 0.5%. Visual examination (Figure 5.5) shows that the data is systematically different than the modeled curve. After the first few sampling intervals, the experimental data are very linear, suggesting that the leach rate for calcium is limited by solubility .

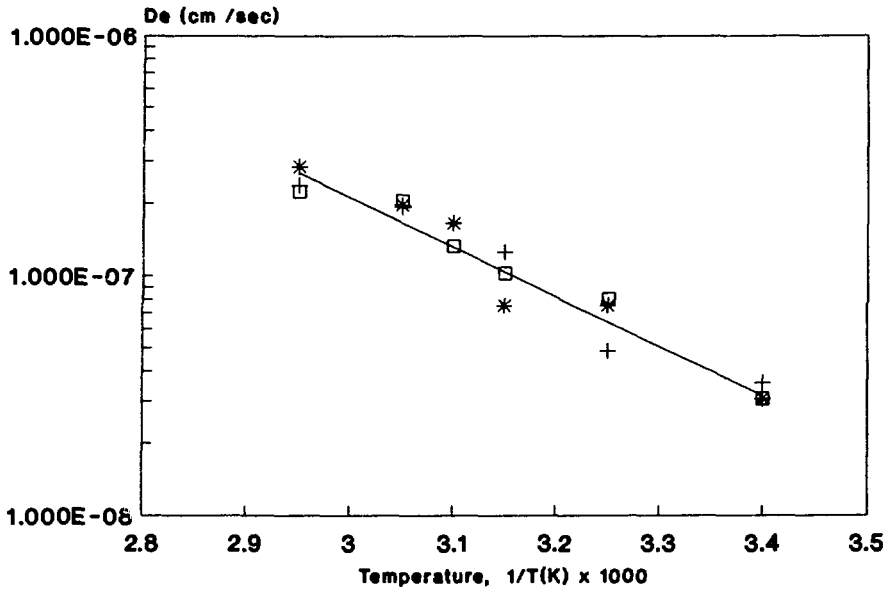


Figure 5.4 The Arrhenius plot for potassium from cement/sodium sulfate waste forms shows a strong correlation between D_e and temperature, as did the plot for sodium.

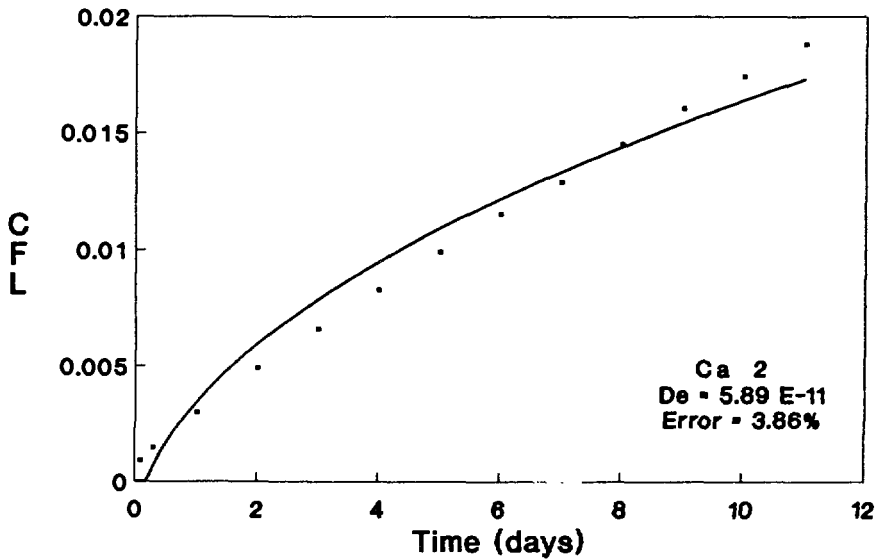


Figure 5.5 The fit of the model to the experimental data taken at 20°C, for calcium leached from cement/sodium sulfate waste forms is poor. The data is linear after the first few points, suggesting that solubility limits control the concentration of calcium in the leachate.

The maximum concentration of calcium in the leachant at 20°C was 4.2 - 4.8 mg/ℓ. Solubilities of various minerals that could be controlling the concentration are listed below:

$$\text{Ca(OH)}_2 = 1030 \text{ mg/}\ell$$

$$\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O} = 810 \text{ mg/}\ell$$

$$\text{CaSO}_4 \cdot 2\text{H}_2\text{O} = 560 \text{ mg/}\ell$$

$$\text{CaSiO}_3 = 33 \text{ mg/}\ell$$

$$\text{CaCO}_3 \text{ (calcite)} = 6 \text{ mg/}\ell$$

While these concentrations do not take into account the pH of the solution nor the effects of the presence of other ions, it is obvious that CaCO₃ controls the concentration of calcium in the leachate.

Increasing temperature tends to improve the fit of the model to the data during the early sampling intervals, implying that releases controlled by diffusion become proportionately more important at elevated temperatures.

The Arrhenius plot (Figure 5.6) shows the response of D_e to increasing temperature. These data give a correlation coefficient of 0.91 and an activation energy (E_a) of 10.6 kcal/mole, which is greater than expected for diffusion. The results shown on this figure also can be interpreted as the formation of calcium carbonate maintaining a constant concentration in the leachate between 35°C and 55°C, the supply of CO₂ being limited by diffusion through the container.

5.1.4 Cesium-137. Leaching of cesium-137 from cement/sodium sulfate samples is not controlled by diffusion. One set of samples, those leached at 50°C, have values of E_R that are close to or less than 0.5%, but most others are significantly greater. The trends in the shapes of the CFL versus time plots for cesium are similar to those of potassium. Specifically, the model overestimates the points in the later portion of the experiments (Figure 5.7a and b).

Elevated temperature increases the effective diffusion coefficient. Using the diffusion model, at 20°C the average D_e is 1.26×10^{-7} cm²/s, while at 65°C the average is 4.0×10^{-7} cm²/s, an increase of a factor of 3. At 20°C, a sample (2.45 cm diameter, 2.45 cm height) would be completely depleted in about 120 days, while at 65°C it would be depleted in 25 days.

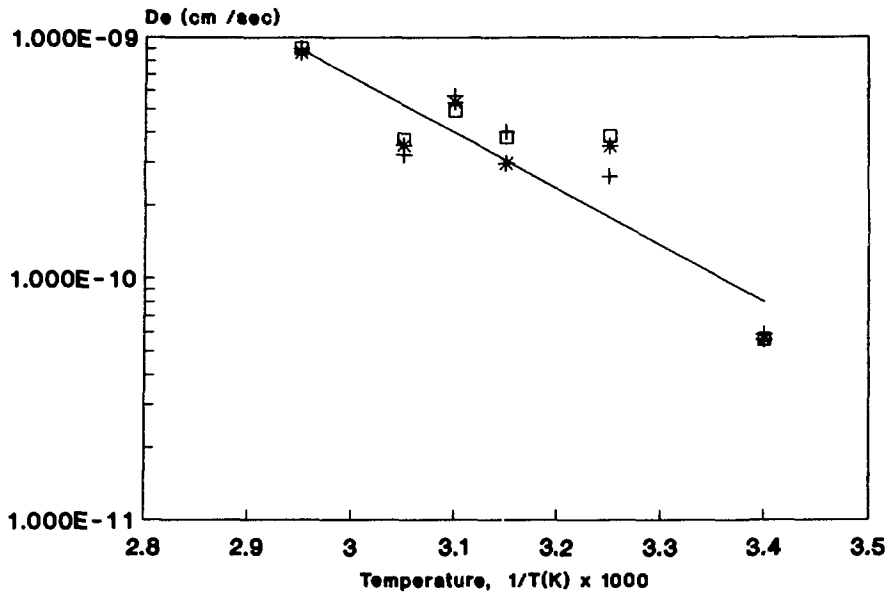


Figure 5.6 Arrhenius plot of calcium leached from cement/sodium sulfate waste forms.

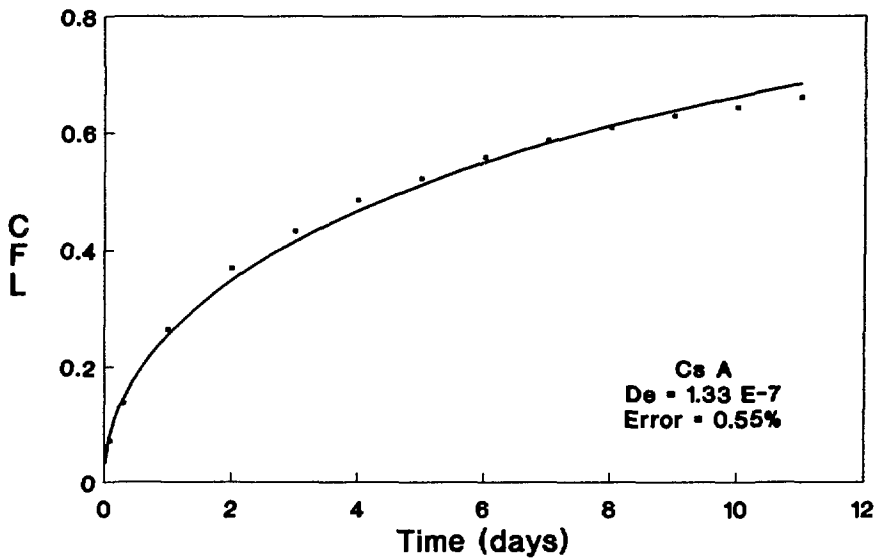


Figure 5.7a The fit of the diffusion model to the leaching data for Cs-137 from cement/sodium sulfate waste form samples, taken at 20°C , is slightly greater than the 0.5% limit for E_R . The model overestimates the data at the last three points.

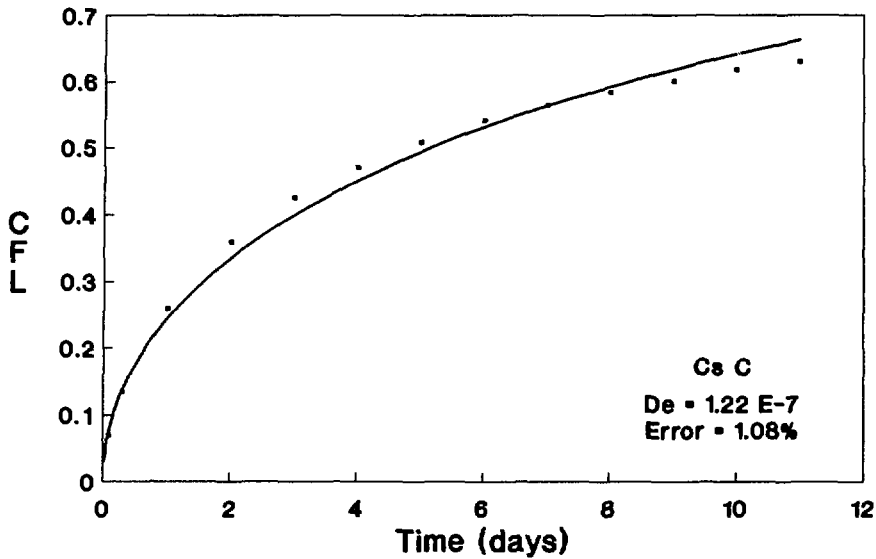


Figure 5.7b Cesium-137 data from a second cement/sodium sulfate sample leached at 20°C shows a worse fit than in Figure 5.7a to illustrate the spread among replicate samples.

The Arrhenius plot for cesium-137 (Figure 5.8) indicates that the effect of temperature on the magnitude of D_e is slightly less than that for other elements. The correlation coefficient for these data is 0.83, indicating that the scatter around the plotted line is high. The activation energy is 6.0 kcal/mole, which is close to that expected for diffusion.

The diffusion model can be forced to fit the cesium (and potassium) data by adjusting the original source term to a lower value (Figure 5.9). Because the source terms have been checked several times, it is certain that the original source terms are not in error. Therefore, the only viable alternative is that some of the cesium-137 is not available for leaching because it has been taken into the solid phase of the sample through adsorption, crystal lattice substitution, or some other mechanism. Portland cement has a very low capacity to take up cesium [16]. However, earlier work in this program has shown that authigenic products, such as CaCO_3 , that form on the surface of cement during leaching, have some capacity to adsorb cesium-137 as the CaCO_3 forms [15]. For these reasons the leaching mechanism of cesium (and potassium) can best be described by diffusion plus adsorption. For optimum results, it may be necessary for the adsorption term to "grow in" with the formation of CaCO_3 .

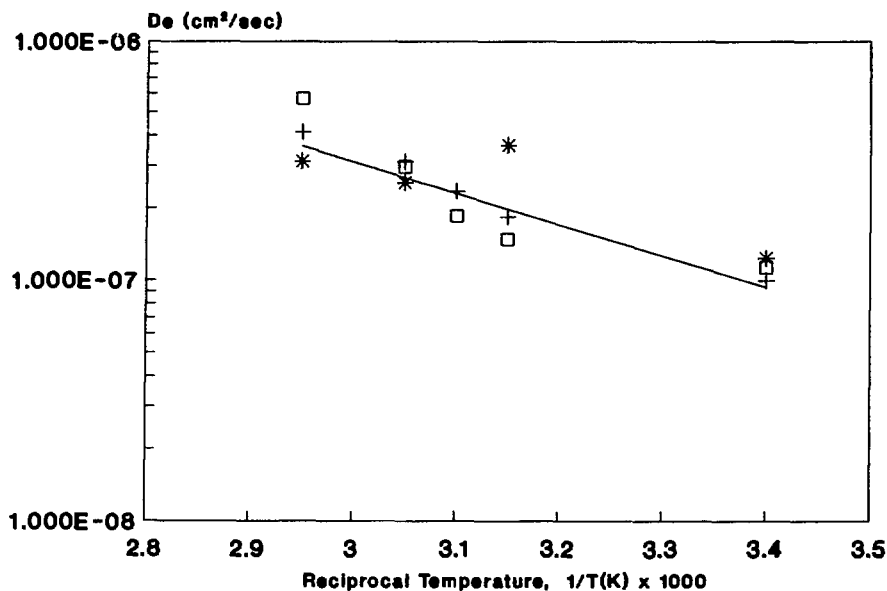


Figure 5.8 The Arrhenius plot for cesium-137 leached from cement/sodium sulfate show that the effect of increasing temperature (the slope) is less than for potassium and sodium.

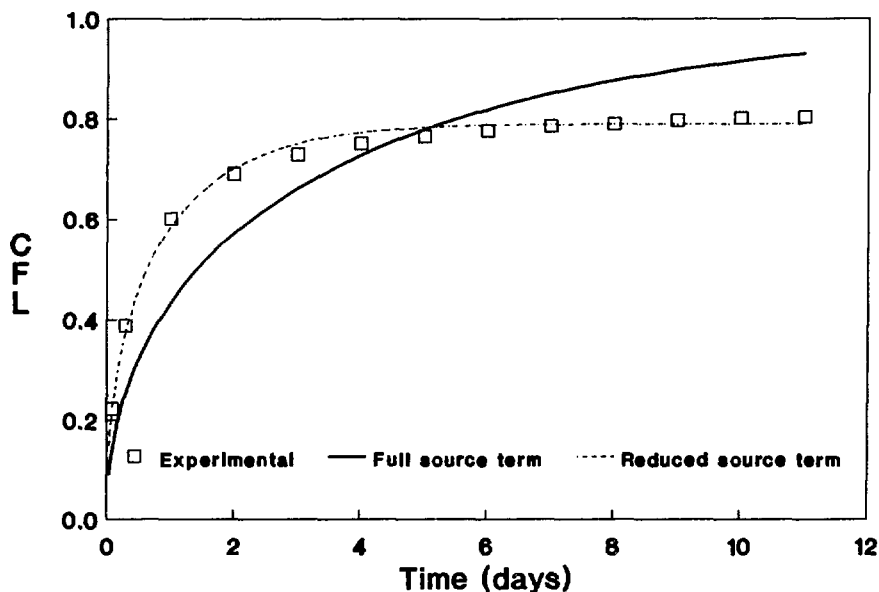


Figure 5.9 Comparison of CFL curves for cesium-137 from a cement/sodium sulfate sample. The dotted curve is normalized by adjusting the source term down by 12%. This improved the goodness of fit from 2.43% for the untreated curve (full source term) to 0.37%.

5.1.5 Strontium-85. Experimental data for the leaching of strontium-85 fits the diffusion model for temperatures between 20°C and 50°C (Figure 5.10). At 55°C, the value for E_R slightly exceeds the 0.50% cut off, and at 65°C E_R has increased to an average 1.49% (Figure 11). This data suggests that the release of strontium-85 is controlled by diffusion at 50°C or below, but above 50°C, leaching is no longer by diffusion alone. For data taken above 50°C, the shapes of the CFL versus time plots for strontium are similar to those for calcium and are more linear than the diffusion curves.

The Arrhenius plot (Figure 5.12) indicates that even though the diffusion model does not fit data taken at 55°C or 65°C, the trend of increasing D_e with increasing temperature remains linear to 65°C with a correlation coefficient of 0.957. The activation energy calculated from this plot is 8.7 kcal/mole. The diffusion coefficient increased from an average 4.7×10^{-10} cm²/s at 20°C, to 3.5×10^{-9} cm²/s at 65°C, an increase of 7.5 times. Using the observed diffusion coefficients with the diffusion model a sample (2.45 cm diameter by 2.45 cm height) leached at 20°C would need more than 20,000 days to reach depletion, while at 65°C it would be depleted in about 2,500 days.

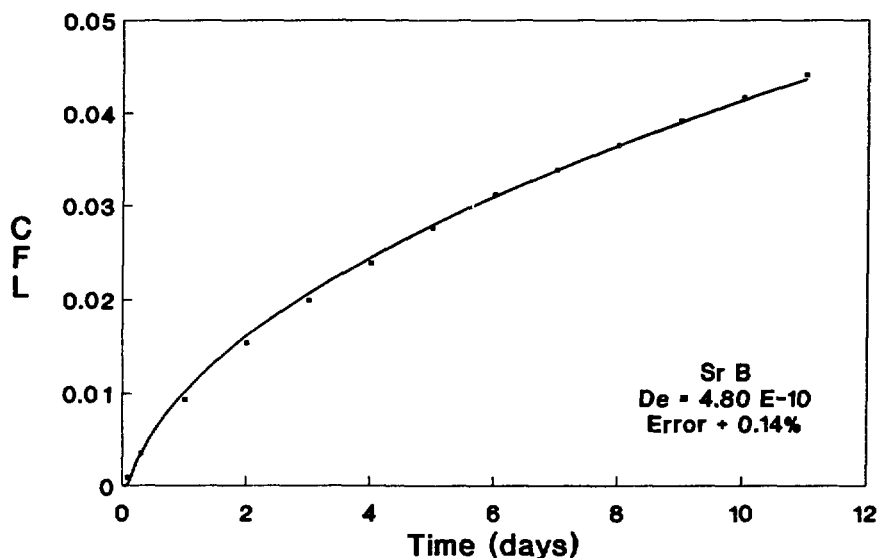


Figure 5.10 The diffusion model fits the leaching data for strontium-85 taken at 20°C for cement/sodium sulfate samples with an error of only 0.14%.

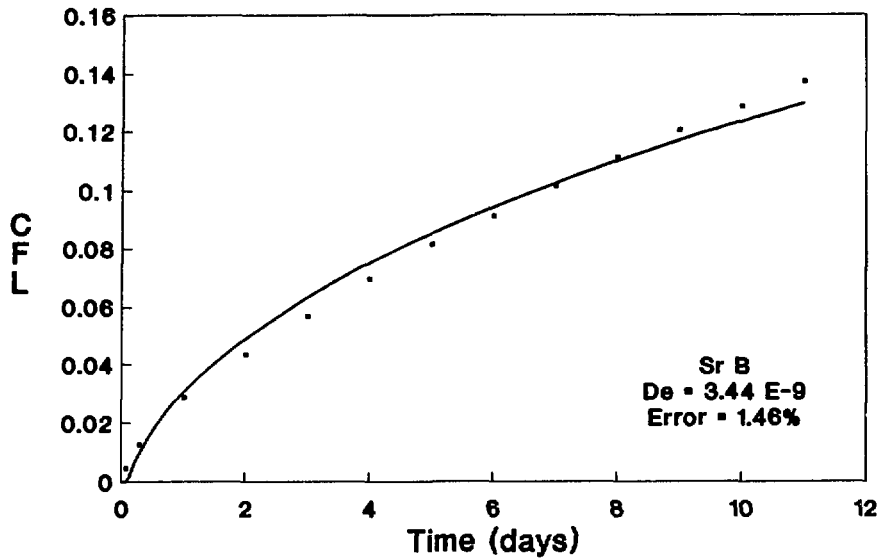


Figure 5.11 At 65°C, the model does not fit the data for strontium-85 leached from cement/sodium sulfate samples within the 0.5% limit. The data is more linear than the diffusion model.

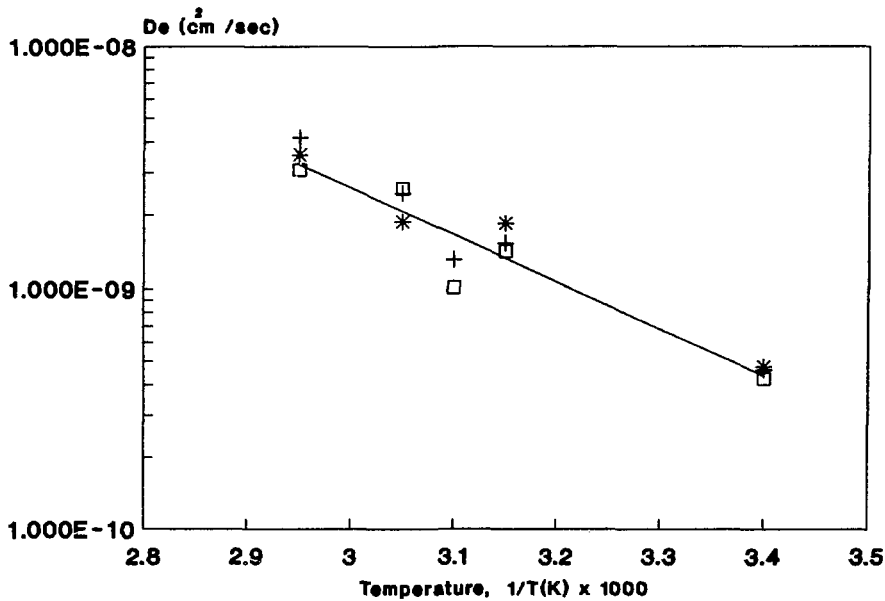


Figure 5.12 The Arrhenius plot for strontium-85 leached from cement/sodium sulfate samples shows a good correlation of D_e with temperature. The correlation coefficient is 0.957.

5.1.6 Conclusions. Cement waste forms containing sodium sulfate leach via three mechanisms under the experimental conditions in the accelerated leach test. Sodium leaches by diffusion. Calcium releases are controlled by solubility. Potassium and cesium-137 leach by diffusion that is modified by adsorption. Strontium-85 leaches by diffusion up to 50°C, and then appears to be controlled by another process.

Some of these mechanisms are the result of the test conditions. For example, calcium releases are controlled by removal of calcium from solution by the formation of CaCO_3 . If the test allowed a large volume of water (in excess of 30 liters), concentrations of Ca would be low enough to ensure that CaCO_3 would not precipitate. The need for a practical test design has precluded consideration of such large volumes. Another consideration, however, is that some carbonation of cement waste forms will take place in the disposal environment. While the rate of carbonate formation in the disposal environment is probably not the same as the rate in the leach test, it is better to observe the effect of carbonation on radionuclide transport during leaching than to deliberately exclude it by manipulating the test procedure.

Although the leaching mechanisms of cement/sodium sulfate waste forms are not generally strictly diffusion, this has little effect on the usefulness of elevated temperature for accelerating leaching. Arrhenius plots of each element examined indicated that increasing temperature systematically increases leachability (Figure 5.13). All of these plots have correlation coefficients that were very close to, or greater than, 0.90. For waste forms containing a simulated waste that is known to react with portland cement, this correlation is considered to be good.

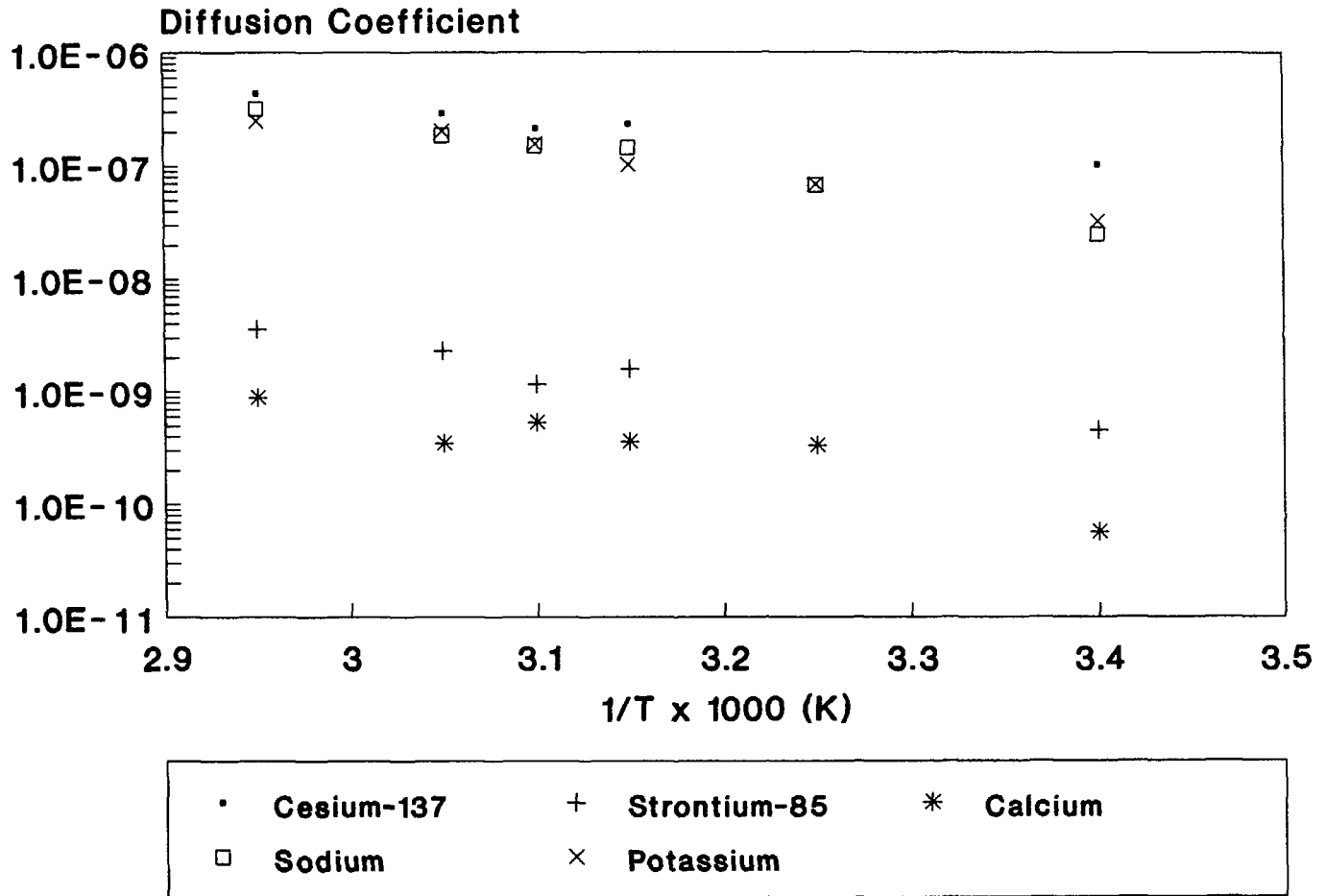


Figure 5.13

Arrhenius plot for cesium-137, strontium-85, calcium, sodium and potassium leached from cement/sodium sulfate samples, showing that leaching of all elements are accelerated by elevated temperature.

5.2 Portland Cement/Incinerator Ash Specimens

Duplicate or triplicate leach tests, with specimens composed of portland cement/incinerator ash using the accelerated leach test method, were conducted at 20°, 35°, 45°, 50°, 55°, and 65°C. Sodium, potassium, calcium, cesium-137, and strontium-85 concentrations were determined in the leachates. Effective diffusion coefficients and values for the relative error in the fit of the diffusion model to the data are given in Table 5.2.

5.2.1 Sodium. Releases of sodium from cement waste forms containing incinerator ash are not controlled by diffusion. Only one out of 15 values of E_R was less than 0.5%, meeting the criterion for diffusion; the rest were significantly greater. The low E_R (0.23%) was associated with a sample that had an anomalously low effective diffusion coefficient. Typical CFL versus time curves (Figure 5.14) show that the data become asymptotic before the model does. This curve is similar in shape to the sodium and cesium curves for portland cement containing sodium sulfate but is steeper. This shape indicates that either the source term is incorrect or that some sodium is not available for leaching, probably through an adsorption process.

Leaching of sodium is accelerated by increasing the temperature (Figure 5.15), but the scatter in the data is large, giving a correlation coefficient of 0.88. This variability is typical of waste forms containing incinerator ash because of the great chemical variability of the ash itself.

5.2.2 Potassium. Leaching of potassium is not controlled by diffusion for cement/incinerator ash waste forms. As with sodium, only one sample out of 15 had an E_R value that indicated diffusion. The remaining E_R values were much greater than the 0.5% cut off. In some cases, such as at 65°C, there is a very large spread in D_e values as well as in E_R . Releases from some samples became asymptotic after only 70 or 80% release (Figure 5.16). This scatter in releases of both sodium and potassium can be attributed to the inhomogeneity of the incinerator ash. For both elements, the ash comprises more than 1/3 of the total source term which is enough to account for the variability in releases. Alternatively, adsorption onto the ash may be involved, which is another process that could be strongly influenced by inhomogeneity of the ash. The linear regression on the Arrhenius plot (Figure 5.17) shows a positive effect on D_e with increasing temperature but the correlation coefficient is relatively low (0.83). The activation energy is 7.0 kcal/mole.

TABLE 5.2

Cement Containing Incinerator Ash

	Sample A		Sample B		Sample C	
	$D_e(\text{cm}^2/\text{s})$	$E_R(\%)$	$D_e(\text{cm}^2/\text{s})$	$E_R(\%)$	$D_e(\text{cm}^2/\text{s})$	$E_R(\%)$
Cesium-137						
20°C	9.66×10^{-8}	3.16	1.20×10^{-7}	2.70	9.68×10^{-8}	2.20
45°C	2.32×10^{-7}	3.42	2.75×10^{-7}	2.77	1.04×10^{-6}	0.72
50°C	5.24×10^{-8}	2.80	6.87×10^{-8}	3.31	6.14×10^{-8}	2.58
50°C (repeat)	1.89×10^{-7}		2.34×10^{-7}		1.62×10^{-7}	
55°C	4.85×10^{-7}	27.40	4.59×10^{-7}	20.00	2.60×10^{-7}	11.50
65°C	2.91×10^{-7}	14.80	1.88×10^{-7}	20.70	2.43×10^{-7}	26.80
Strontium-85						
20°C	1.58×10^{-9}	1.01	1.66×10^{-9}	1.46	1.30×10^{-9}	1.20
45°C	3.42×10^{-9}	0.08	3.44×10^{-9}	0.15	7.13×10^{-9}	0.47
50°C	1.02×10^{-9}	0.04	1.37×10^{-9}	1.62	5.25×10^{-10}	0.04
55°C	1.04×10^{-8}	0.34	6.84×10^{-9}	0.20	4.19×10^{-9}	0.83
65°C	5.00×10^{-9}	1.44	6.10×10^{-9}	1.75	9.13×10^{-9}	1.36
Sodium						
20°C	6.16×10^{-8}	0.23	1.05×10^{-7}	0.90	-	-
35°C	1.88×10^{-7}	3.31	1.22×10^{-7}	8.95	-	-
45°C	1.34×10^{-7}	8.49	1.34×10^{-7}	4.49	1.70×10^{-7}	10.05
50°C	2.39×10^{-7}	1.96	2.43×10^{-7}	3.24	2.19×10^{-7}	0.98
55°C	3.24×10^{-7}	6.10	4.29×10^{-7}	6.48	-	-
65°C	2.50×10^{-7}	9.94	3.71×10^{-7}	1.15	3.90×10^{-7}	1.64
Potassium						
20°C	8.88×10^{-8}	0.97	1.24×10^{-7}	4.60	-	-
35°C	1.59×10^{-7}	9.19	1.51×10^{-7}	8.96	-	-
45°C	1.50×10^{-7}	18.90	1.61×10^{-7}	24.10	1.91×10^{-7}	22.30
50°C	1.99×10^{-7}	5.70	2.91×10^{-7}	6.75	2.15×10^{-7}	4.97
55°C	4.29×10^{-7}	6.84	3.68×10^{-7}	12.10	-	-
65°C	2.58×10^{-7}	16.50	5.87×10^{-7}	2.50	9.09×10^{-7}	0.21
Calcium						
20°C	1.25×10^{-10}	0.86	1.79×10^{-10}	0.93	-	-
35°C	4.49×10^{-10}	0.27	3.16×10^{-10}	0.32	-	-
45°C	3.61×10^{-10}	0.52	4.39×10^{-10}	0.50	4.06×10^{-10}	0.67
50°C	5.74×10^{-10}	0.07	5.54×10^{-10}	0.08	4.55×10^{-10}	0.06
55°C	2.74×10^{-10}	0.47	4.45×10^{-10}	0.39	-	-
65°C	5.09×10^{-10}	0.09	5.28×10^{-10}	0.39	3.87×10^{-10}	0.42

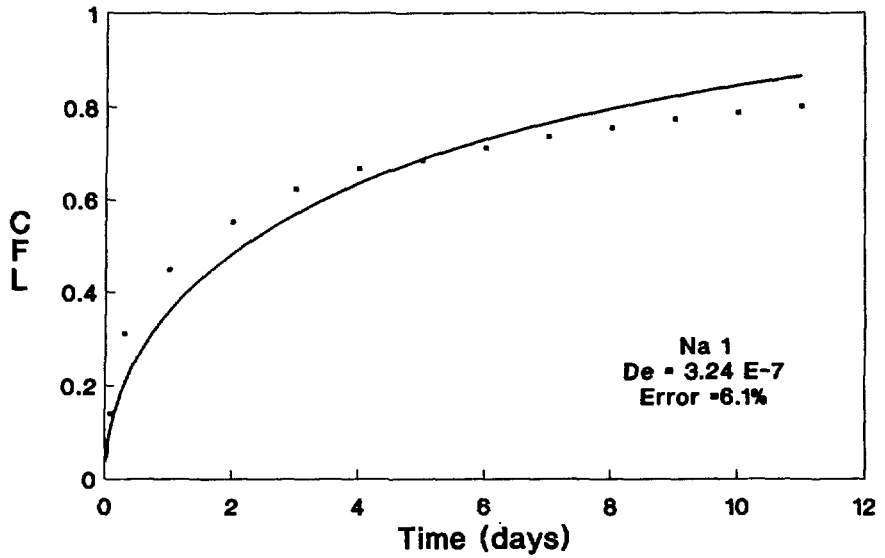


Figure 5.14 Releases of sodium from cement/incinerator ash waste forms are not represented by the diffusion model, as illustrated by this data taken at 55°C.

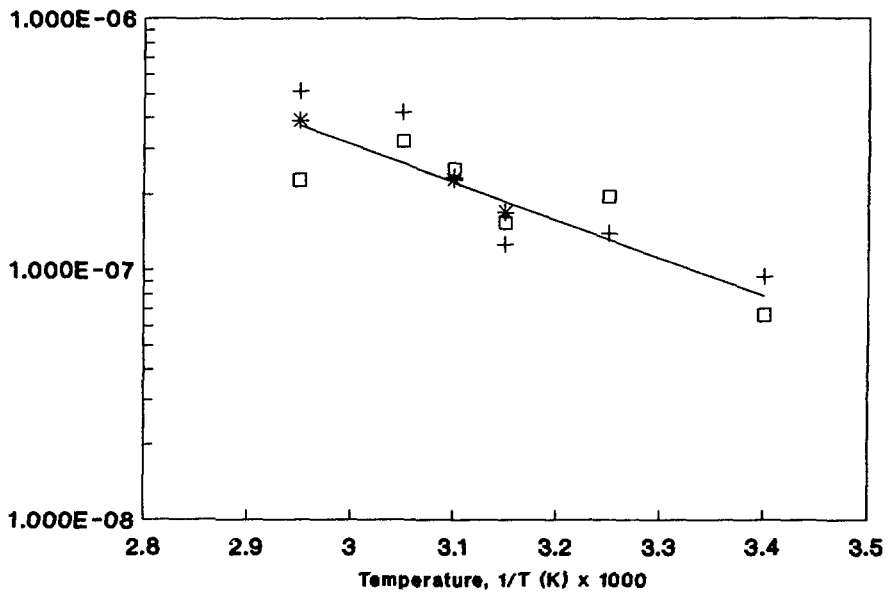


Figure 5.15 The Arrhenius plot of sodium leached from cement/incinerator ash waste forms shows high variability among samples typical of this type of waste form.

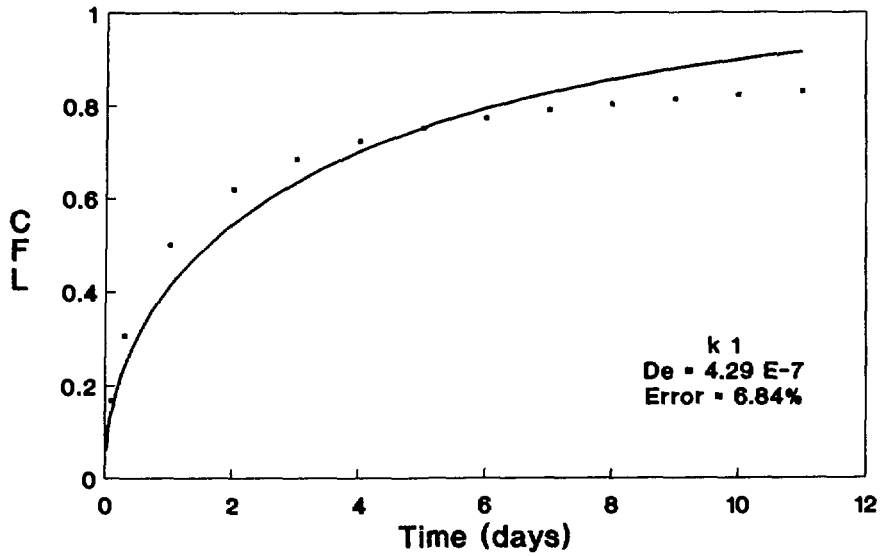


Figure 5.16 Potassium releases from cement/incinerator ash samples cannot be modeled by diffusion as illustrated by this data taken at 55°C.

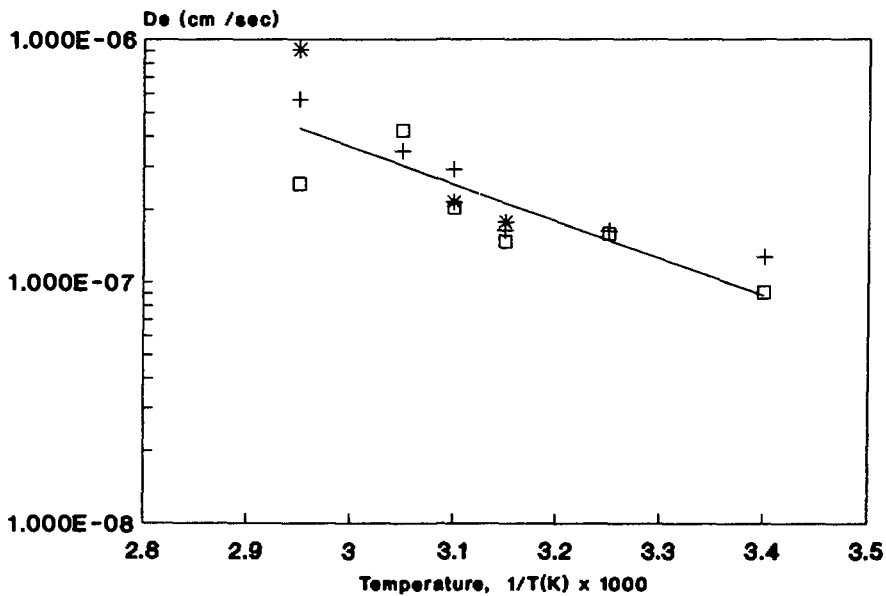


Figure 5.17 Arrhenius plot for potassium released from cement/incinerator ash waste forms shows a poor fit of the data to the regression line.

5.2.3 **Calcium.** Based on the fit of the diffusion model to the data, calcium leaching from cement waste forms containing incinerator ash is controlled by diffusion (Figure 5.18), in contrast to calcium releases from cement/sodium sulfate samples which is solubility limited. Release rates for both types of waste forms are similar, with diffusion coefficients in the order of 10^{-10} cm²/sec. The incinerator ash contributes little to the calcium source term as it contains about 3% of the calcium in the samples. In cases where the E_R value is greater than 0.5%, the experimental data is more linear than the diffusion model, indicating that solubility is becoming important (Figure 5.19). The two samples with the highest E_R values were those leached at 20°C. Considering the variability of these samples, this difference may not be significant.

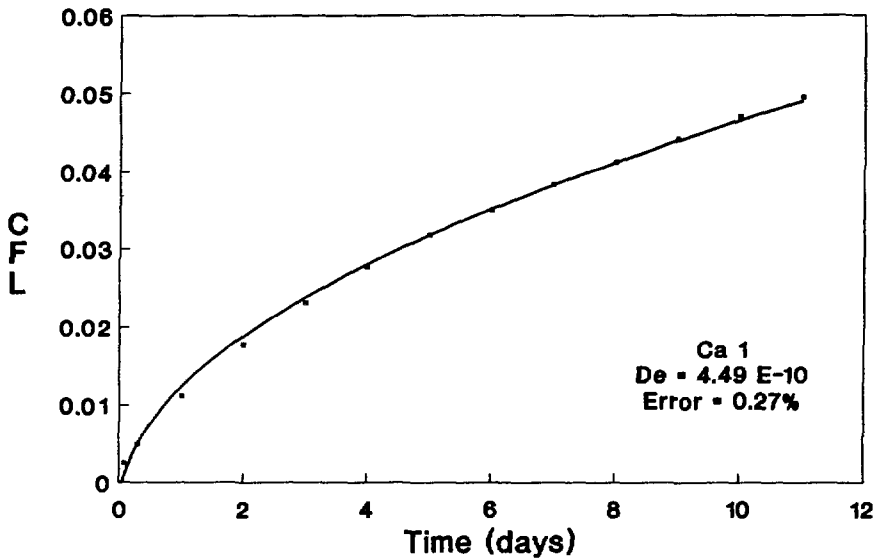


Figure 5.18 Calcium leaching from cement/incinerator ash waste forms at 35°C shows a good fit with the diffusion model.

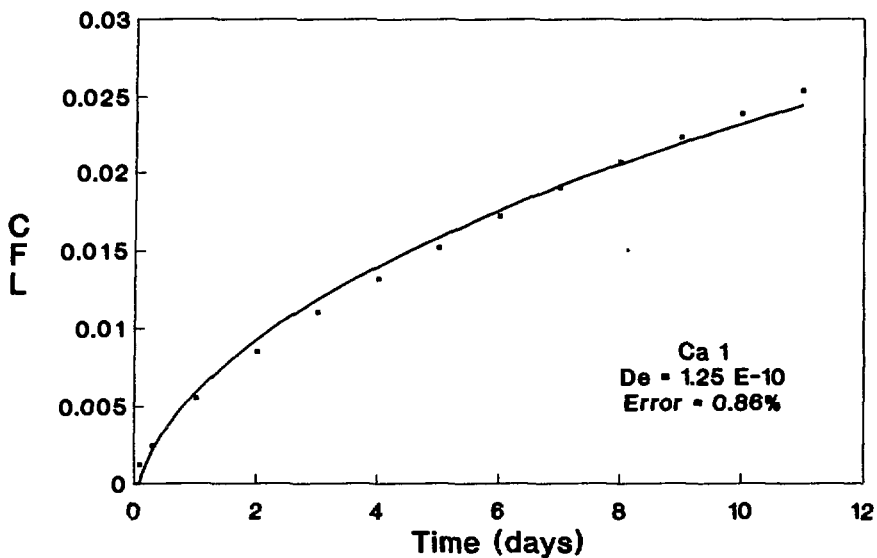


Figure 5.19 Calcium releases from cement/incinerator ash at 20°C do not fit the model very closely. The data is slightly more linear than the model.

The Arrhenius plot (Figure 5.20) for calcium is in contradiction to the modeling results. There is no difference in D_e values with increasing temperature. The reason for this is unknown, but may be the result of calcium reactions with the ash.

5.2.4 Cesium-137. Leaching of cesium-137 from cement/ash samples is not controlled by diffusion. Values for the "goodness of fit" are all greater than 0.5% with some being over 20%. The diffusion model was particularly ill suited for data taken at 55° and 65°C (Figure 5.21). As with sodium and potassium, the curve became asymptotic well below 100% release. In this case, the source term is well known because all Cs-137 was added as a tracer to each sample. This eliminates an erroneous source term as the cause of the poor fit and limits the cause of this observation to adsorption. Batch type adsorption experiments were also performed to determine the capacity of incinerator ash and mixtures of ash and portland cement to adsorb Cs-137 and Sr-85 [1]. Results are reproduced in Table 5.3 and show that about 20% of the Cs-137 and up to 50% of the Sr-85 can be adsorbed by incinerator ash in the presence of portland cement. It is likely that adsorption also is operating for sodium and potassium.

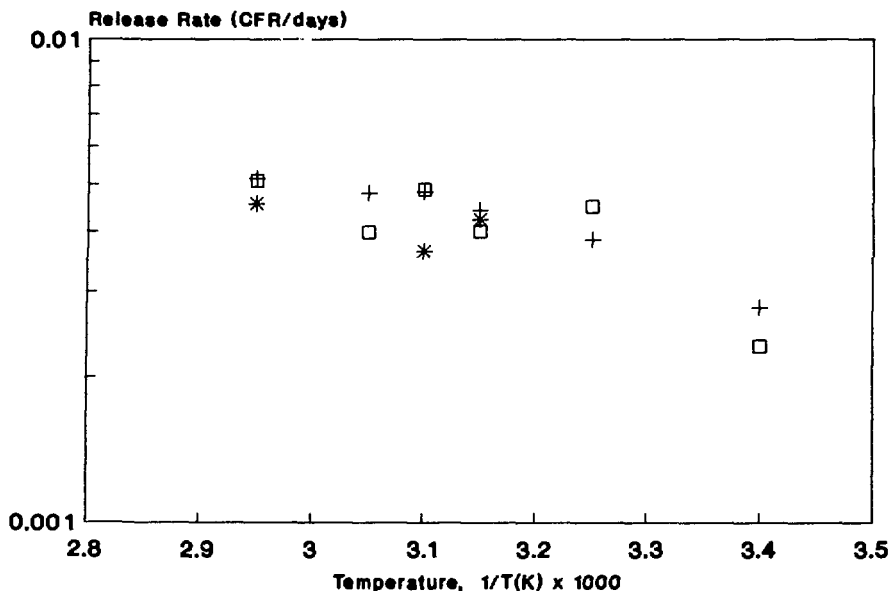


Figure 5.20 Arrhenius plot for calcium from cement/incinerator ash waste forms shows no significant increase in D_e with increasing temperature.

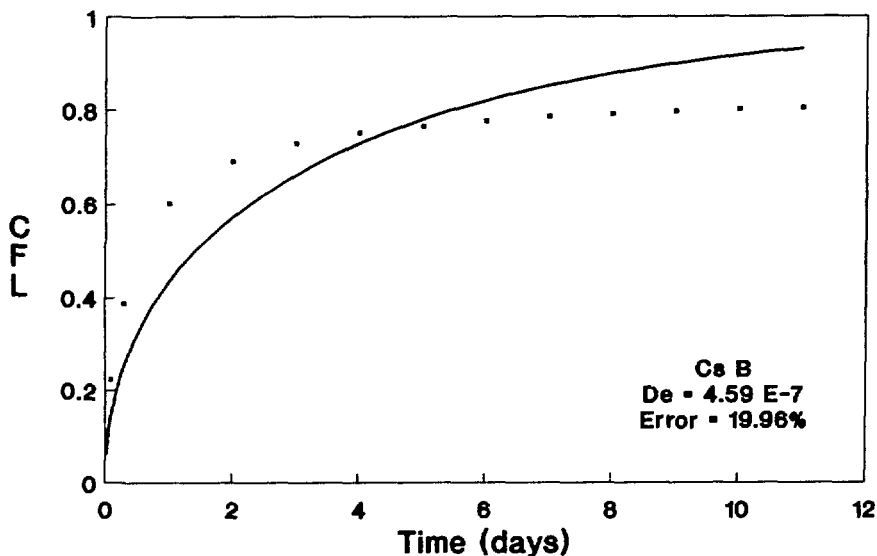


Figure 5.21 Cesium-137 releases from cement/incinerator ash waste forms cannot be fit by the diffusion model; for the cesium data taken at 55°C the curve becomes markedly asymptotic at about 80% release.

TABLE 5.3

Adsorption of Radionuclides by Incinerator Ash
and Cement/Ash Mixtures

<u>Sample Type</u>	<u>Liquid</u>	<u>pH</u>	<u>Percent Adsorption</u>	
			<u>Cs-137</u>	<u>Sr-85</u>
Incinerator Ash	distilled water	11.6	35	56
Incinerator Ash	1M NaOH	13.6	5	81
Cement/Ash (2g ash)	distilled water	13.1	21	49
Cement/Ash (0.76 g ash)	distilled water	12.9	19	38
Cement/Ash (0.50 g ash)	distilled water	12.8	7	20

The Arrhenius plot for cesium-137 (Figure 5.22) can be interpreted in two ways. Using linear regression analysis, a reasonably good fit ($r=0.92$) is obtained for the data taken between 20°C and 55°C. The data taken at 65°C is below the regression line, possibly indicating a departure from the activated leaching process taking place at lower temperatures. Another interpretation is that there is no systematic increase in leaching with elevated temperatures after an initial increase at temperatures greater than 20°C.

5.2.5 Strontium-85. The leaching mechanisms of strontium-85 are mixed. At 20°C and 65°C, the mechanism is not controlled by diffusion (Figure 5.23). The plots of CFL versus time are more linear than diffusion plots, indicating a release limited by solubility. However, at 45°, 50° and 55°C, the E_R values (with two exceptions) indicate that the leaching mechanism is controlled by diffusion (Figure 5.24). Adsorption does not seem to be an important factor in strontium releases. The variability may be a function of the access that carbon dioxide had to the waste forms with some containers sealing better than others. The presence of CO₂ forms CaCO₃ on the surface of cement waste forms and strontium will substitute for calcium in these minerals.

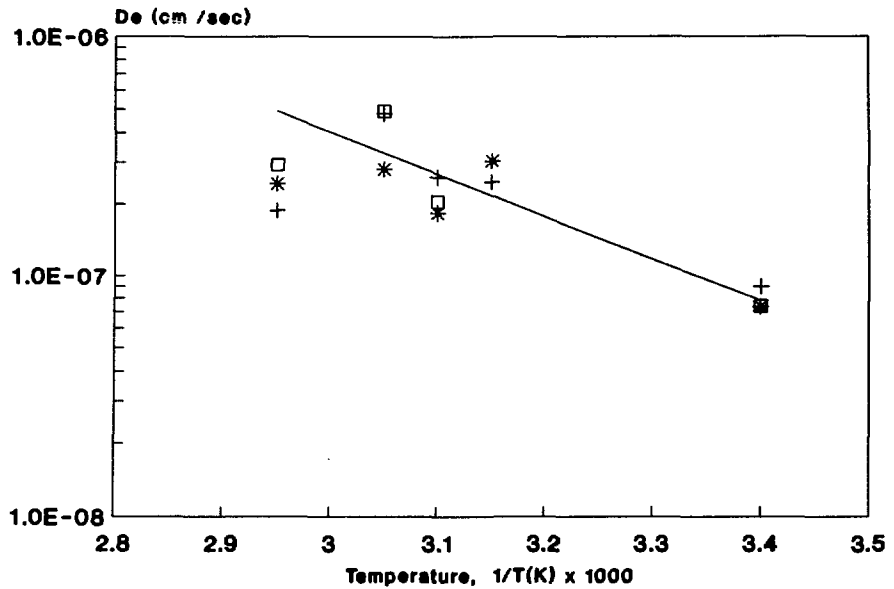


Figure 5.22 Arrhenius plot for cesium-137 leaching from cement/incinerator ash waste forms shows data that can be interpreted in two ways: as a systematic increase in D_e with temperature up to 55°C with a change occurring by 65°C or as an increase in leaching above 20°C , but with no significant change taking place as the temperature increases.

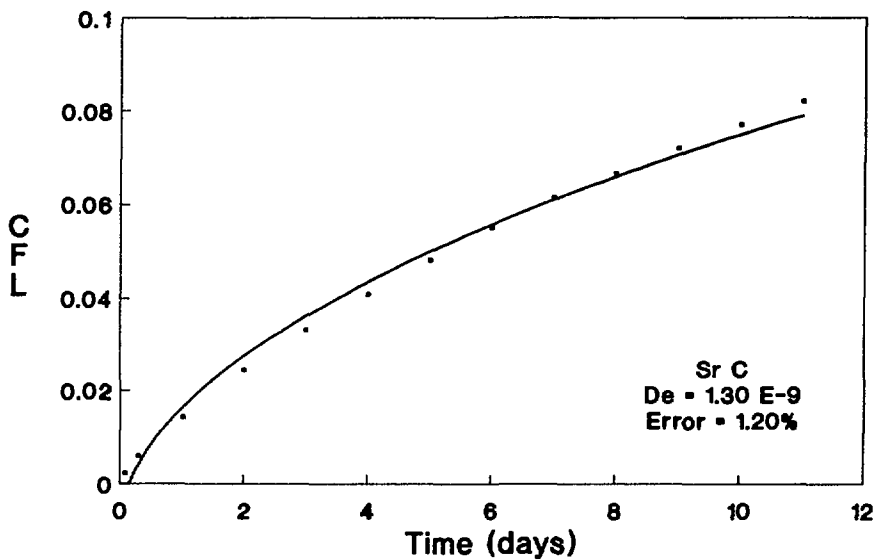


Figure 5.23 Strontium-85 releases from cement/incinerator ash at 20°C do not fit the diffusion model. The experimental data are more linear than the model.

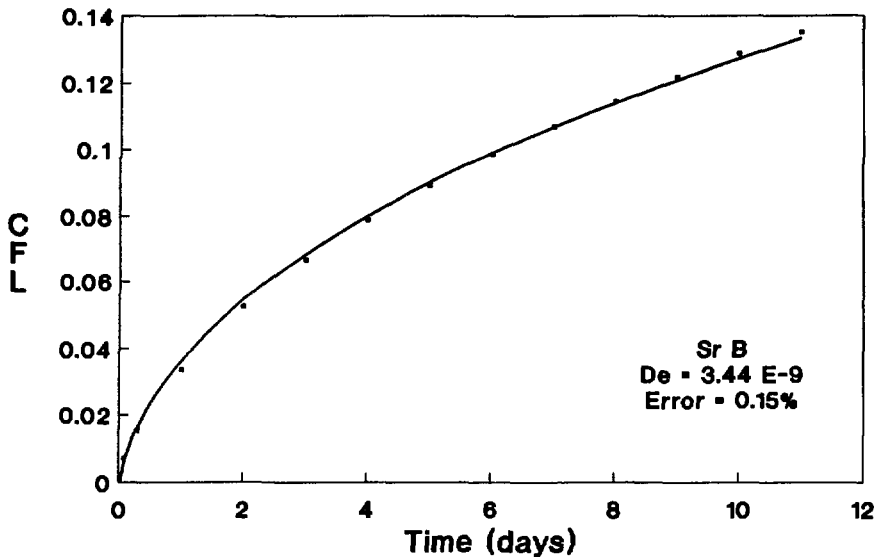


Figure 5.24 Strontium-85 releases from cement/incinerator ash waste forms at 45°C fit the diffusion model closely.

The Arrhenius plot for strontium-85 (Figure 5.25) can be interpreted as a systematic increase in D_e with increasing temperature, having a correlation coefficient of 0.90 and an activation energy of 8.2 kcal/mole. Like the cesium-137 data, however, it could also be interpreted as showing no significant change in D_e between 45° and 65°C after an initial increase at 45°C.

5.2.6 Conclusions. With the exception of calcium, leaching from cement/incinerator ash waste forms is not controlled by diffusion. Typically, plots of CFL versus time become asymptotic at about 80% release, indicating that a portion of the element is not available for release. Most likely, this can be attributed to adsorption onto either the ash or a reaction product of the ash and cement.

Arrhenius plots for cesium-137 and strontium-85 can be interpreted in two ways:

- 1) temperature has no effect after an initial increase in leach rate at temperatures above 20°C.
- 2) temperature causes a systematic increase in leach rate to about 55°C. This is followed by a change in release mechanism as indicated by a drop in D_e at higher temperatures.

Effective diffusion coefficients for strontium-85 and calcium are two and three orders of magnitude lower respectively than the D_e values for cesium-137, potassium and sodium (Figure 5.26).

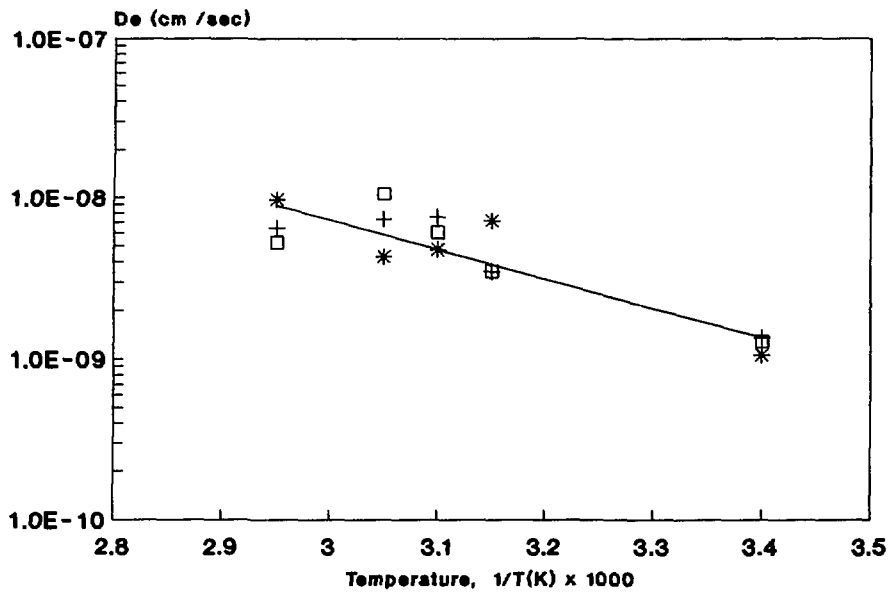


Figure 5.25 The Arrhenius plot for strontium-85 from cement/incinerator ash can be interpreted in two ways: a systematic increase in D_e with increasing temperature or an increase at temperature greater than 20°C , but with no increase in D_e as the temperature is elevated.

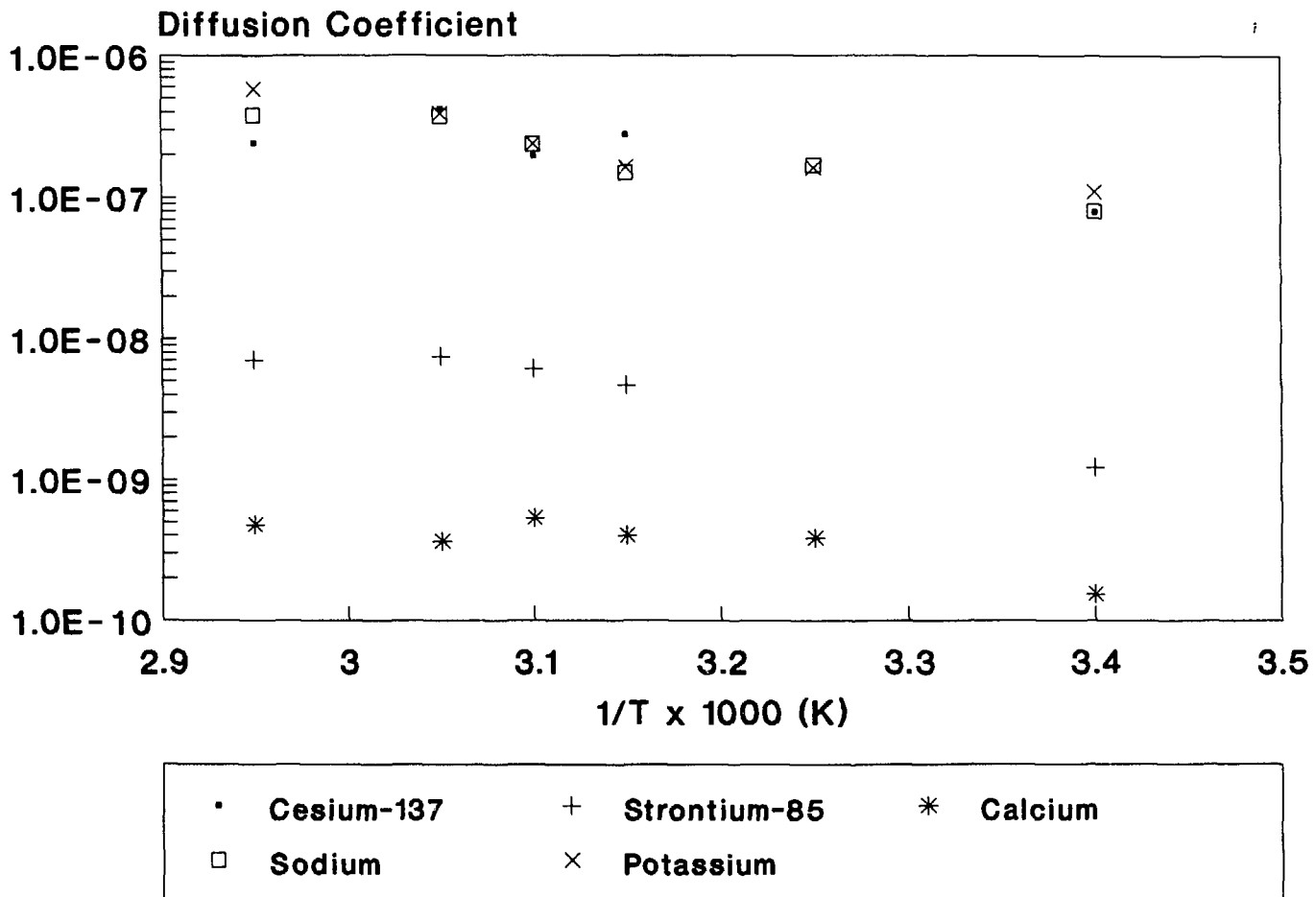


Figure 5.26 The Arrhenius plot for all elements investigated for cement/ash waste forms.

5.3 Vinyl Ester-Styrene/Sodium Sulfate Specimens

Results of leach tests for sodium, cesium-137 and strontium-85 with vinyl ester-styrene (VES) waste forms are given in Table 5.4 as effective diffusion coefficients (D_e) and relative error values (E_R). The experiments were run in triplicate and results are given for each of the samples. As with the cement samples, an E_R value of $\leq 0.50\%$ is used to indicate that diffusion is the process controlling leach rate.

TABLE 5.4
Vinyl Ester-Styrene Containing Sodium Sulfate

	Sample A		Sample B		Sample C	
	$D_e(\text{cm}^2/\text{s})$	$E_R(\%)$	$D_e(\text{cm}^2/\text{s})$	$E_R(\%)$	$D_e(\text{cm}^2/\text{s})$	$E_R(\%)$
Sodium						
20° C	2.79×10^{-10}	4.24	3.10×10^{-10}	3.47	2.49×10^{-10}	3.45
35° C	7.86×10^{-10}	2.84	7.19×10^{-10}	2.94	9.35×10^{-10}	2.82
45° C	7.82×10^{-10}	4.24	7.78×10^{-10}	2.96	5.88×10^{-10}	3.59
50° C	9.10×10^{-10}	0.44	7.47×10^{-10}	0.42	1.17×10^{-9}	0.40
55° C	5.82×10^{-10}	0.89	8.30×10^{-10}	0.28	1.16×10^{-9}	0.41
65° C	2.13×10^{-9}	0.07	1.51×10^{-8}	0.30	6.61×10^{-9}	0.12
Cesium-137						
20° C	5.35×10^{-8}	27.50	5.09×10^{-8}	22.70	5.80×10^{-8}	39.50
45° C	1.23×10^{-7}	1.19	1.52×10^{-7}	0.78	1.65×10^{-7}	0.89
50° C	7.95×10^{-8}	0.48	6.40×10^{-8}	0.83	8.96×10^{-8}	0.70
55° C	1.19×10^{-7}	2.73	1.04×10^{-7}	0.83	1.74×10^{-7}	3.01
65° C	2.17×10^{-7}	5.87	1.67×10^{-7}	5.46	2.72×10^{-7}	7.46
Strontium-85						
20° C	2.88×10^{-8}	2.45	2.91×10^{-8}	1.63	2.63×10^{-8}	3.74
45° C	5.79×10^{-8}	0.41	7.52×10^{-8}	0.16	7.73×10^{-8}	0.28
50° C	6.46×10^{-8}	0.68	5.08×10^{-8}	0.26	6.92×10^{-8}	1.50
55° C	7.08×10^{-8}	0.95	6.16×10^{-8}	0.45	1.04×10^{-7}	1.10
65° C	1.56×10^{-7}	3.37	7.10×10^{-8}	1.08	1.43×10^{-7}	0.23

5.3.1 **Sodium.** Sodium is present in the VES waste forms as particles of dry sodium sulfate salt embedded in the polymer matrix. Sodium comprises about 12% of each waste form and is well-distributed throughout the solid. Sodium sulfate is highly soluble in water and is not expected to be limited by solubility constraints under the experimental conditions used.

Samples leached at 20°, 35°, and 45°C do not leach by diffusion; E_R values range between 2.82% and 4.24%. The data has a different shape than the diffusion curve (Figure 5.27) with the model crossing the data twice. The samples leached at 50°, 55°, and 65°C leached by diffusion (Figure 5.28). With one exception, the E_R values were all below 0.45%. All the samples for this set of experiments were made at the same time and from the same batch of materials. Consequently, the change in leaching behavior is a temperature-induced property of the materials used for the samples.

The effective diffusion coefficients for sodium show that the data taken at 35°, 45°, 50° and 55°C fall very closely together and are not significantly different. The data taken at 6°C has a higher release rate and also greater scatter among the replicates than any other data. Regression analysis of the best fit line on the Arrhenius plot (Figure 5.29) gives a correlation coefficient of 0.788, indicating a poor fit. The averaged diffusion coefficients increased by a factor of 28 between 20° and 65°C.

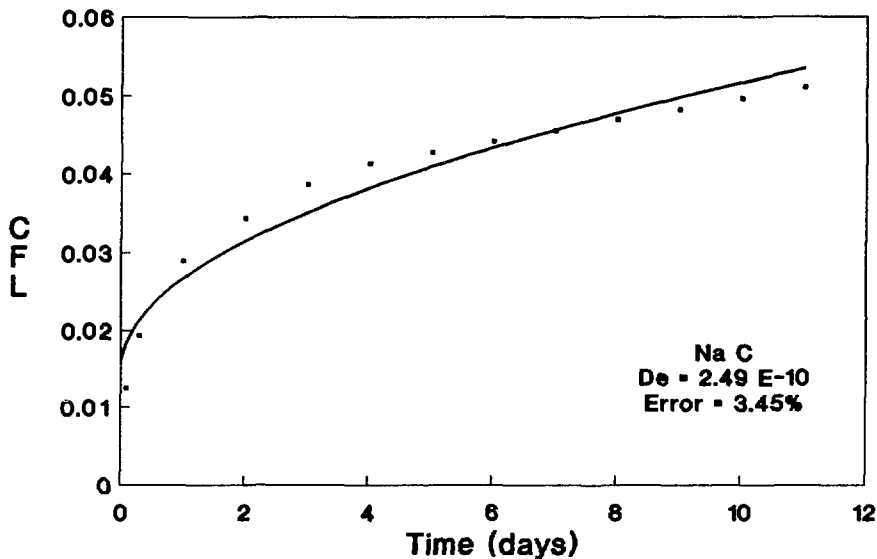


Figure 5.27 Sodium release at 20°C from a VES/sodium sulfate waste form does not fit the diffusion model.

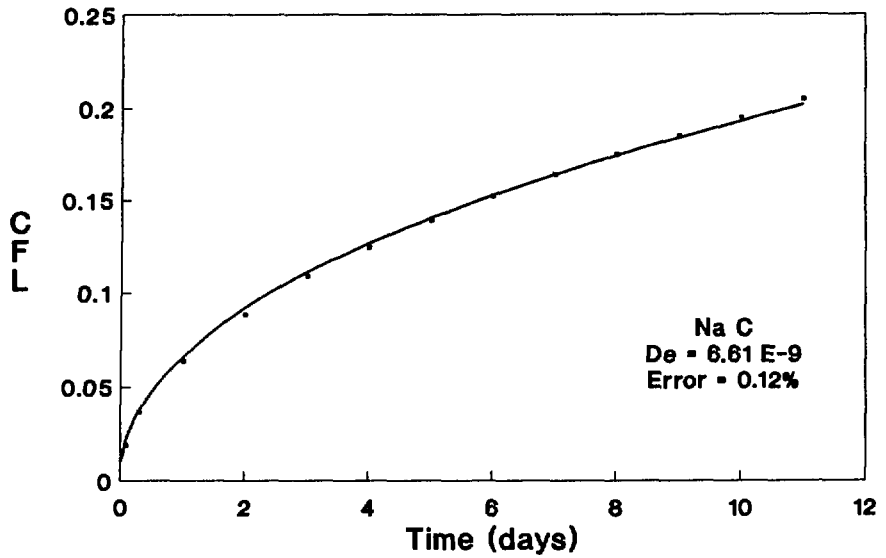


Figure 5.28 At 65°C release of sodium for VES samples fits the diffusion model closely.

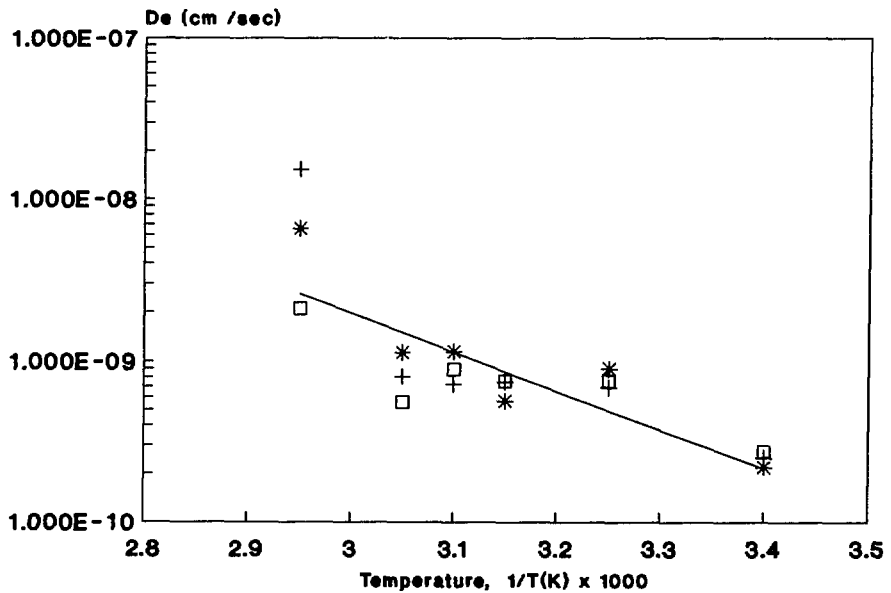


Figure 5.29 Arrhenius plot for sodium from VES/sodium sulfate waste forms gives a poor fit to the regression line. At 65°C the replicates had much greater scatter than usual.

5.3.2 Cesium-137. Cesium-137 is present in VES samples only as an aqueous tracer which was added during the mixing process, before the salt was added. There is less than 1 wt% of tracer in each specimen.

Leaching of cesium is not controlled by diffusion. Only one sample out of 15 has an E_R value that is lower than 0.5%. The samples leached at 20°C have particularly high E_R values ranging between 22.7% and 39.5%. Curves for cesium leaching are similar in shape to those of sodium from experiments run below 50°C and cannot be fit by the diffusion model (Figure 5.30).

Effective diffusion coefficients for cesium do not increase systematically with temperature. Results are scattered and the regression line on the Arrhenius plot (Figure 5.31) has a correlation coefficient of 0.64, a very poor fit. All three 50°C samples have anomalously low releases. The average diffusion coefficient at 65°C is 4.0 times greater than the average at 20°C.

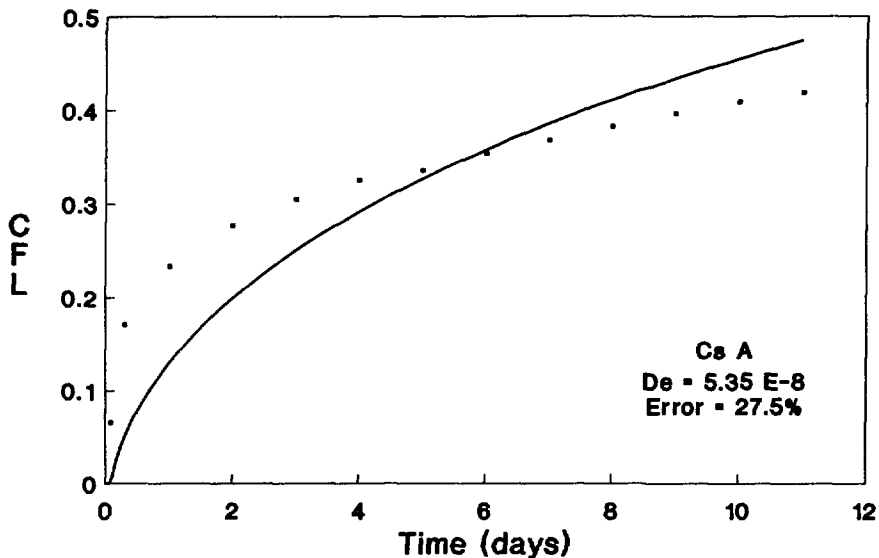


Figure 5.30 Cesium-137 releases from VES/sodium sulfate waste forms at 20°C cannot be modeled by diffusion.

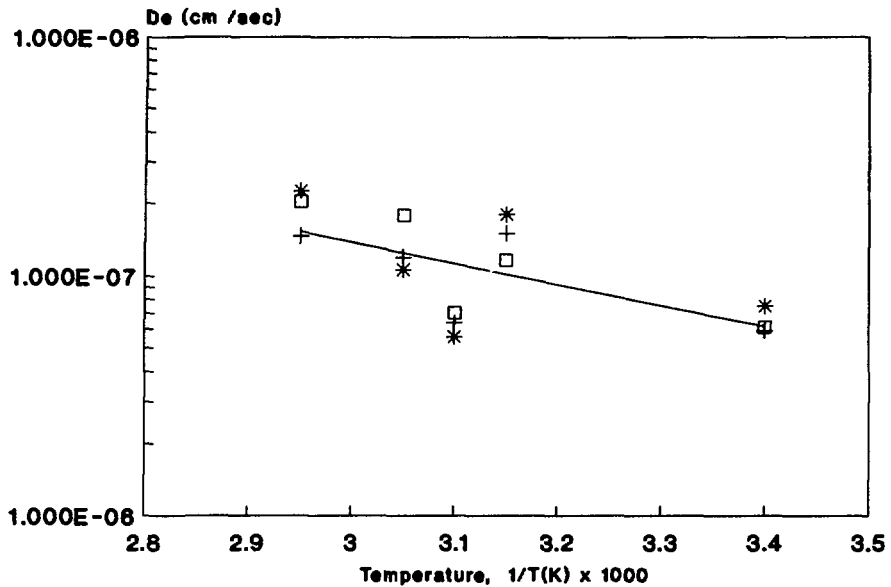


Figure 5.31 The Arrhenius plot of cesium releases from VES/sodium sulfate samples give a correlation coefficient of the regression line of 0.64, a very poor fit.

5.3.3 Strontium-85. Like cesium-137, strontium-85 is added to the VES samples as an aqueous tracer before salt is added to the monomer.

Results from strontium leaching are mixed. For samples leached at 20°C no values of E_R are below the 0.5% cut off. At 45°C, all samples are below 0.5% and at 50°, 55°C, and 65°C, one sample at each temperature is below 0.5%. Within one set of triplicates the variability of E_R is substantial. For example, at 65°C one E_R value was 3.37 while another was 0.23 (Figures 5.32 and 5.33). To determine if this difference is caused by problems with the source term, the source term for one sample was changed repeatedly in the model with no improvement in the fit. Thus, neither the source term nor adsorption is causing the discrepancy between the model and the data. The difference may be a function of the distribution of the small quantity of tracers within each specimen.

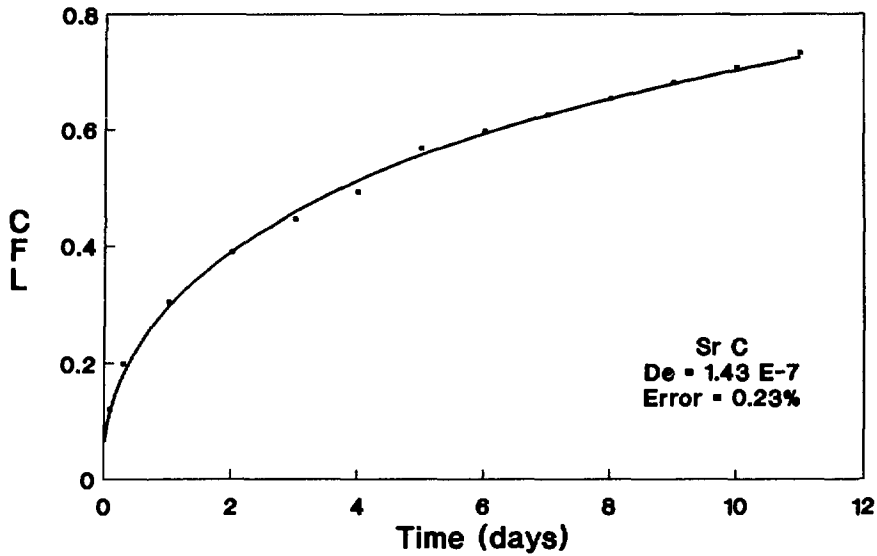


Figure 5.32 Releases of strontium from VES/sodium sulfate samples are variable. In this case (Sample C leached at 65°C) the model and the data fit very closely.

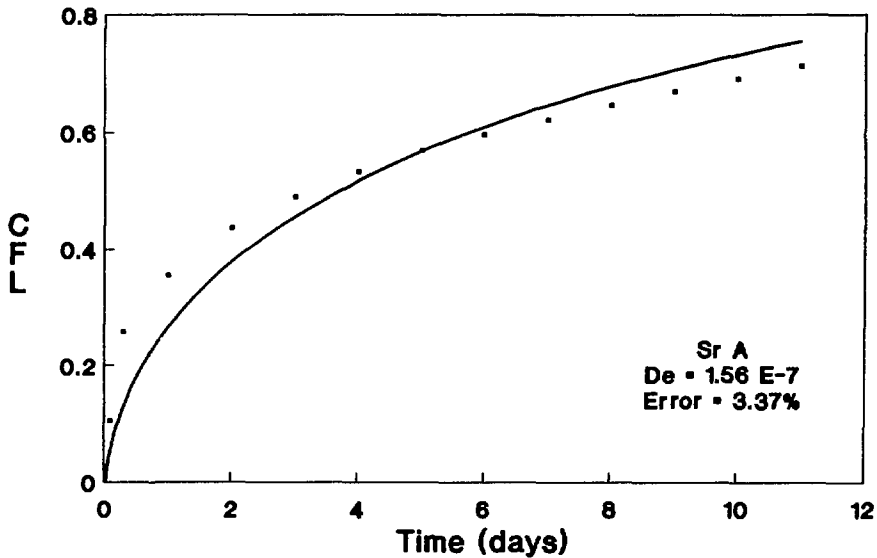


Figure 5.33 Releases of strontium from VES/sodium sulfate samples are variable with regard to the fit of the diffusion model. In this case (Sample A leached at 65°C), the model and the data do not fit.

Effective diffusion coefficients for strontium-85 are similar to those for cesium-137. The Arrhenius plot (Figure 5.34) shows that the scatter in the strontium data is less than the cesium data and shows a better trend of increasing D_e with increasing temperature. Nevertheless, the correlation coefficient is 0.88 which indicates that the scatter around the regression line is high. The increase in average D_e between 20°C and 65°C is a factor of 4.4.

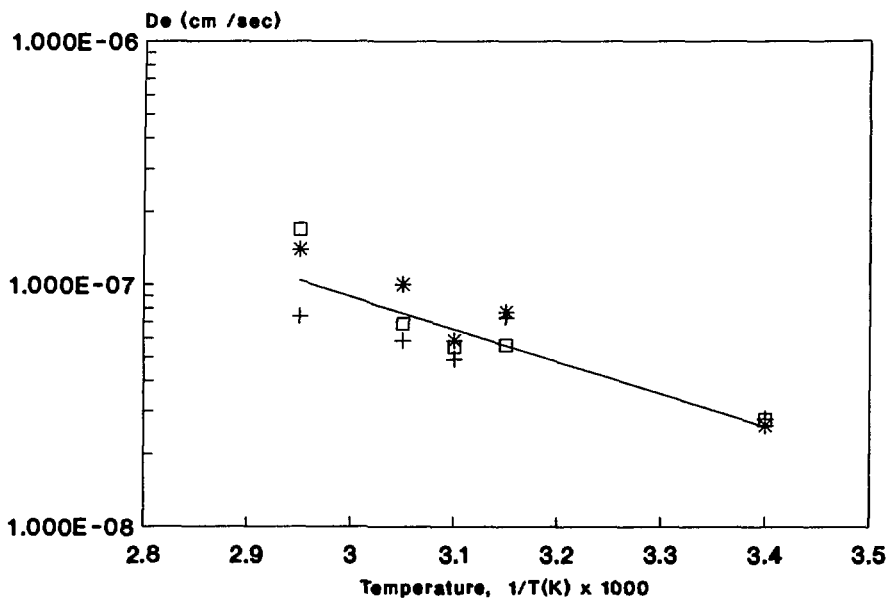


Figure 5.34 Arrhenius plot for strontium leached from VES/sodium sulfate samples indicates a trend of increasing D_e with increasing temperature. The correlation coefficient for the regression line is 0.88.

5.3.4 Conclusions. Leaching of sodium from VES is controlled by diffusion at temperatures of 50°C or greater. However, below 50°C the leaching mechanism is not diffusion. The leaching mechanism of cesium-137 and strontium-85 is not diffusion at any temperature. Some strontium samples do leach by diffusion while others, at the same temperature, do not. This may be the result of different distributions of the small quantity of tracer.

The observation that the release mechanism of sodium changes at 50°C implies that some property of the polymer matrix is altered by temperature. Therefore, only temperatures below 50°C should be used to accelerate leaching from VES waste forms if long-term extrapolations are to be made for sodium. In all cases, temperature was an effective acceleration factor. As shown in Figure 5.35, effective diffusivity of sodium is almost two orders of magnitude lower than cesium and strontium, but the increase in sodium leaching (the slope of the regression line) was much greater than for the two radionuclides by a factor of about 5.

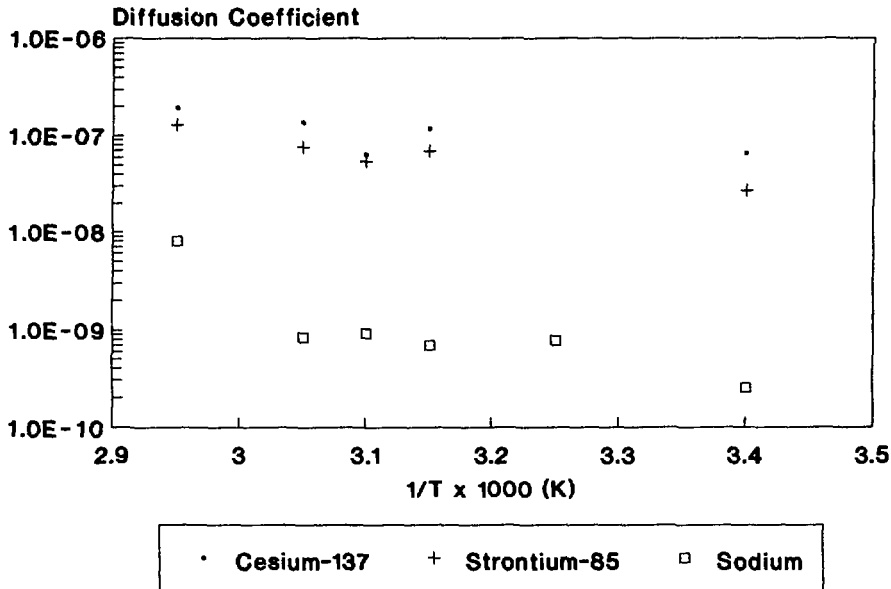


Figure 5.35

Arrhenius plot for releases from VES/sodium sulfate.

6. SUMMARY AND CONCLUSIONS

In FY 1989 the goals of the accelerated leach test program were achieved. A draft accelerated leach test method was submitted to the LLWMP. In addition, another version adapted to the appropriate format was submitted for review by the American Society for Testing and Materials (ASTM). Associated with the test method is a computer program, which was developed for this task, that calculates and models results.

The following conclusions are drawn from the FY 1989 work on development of an accelerated leach test.

- Releases of some elements from certain waste forms (notably sodium from cement/sodium sulfate waste form), are controlled by diffusion under the conditions of the proposed test.
- Leaching of other elements from various waste forms is not controlled by diffusion alone. Other mechanisms, especially adsorption are important.
- Elevated temperature is a useful means of increasing leach rates even though the release mechanisms are not necessarily diffusion alone. This is true for all elements investigated for cement/sodium sulfate waste forms. For cement/ash samples, temperature effectively increases the releases of potassium and sodium. The effect of increased temperature on the leaching of calcium, cesium-137, and strontium-85 is less clear and can be interpreted in two ways:
 - 1) There is no acceleration of leaching after an initial increase in leach rate at temperatures above 20°C.
 - 2) There is a systematic increase in leach rate to about 55°C followed by a change in release mechanism as indicated by a drop in D_c at high temperatures.
- The mechanism of leaching of sodium from VES waste forms changes at temperatures of 50°C or greater, with diffusion operating at the higher temperatures. Release mechanisms of cesium-137 and strontium-85 show no clear pattern.

For FY 1990 the accelerated leach test development program will concentrate on improving the computer program. In particular, the programs data files will be made compatible with LOTUS 1-2-3, making better graphics capabilities available.

The following recommendations are made for future work.

- An interlaboratory round-robin of the accelerated leach test should be run to help validate the method as well as to familiarize potential users with the test.
- Models using diffusion from a finite cylinder are a good first step but more sophisticated models need to be developed and validated.
- Leaching mechanisms of various species of interest, from real waste forms, need to be studied to validate the models. This is especially so for long-lived radionuclides such as ^{14}C , ^{129}I and ^{99}Tc .
- Leaching mechanism and model validation studies need to be performed for special DOE waste forms such as saltcrete from SRP and the grouts being used at Hanford.

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