

CONF-891119--20

BNL-43449

BNL--43449

DE90 003641

THE EFFECTS OF TEMPERATURE ON THE LEACHING BEHAVIOR OF
CEMENT WASTE FORMS - THE CEMENT/SODIUM SULFATE SYSTEM*

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October 1989

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Prepared for the
NATIONAL LOW-LEVEL WASTE MANAGEMENT PROGRAM
UNDER CONTRACT NO. DE-AC02-76CH00016 WITH THE
UNITED STATES DEPARTMENT OF ENERGY

*To be presented at the Material Research Society 1989 Fall Meeting in Boston, Massachusetts, November 27-December 2, 1989.

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THE EFFECTS OF TEMPERATURE ON THE LEACHING BEHAVIOR OF CEMENT WASTE FORMS - THE CEMENT/SODIUM SULFATE SYSTEM *

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ABSTRACT

The leaching mechanisms of simulated low-level radioactive waste forms are being determined as support for development of an accelerated leach test. Two approaches are being used: (1) comparisons of leaching data with results of a model that describes diffusion from a finite cylinder, and (2) observation of the leaching process at temperatures between 20°C and 65°C. To provide results that can be used for modeling, leaching at elevated temperatures must change neither the leaching mechanism nor the structural controls of leaching such as the porosity. Releases of ^{137}Cs , ^{85}Sr , calcium, sodium and potassium from portland cement containing sodium sulfate, as a simulated evaporator sludge, have been determined under a variety of experimental conditions. Data from the leach tests were compared to model results for diffusion from the finite cylinder. While most leaching appears to be diffusion controlled, notable exceptions occur. For all samples activation energies ranging between 6 and 11 Kcal/mole have been calculated from the relationship of the effective diffusion coefficient to increasing temperature, close to the expected value of 5 Kcal/mole for diffusion.

INTRODUCTION

The leaching behavior of cement-based, simulated low-level waste forms was studied at temperatures between 20°C and 65 C as support for the development of an accelerated leach test. In previous investigations [1,2,3,4,5] a variety of factors, such as elevated temperature and increased leachant volume, were examined for their ability to accelerate leaching. Initially, they were studied individually, later the most useful factors were combined to obtain greater release rates.

From this work an accelerated leach test method [6] was developed for low-level radioactive waste forms. The leach test method was designed to minimize experimental artifacts that could be misinterpreted as release mechanisms such as effects of increased ionic concentrations in the leachate. This is particularly important when the data is used for mechanistic interpretations and long-term extrapolations. A computer program associated with the accelerated leach test allows the user to test experimental results against a model for diffusion from a finite cylinder [7,8]. If the model and the data fit within preset criteria then the diffusion model can be used to make projections of releases. Leaching data were analyzed to assess: 1) whether the model for diffusion from a finite cylinder describes leaching from cement based waste forms and 2) whether elevated temperature provides a predictable increase in leach rate. In this paper some of the experimental and modeling work used to validate the test method are presented. Only the work on portland cement containing sodium sulfate is presented here. Results of similar studies with portland cement alone and portland cement containing incinerator ash will be published separately.

METHODS

Releases of ^{137}Cs , ^{85}Sr , calcium, potassium and sodium were investigated for portland type I cement plus 5 wt% sodium sulfate salt. This formulation represents a typical low-level waste form produced from neutralized acid used to regenerate ion exchange resin. The tracers ^{137}Cs and ^{85}Sr were added during production of the samples. Details of composition are given elsewhere [5].

* This work was sponsored by the U.S. Department of Energy Low-Level Waste Management Program under contract No. DE-AC02-76CH00016.

The leach test [6] is a semi-dynamic test in which the leachate is replaced periodically after intervals of static leaching. 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 μ mhos/cm. Specimens are usually tested in triplicate to determine the variation in leaching. Experiments run at elevated temperatures were conducted in an environmental chamber with strict temperature controls. The results of the leach tests are expressed as cumulative fraction leached (CFL) or as an effective diffusion coefficient (D_e), to facilitate alternative methods of treating the data.

A model for bulk diffusion from a finite cylinder is used as a guide to determine if diffusion is the rate controlling transport mechanism during leaching. A value for the optimum D_e value is obtained by first estimating D_e using the semi-infinite medium approach. Then iterations are performed with the finite cylinder model to obtain the D_e value that gives the lowest sum of the residuals for the entire set of data.

The goodness-of-fit between the data and the model result is evaluated by expressing the sum of the residuals as a percentage of the maximum CFL of the experimental data, E_R . If $E_R \leq 0.5\%$, then it is taken to mean that diffusion is the dominant leaching mechanism. Figure 1 shows the relationship between the data from an experiment and the diffusion model when $E_R = 0.51$.

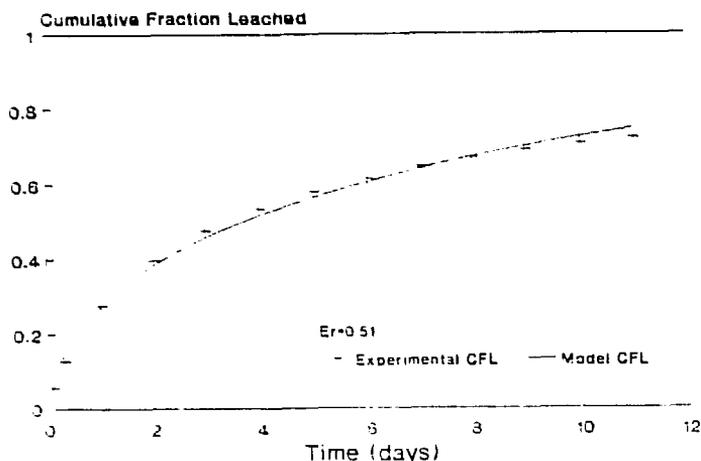


Figure 1. Experimental data are compared to the diffusion model when $E_R = 0.51$. These data are for ^{137}Cs leached from a cement/sodium sulfate sample at 50°C .

RESULTS AND DISCUSSION

Table I contains D_e and E_R values for various elements leached from triplicate samples of cement containing 5 wt % sodium sulfate. The Ca, K and 9% of Na originate in the cement, 91% of the Na is from the sulfate salt and the ^{137}Cs and ^{85}Sr were added as tracers.

Releases of Na generally have values of E_R that are close to or less than 0.50% indicating that diffusion controls releases at all temperatures. The exceptions are two of the three samples leached at 45°C . Leaching of K gives more scattered results with the 45°C samples having especially large errors. All of the Ca results are greater than 0.50% indicating that diffusion does not control the release rate of Ca. Plots of CFL versus time for Ca (figure 2) are more linear than the diffusion curve, illustrating that solubility limits are the leach rate controlling factor. Maximum concentrations of Ca in the leachate are 4.2 - 4.8 mg/l (at 20°C) which is close to the solubility of 6 mg/l for calcium carbonate (this is much lower than the solubility limits of any other major compounds that could be present). Leaching of ^{85}Sr is diffusion controlled between 20°C and 50°C , but at higher temperatures it was not.

TABLE I
Effective Diffusion Coefficients For 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

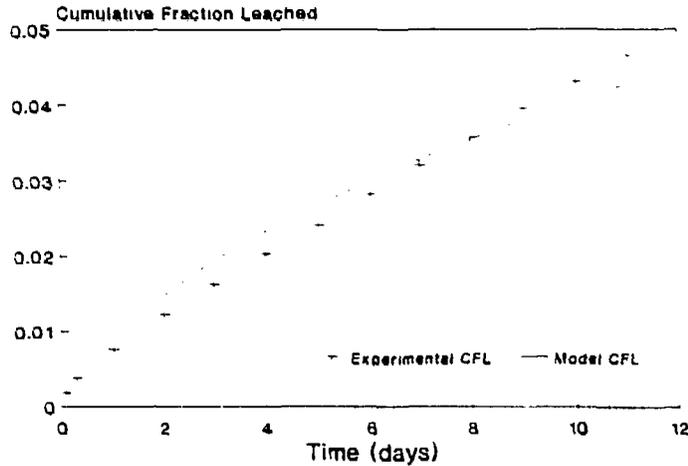


Figure 2. Releases of calcium do not fit the diffusion model. The experiment data are linear after the first few points indicating that solubility limits the concentration of Ca in the leachate.

Releases of ^{137}Cs as indicated by the E_R values, are not diffusion controlled. The data at the end of the experiments typically fall below the model curve. An example is shown in Figure 3. Curve A is the diffusion curve that represents the best fit of the model to the data, giving an E_R value of 2.43%. By adjusting the source term downward by about 12% and generating Curve B, the fit is improved to an E_R of 0.37%. Because the source term has been checked several times, it is certain that the original source terms are not in error. Some of the ^{137}Cs 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 [10]. However, earlier work in this program has shown that authigenic products, such as CaCO_3 , that form on the surface of cement during leaching do have some capacity to adsorb ^{137}Cs and inhibit the movement of dissolved species to the surface of the sample [4,11]. For these reasons the leaching mechanism of cesium (and probably 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 .

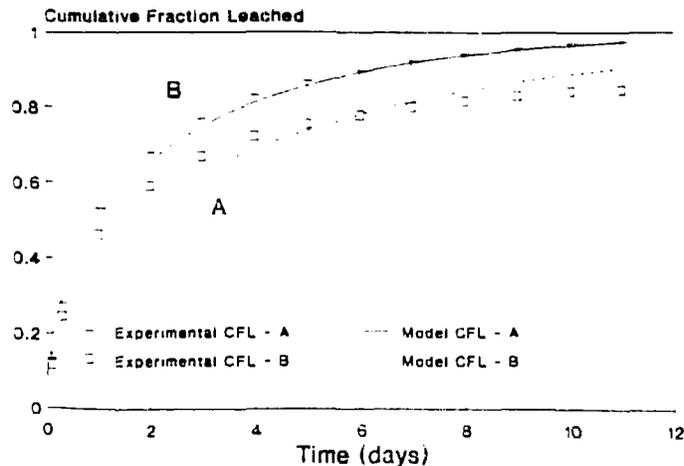


Figure 3. Comparison of CFL curves for ^{137}Cs leached at 65 C. Curve A is the untreated data. Curve B is normalized by adjusting the source term downward by 12%, improving the fit of the model to the data.

If temperature changes neither the mechanism of leaching nor the structural controls on leaching, then an Arrhenius plot of the log of the leach rate as a function of $1/T$ (where T equals temperature in Kelvins) will be linear.

Figure 4 is an Arrhenius plot of averaged D_e values for leaching of cement/sodium sulfate samples. It shows that increasing temperature systematically increases the effective diffusion coefficients. Linear regression of the data, including all triplicates, gives correlation coefficients (r) shown in Table II. Also in table II are activation energies (E_a) calculated from the slope of 16 regression lines. For waste forms containing a simulated waste that is known to react with portland cement, these correlations are acceptable. The activation energies are slightly higher than the 5 Kcal/mole expected for diffusion. This implies that the rate of increase in leaching may not be predictable and will need to be determined empirically for each material tested.

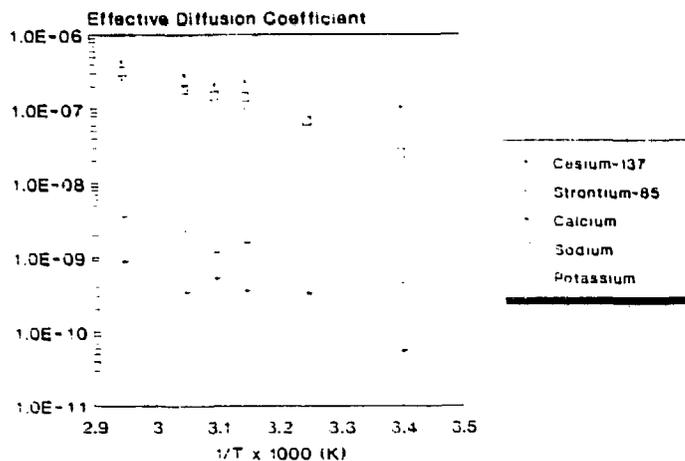


Figure 4. Arrhenius plot showing the response of D_e to increasing temperature for each of the elements studied.

Table II
Correlation Coefficients and Activation Energies
For Cement/Sodium Sulfate Samples

Element	Correlation Coefficient (r)	E_a (Kcal/mole)
^{137}Cs	0.89	6.0
^{85}Sr	0.96	8.7
Ca	0.97	11
K	0.97	9.4
Na	0.91	11

CONCLUSIONS

Cement waste forms containing sodium sulfate leach via three mechanisms under the experimental conditions presented in the accelerated leach test. Sodium leaches by diffusion. Calcium releases are controlled by solubility. Potassium and cesium leach by diffusion that is modified by adsorption probably on calcium carbonate that forms on the surfaces of the waste forms. Strontium leaches by diffusion up to 50 C and then is controlled by another process at higher temperatures.

Although the leaching mechanisms of cement waste forms containing sodium sulfate are not strictly diffusion, this has little effect on the usefulness of elevated temperature for accelerated leaching. Arrhenius plots of the elements studied indicate that increasing temperature accelerates the leach rate.

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