PROGRESS IN DEVELOPMENT OF AN ACCELERATED LEACH TEST FOR LOW-LEVEL RADIOACTIVE WASTE FORMS*

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August, 1987

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Factors that accelerate leaching from solidified low-level radioactive waste are being investigated to develop a short-term leach test that can be used to predict long-term releases. Data from work with portland cement containing radioactive tracers indicate that elevated temperatures (up to 50°C or higher) can accelerate leaching of Cs-137 by at least a factor of eleven without changing the leaching mechanism. An 18 day leach test at 50°C provided the equivalent of 200 days data taken at 20°C. Portland cement containing 5 wt% Na$_2$SO$_4$ (as a simulated evaporator concentrate) also can be accelerated, but to a lesser degree. Solid phase analysis indicated that pore plugging and increased tortuosity may be the cause of the smaller acceleration. Reduced specimen size was also a useful acceleration factor with inhomogeneities not being a problem in very small specimens. Elevated pH and 100 ppm EDTA in leaching solutions increased Sr-85 releases without altering Cs-137 leaching.

INTRODUCTION

Leach tests for low-level radioactive waste have served, in the past, two purposes: (1) to provide data for comparison among solidification agents or additives for waste forms and (2) to meet licensing requirements of the Nuclear Regulatory Commission for shallow land burial disposal (10 CFR 61). In both cases, short-term (90-days) tests typically are considered adequate. A third use of leaching data, which has only recently been applied, is for source term determinations and performance assessment of disposal sites [1,2]. Because projections over long times are necessary for this use, leaching data also should have a relatively long time frame. The accelerated leach test program is attempting to develop a rapid leach test that will give the equivalent of long-term data in a relatively short time.

Because of the large body of information being generated in this work only selected results of our investigations are reported here. This paper gives some results of the Accelerated Leach Test(s) Development program concentrating on data from plain portland cement and portland cement containing 5 wt% sodium sulfate salt. For information on accelerated leaching from other waste forms the reader is referred to the annual and topical reports generated in this program [3-6]. The waste forms being investigated are:

*This work sponsored by the National Low-Level Waste Management Program of the U.S. Department of Energy under contract No. DE-AC02-76CH00016.
A wide variety of potential acceleration factors are being studied including:

- temperature
- size
- leachant volume
- leachant pH
- leachant Eh
- leachants containing complexing agents
- waste loading

RESULTS OF ACCELERATED LEACH TESTS

Several acceleration factors were observed to provide increased leaching in a manner that did not alter the leaching mechanism of either plain portland type I cement or portland cement containing 5 wt% sodium sulfate as a simulated waste. Some acceleration factors increased the leachability of both Cs and Sr. Others increased only releases of Sr. In no case was Co observed in any of the leachate from these cement waste forms. This was expected and desirable because no Co was detected in the baseline leaching studies against which accelerated leaching is compared.

Plain Cement

Temperature

Figure 1 shows the cumulative fraction releases (CFR) of plain cement specimens at 70°, 50°, 40°, 30° and 20°C over a period of 18 days. The 20°C data extended to more than 500 days so the accelerated test results could be compared against it. Results are shown in Table 1 for 18 days accelerated tests. The "equivalent time" is the number of days (at 20°C) it would take to get the same release obtained in 18 days at elevated temperatures. For example, it would take 200 days leaching time at 20°C to get the same results obtained in 18 days at 50°C.
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<th>Temperature (°C)</th>
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Figure 1. Cumulative fraction releases (CFR) of Cs-137 from cement waste forms leached at 20°, 30°, 40°, 50° and 70°C.

Figure 2. Linear correlation plot for plain cement leached at 20°, 30°, 40°, 50° and 70°C. While most data sets are linearly correlated the 70°C data is less linear implying either depletion or a mechanism change is altering leaching.
Figure 2 shows a linear correlation plot of CFR data at various temperatures. To determine if the leaching mechanisms had changed during studies at elevated temperatures the CFR of each set of data, taken at increased temperatures, was plotted against a standard set of data, (in this case CFR at 20°C), so that data points taken at the same time are plotted against each other. If the resultant points lie on a straight line, then the two sets of data are linearly correlated as long as the leaching mechanism remains unchanged. The slope of each line provides a relative measure of the leach rate compared to the standard data. This approach was taken for all acceleration factors investigated.

On Figure 2 the data indicate that leaching at elevated temperatures does not alter the leaching mechanism until at least 70°C is reached. Therefore, it is possible to accelerate leaching of Cs-137 from cement with temperatures up to 50°C, and possibly higher, with at least an eleven-fold increase in leaching and no change in mechanism.

Applications

Application of this work to specific problems where portland cement (without waste) is of concern have been discussed recently. One involves the basement at Three Mile Island where Cs-137, 134 and Sr-90 have sorbed into the concrete walls. Leaching at elevated temperatures (while demineralizing the water) could substantially reduce the time required to minimize this contamination. Another application is for the study of concrete materials to be used as barriers in engineered disposal facilities. Exposure to Cs-137 solutions at elevated temperatures would provide a rapid means of determining effectiveness of various cementitious materials as barriers.

Cement Plus Sodium Sulfate

Waste forms composed of portland cement and 5 wt% sodium sulfate were investigated as one of several typical power reactor wastes. These were subjected to a variety of individual acceleration factors.

Temperature

Elevated temperatures increased leachability of Cs-137 from cement containing 5 wt% sodium sulfate. It also increased the scatter in leaching data. Figure 3 shows median CFR curves for leaching at 20°C, 40°C and 50°C, illustrating that leaching is increased by about a factor of 2 at 40°C and about 3 at 50°C. This data also is shown in Table 1. Linear correlations for all specimens are shown in Figure 4 and indicate the increased general scatter among specimens. Below a CFR of 0.4 (for 40°C specimens) the relationships are linear. This implies that there is no change in leaching mechanism at 40°C. At 50°C there may be a mechanism change. Calculations of activation energies for Cs-137 releases gave an average of 4.84 ± 1.4 which is indicative of diffusion. However, acceleration of Cs-137 releases with this material is not as great as with plain cement. Analysis by scanning electron microscopy shows a possible cause. The surface of an unleached cement specimen is shown
Figure 3. Median CFR values for Cs-137 leached from cement at 20°, 40°, and 50°C.

Figure 4. Triplicate data showing linear correlations for specimens leached at 40° and 50°C plotted against the 20°C baseline data.
in Figure 5. It is an open, porous network of capillary pores. After immersion for 55 days at 50°C, as shown in Figure 6, the surface is covered with small crystals that appear to reduce the porosity. Inside the specimen any bubbles that were open prior to immersion were filled with crystals as in Figure 7. This indicates that significant authigenic mineral growth is occurring throughout the specimen which could: decrease porosity, increase tortuosity or provide additional sorption for Cs-137. Mineral growth may account for the sharp reduction in acceleration at 50°C, but this needs to be investigated further.

Size

Small scale specimens can be used to accelerate the leaching that would be expected from full-scale waste forms [7,8,9]. This was verified for cement specimens containing, sodium sulfate. Figure 8 shows linear correlations for specimens of several sizes which indicate that there is no change in leaching mechanism. The points for $V/S=0.42$ fall below the line because of depletion. In 18 days of leaching the smallest specimens (2.5x2.5 cm) gave the equivalent of 65 days of leaching from the standard size specimens, an increase of 3.6 times. Specimen size also accelerated leaching of Sr-85 from these specimens. In 18 days the smallest specimens leached the equivalent of about 180 days. This a 10-fold increase in leaching.

EDTA

A 100 ppm solution of disodium EDTA was used as a leachant to accelerate releases. There was no significant effect on Cs-137 leaching, but Sr-85 leachability was increased significantly. Figure 9 shows linear correlation plots of triplicate specimens leached in the EDTA solution and in distilled water. EDTA increased Sr releases by a factor of 4.7 such that during an 18 day leach test the equivalent of 85 days release was obtained without altering the leaching mechanism.

Leachant pH

A range of pH values from 3 to 8 were tested for ability to accelerate leaching from cement waste forms. These values were those of the leaching solution prior to use. Leaching of cement will cause the leachant pH to increase as soluble components of cement dissolve. The theoretical pH of distilled water is 7, but is actually around 6 due to dissolution of carbon dioxide from the air. Changing the pH did little to alter the Cs-137 leachability. The linear correlation plot in Figure 10 shows that decreasing the pH increased Sr-85 releases so that at pH 3, for an 18 day leach test, the equivalent of 85 days of baseline data (pH 6) were obtained. Increasing the pH of the initial leaching solution decreased releases of Sr-85.

These changes in Sr-85 release may be due to alteration of the rate of carbonation that occurs on the surface of the cement. By reducing the rate of $\text{CO}_2$ dissolution into the water (by lowering the pH) the effects of carbonation can be eliminated.
Figure 5. Outer surface of an unleached cement sample containing 5% sodium sulfate at a magnification of 400 times. This surface is indistinguishable from that of unleached pure cement.

Figure 6. Outer surface of a leached cement sample containing 5% sodium sulfate after static leaching for 55 days at 50°C. Magnification is 400 times. Profuse crystal growth covers the surface.
Figure 7. A bubble that after leaching was full of crystals. This was typical of voids in the sample indicating that alteration of porosity/tortuosity throughout the specimen is occurring.

SIZE ACCELERATION OF Cs-137 LEACHING FROM CEMENT/SO₄ WASTE

Figure 8. Linear correlation plot showing that small specimens leach Cs-137 faster than larger specimens and that the leaching mechanism is maintained. Inhomogeneities do not cause a change in mechanisms.
EDTA ACCELERATION OF Sr-85 LEACHING FROM CEMENT/SO$_4$ WASTE

Figure 9. Linear correlation plots of Sr-85 from waste forms leached in distilled water and in a 100 ppm EDTA solution.

pH ACCELERATION OF Sr-85 LEACHING FROM CEMENT/SO$_4$ WASTE

Figure 10. Linear correlation plots of Sr-85 from waste forms leached at various pH values.
SUMMARY AND CONCLUSIONS

Releases of Cs-137 can be significantly accelerated by elevated temperature without altering the leaching mechanism. For plain cement, Cs-137 leaching can be accelerated 11-fold by leaching at 50°C, while at 70°C leaching can be accelerated by more than 30 times. At 70°C, however, leaching mechanism changes may take place. At 50°C an 18 day experiment generated data equivalent to 200 days of leaching at 20°C while at 70°C the 18 day experiment gives the equivalent of over 550 days worth of data.

Temperature also accelerated releases of Cs-137 from portland cement specimens containing 5 wt% Na₂SO₄. However, the increase in leach rate was less than that observed for plain cement. At 50°C the increase was about a factor of 3 compared to a factor of 11. Solid phase analysis indicated that mineral growth on surfaces and in the pores of this material may reduce porosity and increase tortuosity enough to alter this rate.

Along with temperature, reduced size also increased the leach rate without altering the mechanism. This was of concern because, with small specimens, minor inhomogeneities could become important. For these specimens this was not the case.

Altering the starting pH of leaching solutions had no effect on Cs-137 leaching, but did increase Sr-85 releases by a factor of almost 5. Similarly, a 100 ppm EDTA leaching solution increased the rate of Sr-85 release.
REFERENCES


