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# LEACHING STUDIES OF LOW-LEVEL RADIOACTIVE WASTE FORMS*

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## DISCLAIMER



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*Work performed under the auspices of the U.S. Nuclear Regulatory Commission.

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## ABSTRACT

A research program has been underway at the Brookhaven National Laboratory to investigate the release of radionuclides from low-level waste forms under laboratory conditions. This paper describes the leaching behavior of Cs-137 from two major low-level waste streams, that is, ion exchange bead resin and boric acid concentrate, solidified in Portland cement. The resultant leach data are employed to evaluate and predict the release behavior of Cs-137 from low-level waste forms under field burial conditions.

## INTRODUCTION

The Rule 10 CFR Part 61, "Licensing Requirements for Land Disposal of Low-Level Radioactive Waste," promulgated by the U.S. Nuclear Regulatory Commission, requires either solidification or the use of a high integrity container for the disposal of Class B and C waste such as ion-exchange resins, filter sludges, and evaporator bottoms (1). An important factor in licensing low-level waste forms for disposal is the potential for release of immobilized radionuclides. Portland cement is by far the most common solidification agent employed by the industry. In order to evaluate the long-term performance of cementitious waste forms, it is important to determine their leaching behavior, the dominant processes controlling radionuclide release, and the geochemical factors that influence leaching under field conditions.

This study describes the leaching behavior of cesium-137 from two major LWR waste streams, that is, ion exchange bead resin and boric acid concentrate, solidified in Portland cement. The investigations include: (a) Scale-up Study-Simulated waste forms of varying volume-to-surface area ratios (V/S) were leached to evaluate the applicability of leach data based on small-scale specimens to predict radionuclide release from a full-scale specimen; (b) Simulated Versus Actual Reactor Waste Study - Radionuclide releases were compared for actual reactor waste forms and their simulants in order to test the validity of studying simulated specimens in laboratory experiments; and (c) Cyclic Leaching Study - Radionuclide releases from waste forms subjected to a range of wet-dry cyclic leaching conditions, simulating realistic field burial conditions, were evaluated.

## EXPERIMENTAL

### Scale-up Study

The test specimens selected for this study were right cylinders with nominal dimensions (diameter x height, cm) of 5 x 10, 15 x 15, and 55 x 55 for the cation-exchange bead resin waste. Corresponding volume-to-geometric surface area ratios (V/S) for these specimens were 0.94, 2.52, and 9.10 cm, respectively. Cation exchange resin/cement test specimens, loaded with Cs-137, were prepared with a waste-to-cement (Portland Type I) ratio of 0.6 and a water-to-cement ratio of 0.4 and cured for a period of 28 days. This formulation was chosen based on earlier process parameter investigations which had established stability regions in terms of the waste form components (resin, water, and cement) for obtaining a free-standing solid product (2). All test specimens were made in duplicate or triplicate except for the 55 x 55 size specimen which was not replicated.

Nominal dimensions of boric acid concentrate test specimens were 5 x 10 and 15 x 15 with corresponding V/S values of 0.94 and 2.52 cm, respectively. The boric acid concentrate (12.0 weight percent) was adjusted to pH 12, spiked with Cs-137, and heated to 77°C prior to solidification in Portland Type III cement. The ratio of waste-to-cement was 0.7.

The test specimens were leached in deionized water using a quasi-static IAEA method (3). However, this method was modified in our laboratory so that the entire surface of the specimen was in contact with the leachant. Initially, the leachant was replaced at daily intervals for the first six weeks, at weekly intervals for the next six weeks, and finally at monthly intervals. The leachant volume, v, was determined by the relationship v/S = 10 cm, where S represents the geometric surface area of the test specimen. All leaching tests were conducted at ambient laboratory temperature (25 ± 5°C).

### Simulated Versus Actual Reactor Waste Study

A boric acid waste concentrate sample from a PWR and a cation-exchange bead resin waste sample from a BWR, both classified as Class A waste on the basis of their radionuclide concentrations, were employed in this study. Five 5 x 10 size waste forms were cast for the two waste types and allowed to cure. Both the PWR boric acid concentrate and the BWR bead resin wastes were solidified in the manner described above for simulated waste forms in the Scale-up study. Except for approximately 60-day curing required for the solidification of reactor boric acid concentrate compared with ≈ 28-day curing for simulated waste, attributed to the presence of inorganic and organic retardants in the former, the waste forms appeared generally similar to those cast from simulated wastes. The V/S values for the two reactor wastes ranged from 0.91 to 0.94 cm. The leaching conditions were identical to those used in the Scale-up study.

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## Cyclic Leaching Study

The waste forms for these tests were right cylinders of 5 x 10 size and contained cation exchange bead resin (IRN-77), loaded with Cs-137, solidified in Portland Type I cement. Following a 28-day cure period, the test specimen was placed in a porous medium contained in a column and leached with deionized water (Figure 1). High density polyethylene beads (≈2 mm in diameter) were selected as the porous medium on the basis of their inert character. The leachant volume for each immersion cycle was again determined by the relationship v/S = 10 cm.

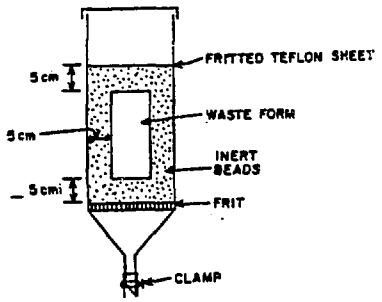


FIGURE 1: SCHEMATIC OF A LEACHING COLUMN USED IN THE CYCLIC LEACHING STUDY

On the basis of the duration of wet and dry periods, two types of wet-dry cycle were selected. For the "constant immersion period experiments," one day of wetting was followed by one, four, six, and 20 days of dry periods corresponding to Experiment Codes B, L, M, and N. A dry period of one day followed by three and six days of wetting, corresponding to experiment Codes C and S, was employed for the "constant dry period experiments." It is important to note that dry periods observed in these experiments do not suggest that the waste form is indeed dry. In actuality, the waste form retains sufficient moisture from the preceding rinse cycle to remain wet. Wet and dry periods in a leaching cycle simply correspond to unsaturated and saturated conditions in the porous medium surrounding the test specimen.

## Leachate Analysis

All acidified leachate aliquots were counted until a minimum of 1,000 counts was accumulated in the "window" set around the Cs-137 photopeak (661.6 keV). Leachate aliquots from some daily, weekly, and monthly renewal periods were composited prior to analysis. Incremental and cumulative fractional releases were calculated using appropriate decay corrections.

## Data Analysis

Incremental fractional release (IFR) and cumulative fractional release (CFR) of a radionuclide from a test specimen are expressed as:

$$IFR = a_n/A_o \qquad (1)$$

$$CFR = \Sigma a_n/A_o \qquad (2)$$

where $a_n$ is the amount of tracer leached from the specimen in the incremental leach time, $A_o$ is the amount of tracer present initially in the specimen, and $\Sigma a_n/A_o$ is the cumulative fraction of tracer leached in the cumulative leach time. The average CFR values were normalized for V/S variation in the test specimens. An initial check as to whether the release is diffusion controlled was made on the basis of plots of CFR versus square root of total immersion time yielding a linear relationship. Effective diffusivity ($D_e$) and incremental leach rates ($R_n$) were calculated from the CFR or IFR data by employing the plane sheet semi-infinite solution of the mass transport equation (4).

# RESULTS AND DISCUSSION

## Scale-up Study

The dominant features that characterize the cesium release behavior from both the boric acid and resin bead waste/cement test specimens are the initial surface-controlled rapid release, followed by release at a lower rate dominated primarily by diffusion. The diffusion-controlled release can be further divided into regions, represented by inflection points on the release curve reflecting the effects of the build up of dissolution products on cesium release kinetics. Suppressed release rates as the leachant renewal frequency is changed from daily to weekly to monthly are attributed to concentration effects in the leachant with respect to cesium (4).

The CFR data for the 5 x 10 size test specimens were employed to determine effective diffusivity values on the basis of the relationship:

$$CFR = 2(S/V)\ (D_e/\pi)^{1/2}(\Sigma t_n)^{1/2} + \alpha \qquad (3)$$

where $D_e$ ($cm^2/s$) is the effective diffusivity; $\alpha$ (cm) is the intercept on the CFR-axis, representing rapid surface-controlled release; and $\Sigma t_n$ is the cumulative leaching time.

Since we are only interested in the dominant rate-controlling mechanism by which cesium is released from the test specimen, we disregarded the initial rapid release ($\alpha$) which gives transient high release rates and is not representative of long-term release from the bulk matrix and selected the release data based on the daily sampling schedule. The concentration effects for this leaching schedule are assumed to be negligible. The cesium release during this time interval may be interpreted to represent conservative cesium release behavior and used for calculating effective diffusivities and predicting cumulative fractional releases in a given time period.

Based on the 5 x 10 size test specimens leach data, effective diffusivities of $1.9 \times 10^{-8}$ and $1.6 \times 10^{-8}$ $cm^2/s$ were calculated for Cs-137 in boric acid and resin waste/cement matrices, respectively. Using these $D_e$ values in Eq. (3), we estimated the CFR from 15 x 15 and 55 x 55 size specimens for two cumulative leach periods. A comparison of the measured and predicted cesium release values for both

the bead resin and boric acid waste specimens is presented in Table 1. For the boric acid waste, the estimated CFR for the 15 x 15 size specimen based on small size test specimen is in good agreement with the measured CFR values. No data are available for large boric acid waste specimens. However, for the bead resin waste specimen, the measured cumulative fractional release values are generally higher than the corresponding estimated values. This is also reflected in the higher diffusivity values for large size specimens calculated on the basis of observed cumulative fractional release. Considering that other intrinsic and extrinsic factors can contribute to even greater uncertainty in CFR values, we believe that laboratory time scale leach data derived from testing of small-scale specimens can be extrapolated on the basis of V/S as a scaling parameter to estimate release from a full-scale specimen. In addition, the overall difference in the calculated diffusivity values for the test specimens ranging in size from 5 x 10 to 55 x 55 do not vary by more than a factor of two, suggesting that small-scale specimen leach data can also be employed to estimate release from full-scale specimens over long time periods.

TABLE 1: MEASURED AND PREDICTED CUMULATIVE FRACTIONAL RELEASE OF Cs-137 FROM LARGE SPECIMENS OF RESIN AND BORIC ACID WASTE

| Nominal Size (cm x cm) | V/S (cm) | Cumulative Leach Time (Days) | Cumulative Fractional Release[a] Measured | Predicted |
|---|---|---|---|---|
| Bead Resin Waste | | | | |
| 15 x 15 | 2.52 | 22 | 0.11 | 0.08 |
| | | 120 | 0.22 | 0.19 |
| 55 x 55 | 9.10 | 39 | 0.04 | 0.03 |
| | | 119 | b | 0.05 |
| Boric Acid Waste | | | | |
| 15 x 15 | 2.52 | 39 | 0.15 | 0.14 |
| | | 150 | 0.25 | 0.25 |
| 55 x 55 | 9.10 | 39 | b | 0.03 |
| | | 150 | b | 0.06 |

[a]Measured and estimated cumulative release include initial release.
[b]Not determined.

## Simulated Versus Actual Reactor Waste Study

The CFR versus leaching time plots for Cs-137 for the PWR boric acid and the BWR resin bead test specimens are shown in Figures 2 and 3. Also depicted in these figures are the CFR data for simulated boric acid and resin bead specimens of similar dimensions and solidified under identical conditions. In order to determine whether diffusion was also the dominant rate-controlling mechanism by which Cs is released from reactor waste specimens, we plotted CFR vs $t^{1/2}$ data for these specimens. A linear relationship between the two variables indicated that diffusion is indeed the principal mechanism of Cs-137 release from reactor waste specimens. Disregarding leach data representing the initial, surface-controlled release, effective diffusivity values of Cs-137 were calculated for both the PWR boric acid and BWR resin waste specimens and their simulants (Table 2).

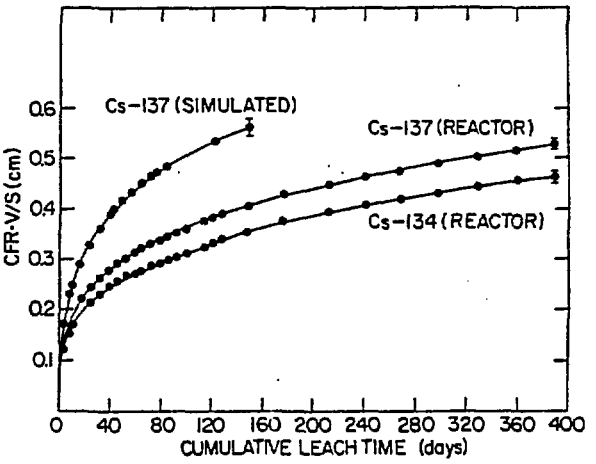


FIGURE 2: NORMALIZED CUMULATIVE FRACTIONAL RELEASE OF Cs ISOTOPES FROM BOTH REACTOR AND SIMULATED BORIC ACID WASTE SPECIMENS

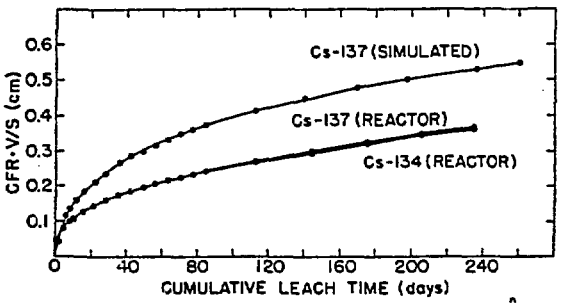


FIGURE 3: NORMALIZED CUMULATIVE FRACTIONAL RELEASE OF Cs ISOTOPES FROM BOTH REACTOR AND SIMULATED RESIN WASTE SPECIMENS

A comparison of Cs-137 release behavior of the two reactor waste types and their simulated counterparts indicates that the calculated diffusivity values vary by a factor of approximately three, with lower values observed for the reactor specimens in both cases. Inspite of the possibility of large variations in the reactor waste streams employed in this study, it is important to note that a general correspondence exists between the leaching behavior of the two sets of specimens in terms of cesium release. As discussed above, the $D_e$ values based on small-scale specimen leach data can be employed to extrapolate the release of Cs from full-size specimens and over long time periods. Since the

magnitude of variability in $D_e$ values for reactor and simulated test specimens is rather small, it is reasonable to assume that Cs-137 leach data derived from testing of simulated waste specimens can be employed to evaluate and predict the release behavior of reactor wastes, provided the specimens are prepared and leached under identical conditions.

TABLE 2: EFFECTIVE DIFFUSIVITY OF Cs-137 FOR BOTH REACTOR AND SIMULATED WASTE SPECIMENS

| Waste Type | Effective Diffusivity[a] ($D_e$, $cm^2/s$) |
|---|---|
| Reactor Boric Acid Waste | $0.7 \times 10^{-8}$ |
| Simulated Boric Acid Waste | $1.9 \times 10^{-8}$ |
| Reactor Resin Bead Waste | $0.5 \times 10^{-8}$ |
| Simulated Resin Bead Waste | $1.6 \times 10^{-8}$ |

[a]Calculated on the basis of semi-infinite diffusion model from CFR values based on the daily leachant replenishment schedule (5).

## Cyclic Leaching Study

Constant Immersion Period Experiments. In a preliminary analysis of leach data for wet-dry cycle experiments (6), we reported that Cs release when considered as a function of actual immersion time (total length of the wet periods of wet/dry cycles) remained relatively constant, irrespective of the varying lengths of dry periods in a cycle. Additional experiments were initiated with longer dry periods of up to 3 weeks to establish the effect of extended dry periods on the overall release of radionuclides.

The leach rates observed for cesium in a given total immersion period are greater than those based on the IAEA test. Furthermore, there is a distinct trend of increasing Cs release with increasing length of dry period in a cycle. As an example, Figure 4 shows the observed enhancement in the leach rates of Cs-137 for total immersion periods of 20, 30, and 35 days as a function of increasing length of dry period in a cycle. The leaching modes B, L, M, and N represent dry periods of 1, 4, 6, and 20 days, respectively, followed by a constant one-day wet period.

It seems that during the dry period of the leach cycle the specimen leached surface is replenished with cesium, diffusing from the relatively enriched sub-surface zones, and subsequently released during the next rinse cycle. Such a mechanism for Cs mobilization and transport in the saturated waste from during the dry period would explain the observed enhancement in Cs release with increasing length of dry period. Additional experiments are underway to further evaluate the significance of this process on the overall release of radionuclides.

Constant Dry Period Experiments. In contrast to the release behavior of Cs under constant immersion period experiments deacribed above, we observe a consistently lower release of the radionuclide as the length of leachant residence time increases. Considering the cyclic leaching data for variable wet periods (3- and 6-day wet periods in experiments C and S) along with the quasi-static and static leach data reported elsewhere (7), we present cesium leach rate data as a function of leaching mode representing increasing leachant residence time for 25-, 30-, 35-, 40-, and 45-day immersion periods (Figure 5). These data show clearly a lower radionuclide release with increasing leachant contact time, attributed to a saturation effect resulting from build up of dissolution products due to decreasing frequency of leachate sampling or leachant renewal.

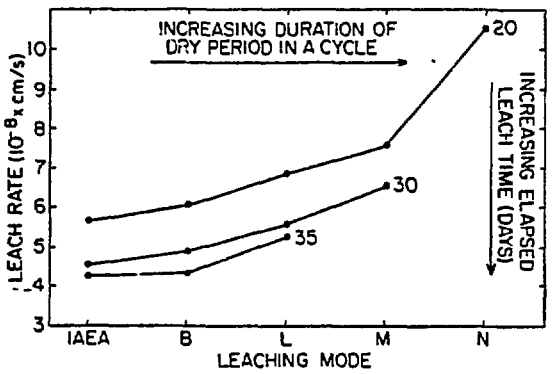


FIGURE 4: Cs-137 LEACH RATES AS A FUNCTION OF LEACHING MODE REPRESENTING INCREASING LENGTH OF DRY PERIOD IN A CYCLE

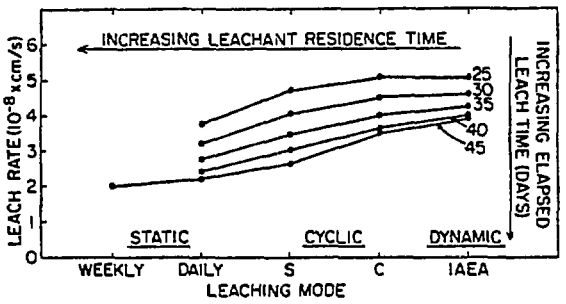


FIGURE 5: Cs-137 LEACH RATES AS A FUNCTION OF LEACHING MODE REPRESENTING INCREASING LEACHANT RESIDENCE TIME

Overall, the leach rate-limiting conditions of the IAEA leaching test reflect conservative estimates of Cs-137 release for short dry-period and longer wet-period experiments. In contrast, for extended dry period experiments, enhanced cesium release is observed relative to that based on IAEA test, representing continuously saturated conditions.

These results indicate that radionuclide releases observed in the laboratory under continuously saturated leaching conditions as represented by conventional leaching tests can be significantly different from that observed under anticipated field

conditions. At least for Cs, we know that extended dry periods, following an initial wetting period, can bring about a significant increase in the overall release. On the other hand, solubility-limiting leaching conditions such as "the bathtub effect" encountered at Maxey Flats and West Valley shallow land burial sites tend to suppress radionuclide release, resulting in lower net releases compared to those based on the IAEA test.

## SUMMARY AND CONCLUSIONS

The results of a scale up study involving test specimens consisting of simulated ion exchange resin and boric acid concentrate waste solidified in Portland type cements show that cesium release can be represented by a diffusional mass transport relationship based on a semi-infinite plane sheet diffusion model. Knowing the calculated diffusivity for cesium based on small-scale specimen leach data and using the volume-to-surface area ratio (V/S) as a scaling parameter, it was possible to estimate cesium release from large specimens. Comparison of predicted and observed cesium releases shows reasonable agreement.

A comparison of Cs-137 release behavior of actual reactor bead resin and boric acid concentrate wastes solidified in Portland cement and their simulants shows considerable similarity in terms of the principal rate-controlling release mechanisms, with diffusion being the dominant process. Considering a relatively small variability in the effective diffusivity values of Cs in the two sets of specimens, it can be concluded that leach data based on testing of simulated test specimens can be employed to evaluate and predict the release behavior of cesium from actual reactor ion exchange resin and boric acid concentrate wastes.

The results of the cyclic leaching study indicate that, for a constant wet period and extended dry periods, the leach rates observed for cesium in a given total immersion time are far greater than those based on conventional laboratory tests such as the IAEA test, which represents continuously saturated leaching conditions. The observed enhancement in cesium release with increasing length of dry period is believed to be a result of replenishment of the leached specimen surface with cesium, migrating from the sub-surface zones, during dry periods of a leaching cycle. In contrast to the release behavior of Cs under extended dry periods in a leaching cycle, consistently lower releases are observed with increasing length of wet periods in a leaching cycle. Suppressed radionuclide release with increasing leachant residence time is attributed to a saturation effect which is a result of decreasing frequency of leachate sampling or leachant renewal.

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