CONF-8509121 -- 17

RECEIVED BY OSTI OCT 28 1985

BNL-NUREG--37071

BNL-NUREG-37071

TI86 001738

LEACHING STUDIES OF LOW-LEVEL RADIOACTIVE WASTE FORMS*

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ABSTRACT

A research program has been under way at the Brookhaven National Laboratory to investigate the radionuclide release behavior of ion exchange bead resin waste solidified in Portland cement. An important aspect of this program is to develop and evaluate testing procedures and methodologies which enable the long-term performance evaluation of waste forms under simulated field conditions.

Cesium and strontium release behavior using a range of testing procedures, including intermittent leachant flow conditions, has been investigated. For cyclic wet/dry leaching tests, extended dry periods tend to enhance the release of Cs and suppress the release of Sr. Under extended wet period leaching conditions, however, both Cs and Sr exhibit suppressed releases. In contrast, radionuclide releases observed under continuously saturated leaching conditions, as represented by conventional leaching tests, are significantly different. The relevance and applicability of these laboratory data obtained under a wide range of leaching conditions to the performance evaluation of waste forms under anticipated field conditions is discussed.

INTRODUCTION

The Rule 10 CFR Part 61 promulgated by the U. S. Nuclear Regulatory Commission requires either solidification or the use of high integrity containers for the disposal of several classes of low-level radioactive waste. Primary concerns in licensing radioactive waste forms and containers are their dimensional stability and the potential for release of the immobilized radionuclides.

Primary emphasis for evaluating the release of immobilized radionuclides from solidified wastes has been placed on the establishment of uniform leaching test conditions (American Nuclear Society, 1984; Hespe,

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

1971). These tests simulate leaching conditions representing a flooded or a temporally saturated burial environment. Leaching procedures outlined in these conventional tests are primarily designed to permit inter-laboratory comparisons for evaluation of waste form products rather than the simulation of disposal environments encountered at burial sites.

Accordingly, experiments were initiated at the Brookhaven National Laboratory to study the leaching behavior of cement/resin waste forms under a range of burial environments simulating intermittent leachant flow conditions. In earlier reports, Dayal et al. (1985, 1984) presented cesium and strontium release data based on wet/dry cyclic leaching conditions. In this report, e provide experimental details, current status of ongoing experiments,and the Cs-137 and Sr-85 release data showing the effects of variable wet and dry leaching periods on the overall release of radionuclides.

EXPERIMENTAL

Preparation of Waste Forms

The test specimens selected for this study were right cylinders with nominal dimensions of 5 x 10 (diameter x height, cm). The simulated waste consisted of Na-saturated organic cation exchange bead resin (Rohm and Haas, IRN-77) spiked with Cs-137 and Sr-85 such that each specimen contained approximately 100 and 200 microcuries, respectively, of these radionuclides. For solidification, a slurry of the constituents was prepared in a batch mode with a waste-to-cement (Portland Type I) ratio of 0.6 and a water-to-cement ratio of 0.4. The slurry was poured into individual molds which were capped and cured for a period of 28 days in the laboratory. This formulation was chosen based on earlier process parameter investigations which had established stability regions in terms of waste form components (bead resin, water, and cement) for obtaining a free-standing solid product of sufficient compressive strength (Manaktala and Weiss, 1980). Salient characteristics of the waste forms employed in these experiments are presented in Table 1. More detailed information on the preparation of test specimens is available elsewhere (Dayal et al., 1983).

Leaching Column Configuration and Characteristics

The leaching apparatus basically represents a flow through system in which a test specimen is placed in a porous medium contained in a polyethylene tube fitted with flat rigid filter supports at the top and bottom (Figure 1). The funnel-shaped bottom of the leaching column is equipped with a clamp, which allows the leachant flow to be regulated in a cyclic mode. No provision was made to exclude atmospheric CO_2 or oxygen from the system. The cylindrical test specimen was placed axially in the leaching column and surrounded on all sides by a 5-cm thick layer of porous packing material consisting of inert high density polyethylene (HDPE) beads obtained from Dow Chemical Company. On the basis of preliminary sorption tests, the HDPE beads were found to be relatively inert with respect to Cs-137, Co-60, and Sr-85. Water retention tests showed that relative to the total void space of the bead column, a very small fraction of water (<5%) resides in the column upon draining under gravity. This indicates that the bead column remains practically unsaturated during the dry period, following an immersion cycle. The combination of both low water retention capacity and the lack of reactivity with radionuclides was the deciding factor in favor of using HDPE beads as the porous medium. A summary of the leaching column characteristics, without the waste form, is given in Table 2.

TABLE 1. CHARACTERISTICS OF TEST SPECIMENS EMPLOYED IN COLUMN LEACHING EXPERIMENTS

Parameter	Value for Experiment Code N[a]	Range for all Waste Forms Used
Weight (upon 28-day curing), g	287	284-396
Weight upon saturation, g	293	b
Oven dry weight, g	233	b
Moisture content at saturation, %	26	b
Estimated amount of cement in waste form, g	181	181-250
Estimated amount of bead resin in waste form, g	36	36-50
Diameter, cm	4.7	4.7-5.2
Height, cm	9.4	9.2-10.4
Volume (V), cm^3	163	160-221
Surface area (S), cm^2	173	172-212
V/S, cm	0.94	0.93-1.04
Bulk density, g/cm^3	1.8	1.8
Estimated porosity, %	26[c]	b

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[a] Average for two waste forms used in Experiment N.
[b] Not determined.
[c] Based on water content upon saturation.

Leaching Conditions

Basically three types of leaching tests were considered: (a) cyclic wet/dry leaching; (b) modified IAEA leaching representing continuously saturated conditions with periodic leachant replenishment; and (c) solubility-limiting leaching representing no leachant replenishment. Deionized water was employed as a leachant in all experiments described in this report. The leachant volume during each replenishment or immersion period was based on the relationship v/S = 10 cm, where v represents the leachant volume, and S is the geometric surface area of the test specimen. Thus for a typical 5 x 10 size specimen, with a surface area of 180 cm^2, the leachant volume employed was 1800 mL. All experiments were conducted in duplicate or triplicate at ambient room temperature.

Information on various leaching modes used in the cyclic wet/dry leaching experiments is given in Table 3. After a predetermined dry period, the column was refilled with fresh leachant totally immersing the specimen for the duration of the wet cycle. In most experiments (B, L, M, and N), the immersion time (t_w) was kept constant at one day, while the dry period (t_d) was varied from one to twenty days, referred to as variable dry period experiments. In experiments C and S, however, the dry period of one day was kept constant while the length of wet period was varied from three to six days, referred to as variable wet period experiments.

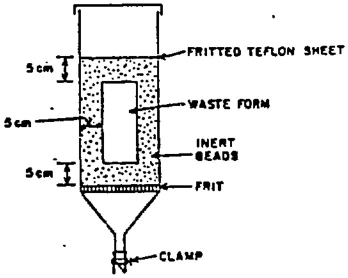

Figure 1. Schematic of a column leaching apparatus employed for leaching under intermittent leachant flow conditions.

TABLE 2. LEACHING COLUMN CHARACTERISTICS[a]

Parameter	Value
Dimensions (diameter x height), cm	15 x 20
Volume (nominal), cm^3	3530
Air dry wt. of beads in column, g	≈2140
Saturated wt. of beads (dewatered), g	≈2240
Moisture retention capacity, %	4.5
Hydraulic conductivity, cm/s	1.2×10^{-1}
Bulk density (D_b), g/cm^3	0.61
Particle density, D_p	0.96
Packing density or fraction, (D_b/D_p), %	63
Porosity, %	37

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[a] Waste form not included.

It is important to note that during the dry periods observed in these experiments the waste form is not necessarily dry, free of water. In actuality, the waste form retains sufficient moisture from the preceeding wet cycle to remain largely saturated during the experimental dry period. Flow rates corresponding to wet/dry leaching conditions calculated on the basis of leachant volume in contact with the waste form over the duration of the wet/dry cycle vary from 0.62 mL/min for Experiment Code B to 0.06 mL/min for Experiment Code N. More detailed description of these experiments is given elsewhere (Morcos and Dayal, 1982).

TABLE 3. WET/DRY CYCLIC LEACHING CONDITIONS

Experiment Code	Wet Period (t_w, days)	Dry Period (t_d, days)	Cycle Length ($t_w + t_d$, days)	Number of Cycles
<u>Variable Dry Period Experiments</u>				
B	1	1	2	85
L	1	4	5	39
M	1	6	7	28
N	1	20	21	21
<u>Variable Wet Period Experiments</u>				
C	3	1	4	46
S	6	1	7	13

For the modified IAEA leaching, the method described by Hespe (1971) was modified in our laboratory so that the entire surface of the specimen was in contact with the leachant (Arora and Dayal, 1984a; Dayal et al., 1983). The leachant was replaced periodically, simulating a flowing system with a variable flow rate resulting from changing frequency of leachant renewal with time. Following the first leaching period of 100 minutes, the leachant was renewed daily, except weekends, for the first six weeks. Subsequently, the daily leachant renewal frequency was changed to weekly for the next six weeks, and finally, to monthly until the experiments were terminated. During the immersion period, the v/S ratio was kept constant at 10 cm. The daily leachant renewal frequency corresponds to an equivalent flow rate of 1.25 mL/min. Reference flow rates suggested for MCC-4 leach test employed for simulating high level waste repository conditions are 0.1, 0.01, and 0.001 mL/min (Materials Characterization Center, 1981).

Static tests were conducted to simulate solubility-limiting conditions in which the leachant was not renewed. A 100 mL aliquot of the leachate was sampled periodically, analyzed, and subsequently returned to the leaching vessel so that the v/S ratio was kept constant at 10 cm (Dayal et al., 1985). More details on leaching methodology and counting procedures were described in previous reports issued in this program (Arora and Dayal, 1984b; Dayal et al., 1983).

Based on leachate analysis, incremental releases of Cs-137 and Sr-85 were measured at the end of each wet cycle in the cyclic leaching experiments. In the modified IAEA and static leaching tests, radionuclides were measured in solution at the end of each immersion or sampling period. Normalized to the initial activity of each radionuclide present in the test specimen, the leaching data were reduced in the form of incremental fractional release (IFR) and cumulative fractional release (CFR) of a radionuclide expressed as

$$IFR = a_n/A_0 \qquad (1)$$

$$CFR = \Sigma a_n/A_0 \qquad (2)$$

where a_n is the amount of tracer leached from the test specimen in incremental leaching time, A_0 is the amount of tracer present initially in the specimen, and Σa_n is the cumulative amount of tracer leached out of the test specimen in cumulative leaching time.

RESULTS AND DISCUSSION

The CFR data for Cs-137 and Sr-85 (normalized for V/S variations in test specimens) vs total elapsed leaching time for the various wet/dry cyclic leaching conditions were presented in previous reports (Dayal and Arora, 1985; Arora and Dayal, 1984a). For both radionuclides, it was observed that the modified IAEA leaching data represent conservative estimates of the releases observed under wet/dry cyclic conditions. This is to be expected considering that IAEA leaching data represent releases measured on a daily basis during the daily leachant renewal frequency period, while in the wet/dry cyclic experiments no releases are measured during the dry periods. In other words, for a given elapsed experimental time of say, 30 days, there are thirty data points for the IAEA test as opposed to 15 data points for the cyclic Experiment B (one-day wet/one-day dry) and only 6 data points for Experiment L (one-day wet/four-day dry). Therefore, for a valid comparison of the observed releases under the range of leaching conditions employed in this study, only the actual immersion periods must be considered. Accordingly, we calculated incremental leach rates for both Cs-137 and Sr-85 based on IFR data and the actual immersion periods using the relationship (Ogard and Bryant, 1982)

$$R_n = \frac{a_n}{A_0} \bigg/ (S/V)(t_n - t_{n-1}) \qquad (3)$$

where

R_n = leach rate (cm/s)
S = exposed surface area of specimen (cm^2)
V = volume of specimen (cm^3)
t_n = cumulative leachant renewal period (s), and
$t_n - t_{n-1}$ = duration of leachant renewal period (s)

The elevated releases observed during the initial immersion periods, attributed to a "washing-off" effect from surface related processes, were disregarded because they give transient high leach rates and are not representative of the bulk matrix leaching characteristics (Dayal et al., 1983).

Cs-137 Release Behavior

Variable Dry Period Experiments

In a preliminary analysis of leaching data for wet/dry cycle experiments (Dayal et al., 1984), 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. However, on the basis of additional experimental data with longer dry periods of up to 3 weeks we observed that the leach rates for cesium in a given total immersion period are greater than those based on the IAEA test. Furthermore, there is a distinct trend of progressive increase in Cs release with increasing length of dry period in a cycle. As an example, Figure 2 shows the observed enhancement in leach rates of Cs-137 for one-day immersion period measured at 20-, 30-, and 35-day leaching times as a function of increasing length of dry period in a cycle.

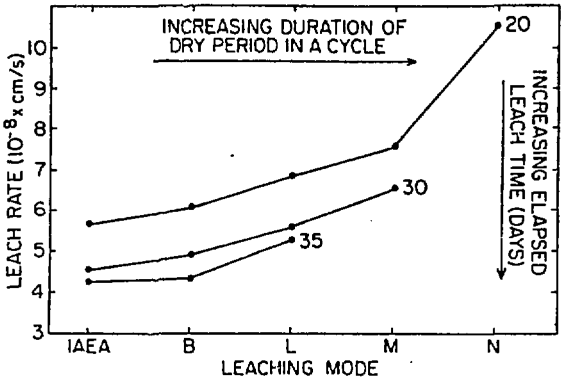

Figure 2. Cs-137 leach rates as a function of leaching mode representing increasing length of dry period in a cycle. The leach rates are given for 20-, 30-, and 35-day leaching periods.

It seems that during the dry period of the leaching cycle the specimen leached surface is replenished with cesium derived from the relatively enriched sub-surface zones, and subsequently released during the next rinse cycle. As discussed in earlier reports (Dayal and Arora, 1985; Dayal et al., 1984), such a mechanism for Cs mobilization and transport in the waste form during the dry period would explain the observed enhancement in Cs release with increasing duration of dry period.

Variable Wet Period Experiments

In contrast to the release behavior of Cs under variable dry period experiments described above, we observe a consistently lower release as the length of leachant residence time increases. This is evident from the leach rates based on IAEA and static tests which show a distinct trend of lower leach rates with decreasing leachant renewal or leachate sampling frequency, with the leach rates based on static test being consistently lower than those based on the IAEA test (Figure 3).

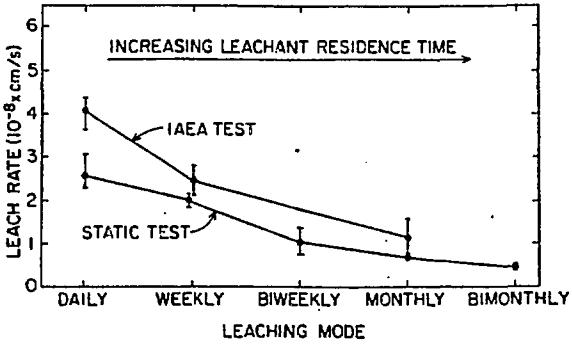

Figure 3. Cs-137 leach rates as a function of leachant renewal and leachate sampling frequency in IAEA and static tests.

Leach rate data for variable wet periods (3- and 6-day wet periods in experiments C and S), along with the modified IAEA and static leaching data reported previously (Dayal et al., 1983), are presented in Figure 4. These data show clearly suppressed radionuclide release with increasing leachant residence time, attributed to saturation effect resulting from build up of dissolution products due to decreasing frequency of leachate sampling or leachant renewal.

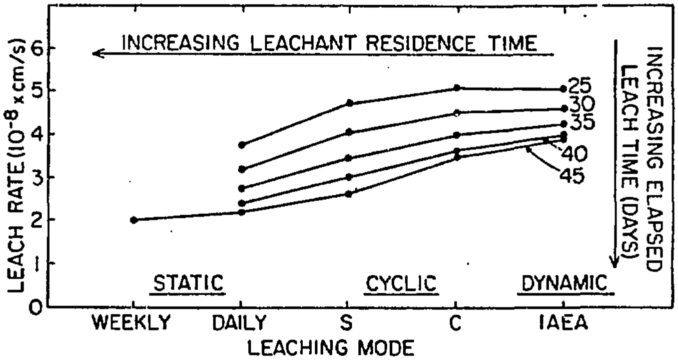

Figure 4. Cs-137 leach rates as a function of leaching mode representing increasing leachant residence time. The leach rates are given for 25-, 30-, 35-, 40-, and 45-day leaching periods.

Sr-85 Release Behavior

Variable Dry Period Experiments

The overall release of strontium is significantly lower than that of

Cs. Furthermore, a systematic decrease in the release rate of Sr is observed with increasing length of dry period in a leaching cycle (Figure 5). Decreasing rates of Sr release with increasing length of dry periods is believed to be a result of different degrees of curing (length of dry periods) of the cementitious matrix incorporating strontium. The longer the duration of dry period in a cycle, the greater is the curing time. For example, minimal Sr release is observed in the six-day dry cycle experiment M in which the curing time corresponds to ≈160 days in an experimental elapsed leach time of ≈190 days. In comparison, significantly higher release of Sr is observed in the one-day dry cycle experiment B in which the curing time for experimental elapsed leach time of ≈190 days corresponds to 95 days. Therefore, it appears that the observed dependence of decreasing Sr release with increasing length of the dry cycle can be attributed to increased curing of the test specimen during dry periods of the experiments. Accordingly, strontium releases observed under conventional IAEA test conditions with no curing represent conservative estimates of releases anticipated under unsaturated field leaching conditions. Further interpretation of Sr release data is presented in previous reports (Dayal and Arora, 1985; Dayal et al., 1984).

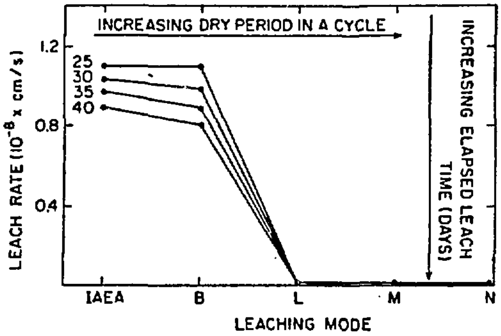

Figure 5. Sr-85 leach rates as a function of leaching mode representing increasing length of dry period in a leaching cycle. The leach rates are presented for 25-, 30-, 35-, and 40-day leaching periods.

Variable Wet Period Experiments

The effect of saturation on the overall release of Sr-85 is also evident from Figure 6. Like cesium, strontium leach rates exhibit a steady decrease with decreasing frequency of leachant replenishment or leachate sampling in modified IAEA or static tests, respectively (Figure 6). This is believed to be a consequence of a buildup of dissolution products due to infrequent leachant renewal intervals or leachate sampling. As expected, the saturation effect is more pronounced under solubility-limiting leaching conditions.

Figure 7 presents Sr-85 leach rates based on static, modified IAEA, and cyclic Experiment C (one-day dry, followed by three-day wet) leaching modes, representing increasing leachant residence time for 25-, 30-, 35-, 40-, and 45-day immersion periods. Although the data show distinctly lower leach rates under static leaching as opposed to those observed under modified IAEA leaching conditions, the cyclic leaching data (leaching mode C) do not follow the trend expected based on a saturation effect alone. More data based on additional cyclic leaching mode are required to conclusively establish the effect of saturation on strontium release during extended wet periods of wet/dry cyclic leaching.

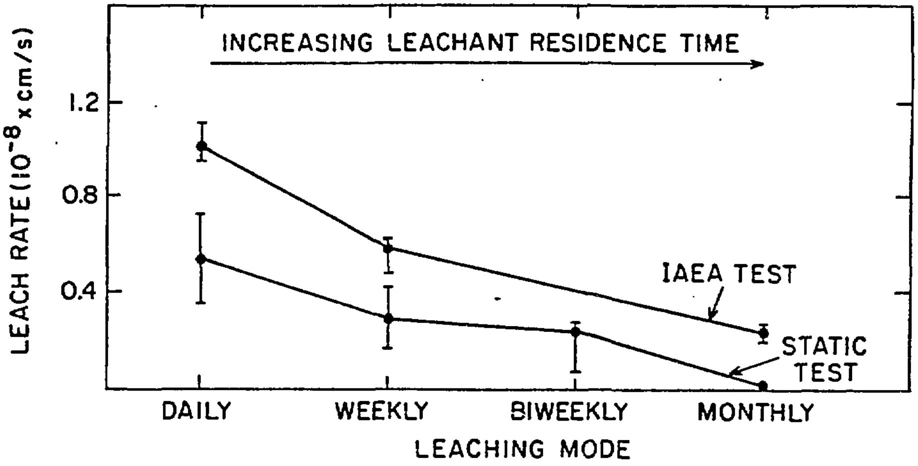

Figure 6. Sr-85 leach rates as a function of leachant renewal and leachate sampling frequency in modified IAEA and static tests.

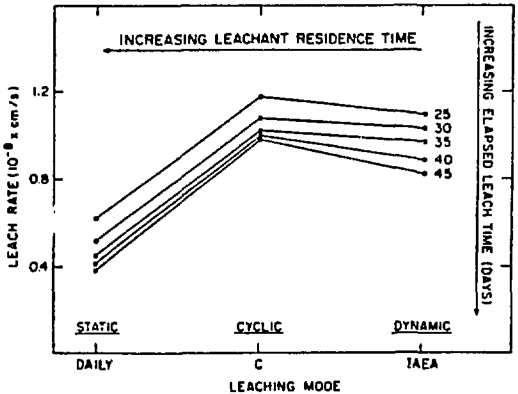

Figure 7. Sr-85 leach rates as a function of leaching mode representing increasing leachant residence time. The leach rates are given for 25-, 30-, 35-, 40-, and 45-day immersion periods.

Contrasting Release Behavior of Cs-137 and Sr-85

As displayed in a composite plot shown in Figure 8, the leach rate-limiting conditions represented by the conventional IAEA leaching test reflect conservative estimates of Cs-137 release for variable wet period experiments. For extended dry period experiments, however, enhanced cesium release is observed relative to that based on IAEA test, representing continuously saturated conditions. Fractional leachant contact time in Figure 8 represents the fraction of the time during which the specimens are actually contacted with the leachant in a given leaching cycle.

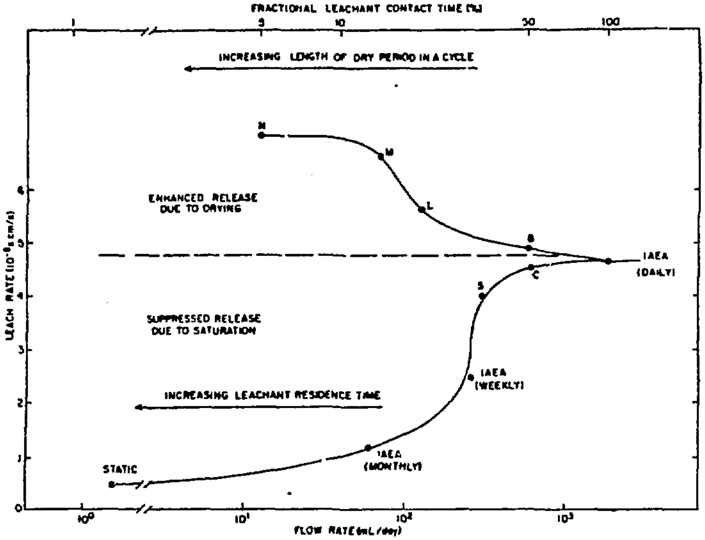

Figure 8. Cs-137 leach rates as a function of flow rate showing the effect of increasing leachant residence time (bottom curve); and as a function of fractional leachant contact time showing the effect of increasing dry periods in a leaching cycle (upper curve). The leach rate data are given for a 30-day immersion period.

In contrast, the effect of extended dry periods and variable wet periods on the overall release of Sr-85 is shown in Figure 9. Unlike the release behavior of Cs, strontium release is significantly lower and exhibits a systematic decrease with increasing length of the dry period in a leaching cycle.

As discussed in earlier reports (Dayal and Arora, 1985; Dayal et al., 1984), the observed differences in the release behavior of Cs and Sr can be attributed to different mechanisms by which these radionuclides are mobilized and transported from the bulk matrix into the leachant. In case of cesium, diffusion is the principal release mechanism. Ion-exchange of cesium from the bead resin and dissolution of cesium compounds are too rapid to be rate-controlling. Strontium, on the other hand, is incorporated into the cement matrix during curing of the waste form. Consequently, release of strontium involves matrix dissolution and subsequent diffusion of strontium into the leachant. Because of an additional rate-controlling, dissolution step, the observed release rate of strontium is lower than that of cesium.

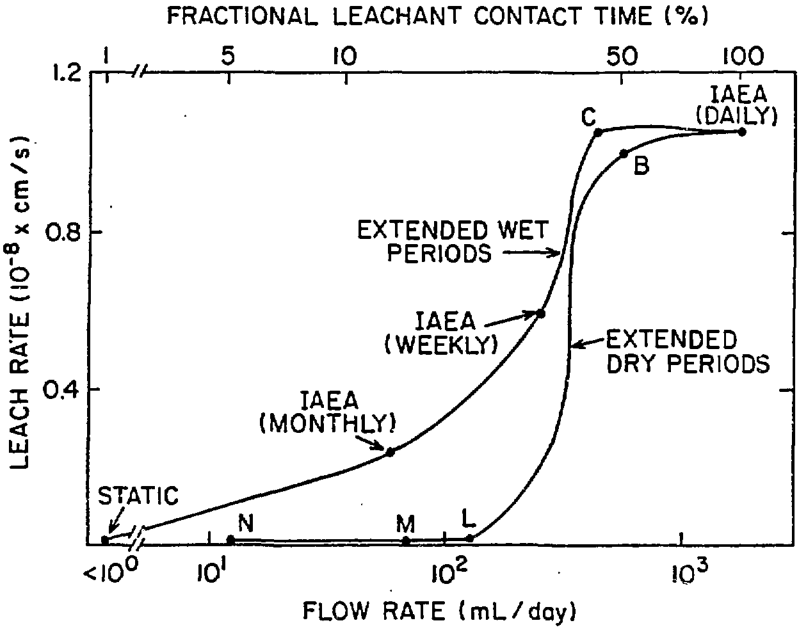

Figure 9. Sr-85 leach rates as a function of flow rate showing the effect of increasing leachant residence time (upper curve); and as a function of fractional leachant contact time showing the effect of increasing dry periods in a leaching cycle (bottom curve). The leach rates are given for a 25-day immersion period.

Practical implications of the results of this study are that radionuclide releases observed in the laboratory under continuously saturated leaching conditions as represented by conventional leaching tests can be significantly different from those observed under anticipated field conditions. In particular, extended dry periods tend to enhance the release of Cs and suppress the release of Sr. Under extended wet period leaching conditions, however, both Cs and Sr exhibit suppressed releases.

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