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TOPICAL REPORT

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ABSTRACT

Leach testing was conducted on two types of reactor wastes (resin beads from a BWR and boric acid concentrate from a PWR) solidified in cement. In these wastes, Cs-134,137 isotopes were the most mobile constituents followed by Sr-90. Co-60 was found to be the least mobile. Effective diffusivities of these radionuclides were $\sim 10^{-9}$ cm^2/s for Cs-isotopes, $\sim 10^{-11}$ cm^2/s for Sr-90, and $\sim 10^{-13}$ cm^2/s for Co-60.

A comparison of the release of Cs-137 from these wastes and the results of our previous study in which simulated counterparts of these reactor wastes were solidified and leached under identical conditions show a general correspondence in their release behavior. Radionuclide release data generated at EG and G, Idaho, in which test specimens from the same batch of the PWR boric acid waste were solidified in-plant employing a commercial proprietary process, exhibited significantly higher releases of Cs-137, Sr-90, and Co-60 (approximately two to four orders of magnitude difference in effective diffusivity values) in comparison to those observed at BNL. Greater radionuclide releases in the EG and G data set were attributed to higher waste-to-cement ratio and variance in the solidification agent used.

Leachability index (LI) values were calculated for determining regulatory compliance of waste forms. Both the BNL and EG and G release data meet the proposed NRC guidelines on leachability criteria ($LI \geq 6.0$). Also summarized are the limitations in the use of LI values for demonstrating regulatory compliance.

CONTENTS

FIGURES

TABLES

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EXECUTIVE SUMMARY

The present study was initiated to compare radionuclide leachability of reactor waste cement composites and their simulants. This study is part of a major ongoing study at the Brookhaven National Laboratory (BNL) to generate a data base which will assist the Nuclear Regulatory Commission in the development of test procedures and methodologies for the prediction and extrapolation of waste form leachability. Boric acid reactor waste from a PWR and ion-exchange resin waste from a BWR were solidified in Portland type cements to give 5-cm diameter x 10-cm height cylindrical composites. Radionuiclide release data obtained by EG and G, Idaho, in which test specimens from the same batch of PWR boric acid waste were solidified at the commercial power plant using a vendor supplied proprietary process are also compared.

Experimental results show that, except for a prolonged time period required for the curing of PWR boric acid composites (28 days for simulated versus approximately 80 days for reactor waste) attributable to the presence of retardants in reactor waste, solidification of reactor wastes is amenable to BNL developed formulations and procedures for at least resin bead- and boric acid-type LWR wastes.

Radionuclide release behavior was expressed as either incremental fractional release (IFR) or the cumulative fractional release (CFR). The Cs-134,137 isotopes were the most mobile constituents followed by Sr-90 in both the PWR boric acid and BWR resin waste composites. Co-60 was found to be the least mobile. Radionuclide release behavior is characterized by initially rapid release, presumably a surface-controlled phenomenon, followed by predominantly diffusion-controlled release at a lower rate. At longer immersion intervals, however, the influence of saturation effect resulting from an accumulation of leached by-products further depressed the radionuclide leach rates. The release behavior of the two cesium isotopes was similar. Effective diffusivity values of Cs-137 in the diffusion-controlled region were ~7 x 10^{-9} and ~5 x 10^{-9} cm^2/s for the PWR boric acid and BWR resin composites. For Sr-90 and Co-60, these values are two to four orders of magnitude lower than that for Cs-137, attributable to the effect of chemical interactions of these isotopes within the cement matrix. Radionuclide diffusivity data, in addition to determining regulatory compliance, are a prerequisite for predicting release from full-size waste forms on the basis of leach data from small-scale laboratory size specimens and for extrapolation to predict the long-term behavior.

A comparison of Cs-137 release behavior of the two reactor waste types and their simulants indicated lower release from reactor waste composites resulting in three to four-fold reduction in their effective diffusivity values. However, since the leach behavior of both the reactor wastes and their simulated counterparts exhibited considerable similarity, it appears reasonable to asssume that Cs-137 leach rate derived from testing of simulated waste composites can be employed to evaluate and predict the release behavior from reactor wastes, provided the specimens are prepared and leached under identical conditions.

The EG and G release data on waste forms solidified from the same batch of PWR boric acid waste exhibit significantly higher releases of Cs-137, Sr-90 and Co-60 (approximately two to four orders of magnitude difference in effective diffusivity values)in comparison with the release data observed at BNL. The results of two data sets are not directly comparable because of the higher waste-to-cement ratio employed in EG and G samples (0.7 for the BNL versus 1.0 for EG and G) and variance in the solidification agents used. A combination of these variables resulted in higher matrix porosity and consequently gave higher radionuclide releases for the EG and G composites.

In accordance with NRC Branch Technical Position recommendations on waste forms, Leachability index (LI) values were calculated from the effective diffusivity data on the basis of ANS 16.1 test procedure for determining regulatory compliance. Both the BNL and EG and G release data meet the proposed NRC guidelines on leachability criteria ($LI \geq 6.0$). The leachability index values for a given radionuclide were found to be sensitive to a number of factors such as leachant renewal frequency, solidification formulation, and leachant composition, as well as the methodology employed in the calculation of LI (such as the IFR or CFR data based or the semi-infinite vs finite source model for calculating effective diffusivity). However, the influence of these variables for regulatory compliance of the two reactor waste composites was found to be minimal.

1. INTRODUCTION

The disposal of low-level radioactive waste is governed by the regulations outlined in the recently enacted Rule 10CFR, Part 61, "Licensing Requirements for Land Disposal of Radioactive Wastes" (Code of Federal Regulations, 1983). The NRC Technical Position (TP) on Waste Form provides guidelines for compliance with these requirements (Higginbotham, 1983). Liquid wastes must be solidified while either solidification or the use of a high integrity container is specified for the disposal of Class B and C solid wastes. For solidification process control, the TP specifies minimal free liquid (<0.5%) and the waste composites to be monoliths of sufficient mechanical strength to provide necessary resistance to disintegration upon prolonged exposure to air or water.

Most waste solidification studies reported in the literature and at Brookhaven National Laboratory (BNL) have involved the use of simulants of waste streams generated in power plant operations. Results of these investigations have demonstrated that certain pretreatments for different types of wastes are required prior to solidification for obtaining a monolithic product of high integrity (Morcos et al., 1982; Manaktala and Weiss, 1980). Research conducted at BNL has established stability regions for the solidification of simulated ion exchange resin and boric acid-type wastes in terms of waste, water, and Portland cement.

Another important consideration for demonstrating waste form acceptability pertains to radionuclide leachability. Primary emphasis in leachability investigations reported in the literature has been devoted toward establishing uniform leach test conditions to provide intercomparison of the leachability of different waste forms (American Nuclear Society, 1984; Materials Characterization Center, 1981; International Standards Organization, 1979; Hespe, 1971). Mostly solidified simulated wastes were employed in these studies (Christensen, 1982; Moore et al., 1977). Research conducted recently at BNL and currently underway to develop a data base for predicting radionuclide releases in realistic disposal environments has also employed simulated waste forms (Dayal et al., 1983a; 1983b).

Croney (1984), Kalb and Colombo (1984), Neilson et al. (1983), Zange et al. (1983), and Celeri et al. (1982) recently provided information on the leachability of radionuclides present in actual reactor wastes. However, none of these studies have compared leach data based on actual reactor wastes with those derived from simulated wastes. Since leach testing of simulated wastes is a common practice in most laboratories, we undertook this study to compare the leach data generated from simulated and actual reactor waste composites in order to test the validity of studying simulants of actual reactor wastes.

The principle objective of the present study is to evaluate the cement solidification of reactor boric acid and resin wastes and to assess the leach behavior of radionuclides present in solidified wastes. The leach data are compared with the results of our previous study involving simulated wastes streams. In conjunction with the recently completed scale-up study (Dayal et al., 1983a), an additional objective of this investigation is to estimate radionuclide release from large waste forms on the basis of leach data obtained from small-scale laboratory specimens and to compare the estimated release with the EG and G generated experimental leach data on large waste forms containing the same batch of boric acid waste from a PWR (Croney, 1984).

2. EXPERIMENTAL

2.1 Sample Collection and Waste Composition

The boric acid waste concentrate sample from a PWR was collected by EG and G, Idaho Falls, Idaho on September 24, 1981 and forwarded to BNL. Sodium borate appeared to be the principle component of the waste concentrate with minor amounts of other constituents such as crud-oxidation products, dirt, etc., and is considered to be a typical sample of boric acid concentrate wastes. An insoluble precipitate of unknown chemical composition was observed on the bottom of the two sample containers obtained from EG and G. Data on the radionuclide content of the waste concentrate were provided by Croney (1984) and are presented in Table 2.1. On the basis of radionuclide concentration levels the PWR boric acid waste can be classified as Class A waste.

Table 2.1
Radionuclide Concentrations in LWR Reactor Wastes

Radionuclide	PWR Boric Acid Waste[a] (μCi/mL)	BWR Resin Waste[b] (μCi/g)
Cs-134	$2.0 (\pm 0.2) \times 10^{-3}$	$1.7 (\pm 0.2) \times 10^{-2}$
Cs-137	$7.3 (\pm 0.2) \times 10^{-3}$	$2.7 (\pm 0.1) \times 10^{-2}$
Cr-51	$7 (\pm 1) \times 10^{-3}$	ND
Mn-54	$5.2 (\pm 0.2) \times 10^{-3}$	$6.2 (\pm 0.4) \times 10^{-3}$
Fe-59	$1.5 (\pm 0.4) \times 10^{-3}$	ND
Co-58	$8.9 (\pm 0.1) \times 10^{-2}$	ND
Co-60	$1.0 (\pm 0.1) \times 10^{-1}$	$2.8 (\pm 0.1) \times 10^{-2}$
Zn-65	$1.4 (\pm 0.4) \times 10^{-3}$	ND
Ag-110	$6.1 (\pm 0.6) \times 10^{-3}$	ND
Sb-125	$6.8 (\pm 0.4) \times 10^{-3}$	ND
H-3	$2.0 (\pm 0.01) \times 10^{-2}$	ND
Fe-55	$1.0 (\pm 0.2) \times 10^{-1}$	ND
Ni-63	$7.1 (\pm 0.4) \times 10^{-3}$	ND
Sr-89	$6.8 (\pm 0.8) \times 10^{-6}$	NA
Sr-90	$1.5 (\pm 0.2) \times 10^{-6}$	$1.1 (\pm 0.1) \times 10^{-4}$[c]

[a]Source: Croney (1984)
[b]BNL data (see text).
[c]EAL Corp. (see text).
ND = Not detected.
NA = Not analyzed.

An ion-exchange resin waste sample from a BWR was also collected and provided to BNL under a similar arrangement. The radionuclide concentrations determined at BNL by column extraction of the beads with aqua regia are also presented in Table 2.1. The BWR resin waste can also be classified as Class A waste on the basis of its activity levels.

2.2 Waste Solidification

2.2.1 PWR Boric Acid Waste

Prior to solidification, the settled precipitate in the waste sample was brought into suspension by thorough mixing. The pH of the waste solution was then raised to 12.0 from 7.3 by addition of sodium hydroxide. Next, the waste was heated to 70°C and mixed with Portland Type III cement in a waste-to-cement ratio of 0.7:1 by weight. Five 5-cm diameter x 10-cm height cylindrical forms were cast from this mixture and allowed to cure. Additional details of the formulation and solidification procedure which has been extensively studied in our laboratory on simulated boric acid waste are provided elsewhere (Morcos et al., 1982).

Cement paste setting revealed that ~60 days were required for the solidification of PWR boric acid waste/cement mix. This curing time is more than twice that required to solidify laboratory samples containing simulated boric acid waste in our earlier experiments. Presence of inorganic compounds such as phosphates, silico-fluorides, and boric acid or organic compounds such as derivatives of hydroxylated carboxylic acids and their salts or derivatives of lignin are known to retard the setting of cement paste (Lea, 1971). Some of these constituents have been detected in the PWR boric acid concentrate (Croney, 1984) and may be responsible for prolonging the time necessary for satisfactory cement setting.

After an 86-day cure, the waste forms were removed from the casting containers and visually examined. The solidified forms appeared generally similar to those cast from simulated boric acid waste except that some of the waste forms cast from reactor waste showed crystalline material in thin patches at various points on the surface. The composition and dimensions of five replicate waste forms are presented in Table 2.2.

Table. 2.2
Weight and Dimensions of PWR Boric Acid and BWR Resin Waste/Cement Composites.

Specimen Number	Weight (g)	Radius (cm)	Height (cm)	Surface Area (cm^2)	Volume (cm^3)	V/S (cm)
PWR Boric Acid Composites						
1	289	2.35	8.9	165	154	0.93
2	289	2.35	8.9	165	154	0.93
3	294	2.35	9.1	169	154	0.93
4	288	2.35	8.8	165	153	0.93
5	288	2.35	8.8	169	153	0.91
BWR Resin Composites						
1	285	2.35	9.3	172	162	0.94
2	288	2.35	9.3	172	161	0.94
3	281	2.35	9.1	169	158	0.93
4	293	2.35	9.5	175	164	0.94
5	275	2.35	9.0	168	157	0.93

2.2.2 BWR Resin Waste

A waste-to-cement (Portland Type I) ratio of 0.6 and a water-to-cement ratio of 0.4 was employed in the preparation of five BWR resin bead/cement composites. This formulation was based on earlier process parameter investigations which had established stability regions for obtaining a free standing monolithic product (Manaktala and Weiss, 1980). The waste forms were removed from the casting containers after a 28-day cure and showed no unusual deposits upon visual examination. The weight and dimensions of five replicate waste forms are presented in Table 2.2.

Both the PWR boric acid and BWR resin waste/cement composites prepared for leach studies remained as solid monoliths upon air dry curing, upon initial contact with water, and upon extended immersions in water during leach testing. The absence of any visible physical deterioration during leach testing of either the boric acid or resin bead/cement composites provides reasonable assurance that solidification is complete and attests to the versatility and effectiveness of the pretreatment and solidification technique for obtaining satisfactory solidification. Since the regulatory aim of solidification is to obtain a free standing monolith, our observations show that while no single formulation is useful for the treatment of all waste types, satisfactory immobilization of actual reactor wastes can be achieved by employing the techniques developed at BNL on simulated waste streams.

2.3 Waste Composite Leaching and Leachate Analysis

The methods used for waste composite leaching and for leachate analysis were similar to those used in earlier studies (Dayal et al., 1983a; Morcos et al., 1982). The test specimens were leached in deionized water using a modification of the IAEA method (Hespe, 1971). This method was modified in our laboratory so that the entire surface of the specimen was in contact with the leachant. The leachant was replaced periodically. Following the first leaching period of 100 minutes for the boric acid waste composites, the leachant was renewed daily, except weekends, for the first nine 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. An essentially similar leachant renewal frequency schedule was maintained for the leaching of resin waste composites. All test specimens were leached in three or five replications to determine the variability in leach data.

The leachant volume was determined by the relationship $v/S = 10$ cm, where v represents the leachant volume and S, the geometric surface area of the test specimen. Leach testing was carried out in two sets of polyethylene test vessels. The test specimen was placed in one vessel which contained fresh leachant. The other vessel contained the leachate from the preceeding leaching period. The leachate was acidified with HNO_3, an aliquot of which was saved for subsequent chemical and radionuclide analysis. The remaining liquid was discarded and the test vessel washed. Fresh leachant was allowed to equilibrate at room temperature overnight before transferring the test specimen from the other vessel. All leach tests were conducted at ambient temperature in the laboratory ($25 \pm 5^{o}C$).

Acidified leachate aliquots were counted until a minimum of 1,000 counts were accumulated in the "windows" set around the Cs-137, Cs-134, and Co-60 photo peaks. These three γ-emitters were the only ones which could be determined in the leachates with sufficient accuracy. For Sr-90 analysis (conducted by EAL Corporation of Richmond, California), a given volume of leachate aliquot was equilibrated with a known amount of yttrium carrier. The yttrium was separated, chemically purified by fluoride, hydroxide, and oxalate precipitation, and converted into oxide. The yttrium oxide was weighed and mounted on a low background planchet with copper backing and counted for beta on a low background beta counter. The Y-90 data were processed by least square analysis upon correction for chemical yield, sample self-absorption, incomplete Y-90 in-growth, and decay. Leachate aliquots from some daily, weekly, and monthly renewal periods were composited prior to analysis. Incremental fractional and cumulative fractional releases of radionuclides were calculated using appropriate corrections for decay.

3. RESULTS AND DISCUSSION

3.1 Evaluation of Leach Data from Reactor Waste Composites

The incremental fractional release (IFR) and cumulative fractional release (CFR) of a radionuclide from a test specimen is expressed as

$$IFR = {}^{a}n/A_o \tag{3.1}$$

$$CFR = \Sigma^{a}n/A_o \tag{3.2}$$

where a_n is the amount of tracer leached from the composite in 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 out of the composite in cumulative leach time. The CFR versus time plots for Cs-137, Cs-134, Sr-90 and Co-60 from the PWR boric acid waste composites are presented in Figure 3.1. Corresponding CFR versus time plots for the BWR resin bead composites are shown in Figure 3.2. Also depicted in Figures 3.1 and 3.2 for discussion in a later section are the CFR data (data presently available for Cs-137 release only) for simulated boric acid concentrate/cement and resin bead waste/cement forms of similar dimensions (5-cm diameter x 10-cm height) reported previously (Dayal et al., 1983a). The vertical error bars in these figures represent variations in leach data based on three or five replicate samples. The average CFR values were normalized for V/S variation in the waste composites.

Experimental leach data presented in Figures 3.1 and 3.2 show incongruent release of radionuclides with the following order in terms of their cumulative release in a given time

PWR Boric Acid Waste:

$$\text{Cs-137} > \text{Cs-134} > \text{Sr-90} > \text{Co-60} \tag{3.3}$$

BWR Resin Bead Waste:

$$\text{Cs-137} \simeq \text{Cs-134} > \text{Sr-90} \tag{3.4}$$

These data also suggest that radionuclide leachability from waste composites is characterized by relatively higher release rates in initial stages followed by a progressive decline in the release rate with time. In our previous work on radionuclide release behavior from simulated waste forms, similar observations were reported for Cs-137 release (Dayal et al., 1983a). In that study, we attributed the initially rapid release to be surface-controlled, followed by a diffusion-controlled release over extended leach periods. Other investigators have also reported the dominance of surface effects on the initial release of radionuclides from waste composites (Matsuzuru et al., 1977b; Moore et al., 1977).

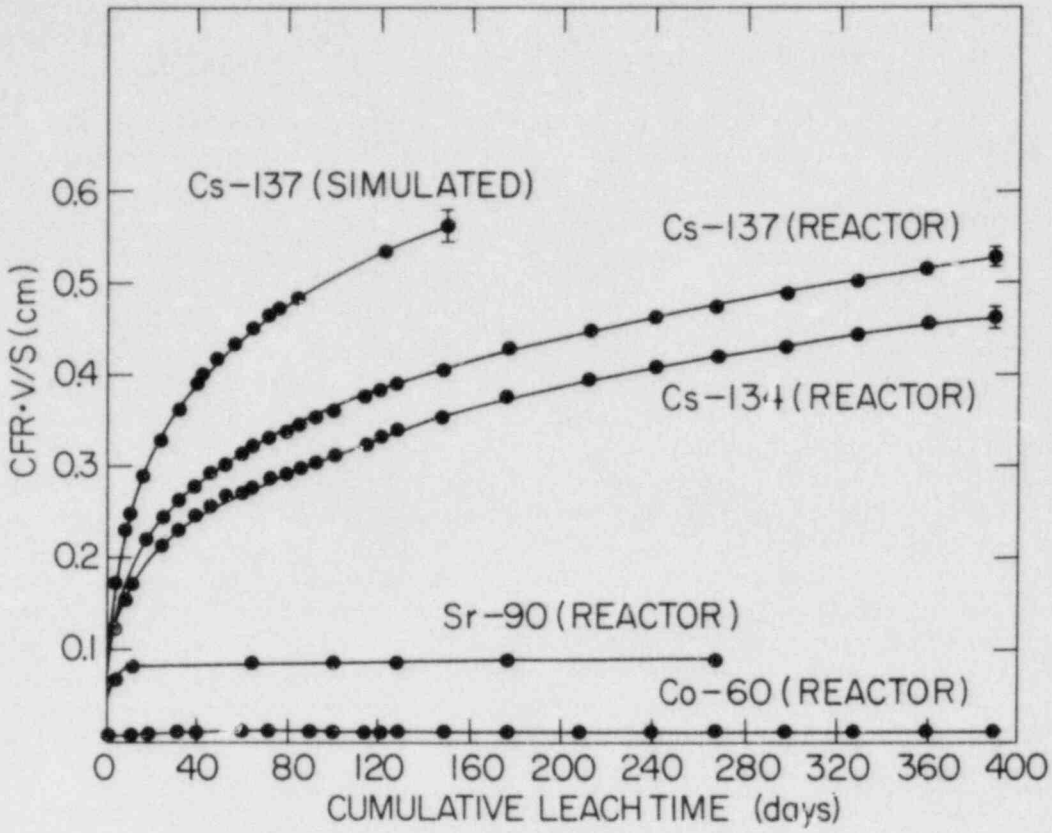

Figure 3.1 Normalized cumulative fractional release of radionuclides for PWR boric acid waste composites. Simulated waste form leach data from Dayal et al. (1983a).

The results of Cs-137 release from the BWR resin waste composites indicate that ~37 percent of the initial radiocesium has leached upon 235 days of continuous leaching. A similar release is observed for Cs-134 over a comparable leaching time (Figure 3.2). For the PWR boric acid specimens, however, Cs-137 release of 53 percent in a leach span of 389 days is slightly higher than that of Cs-134 (46 percent) in the same leach period. Although one generally expects a basic similarity in the release behavior of these two isotopes of cesium because of their similar chemistries, the observed difference may possibly be related to a small error in the amount of either Cs-137 or Cs-134 present initially in the specimen. It should be noted that in the BWR resin waste leaching studies, as discussed later, no difference in the release behavior of the two Cs-isotopes was observed.

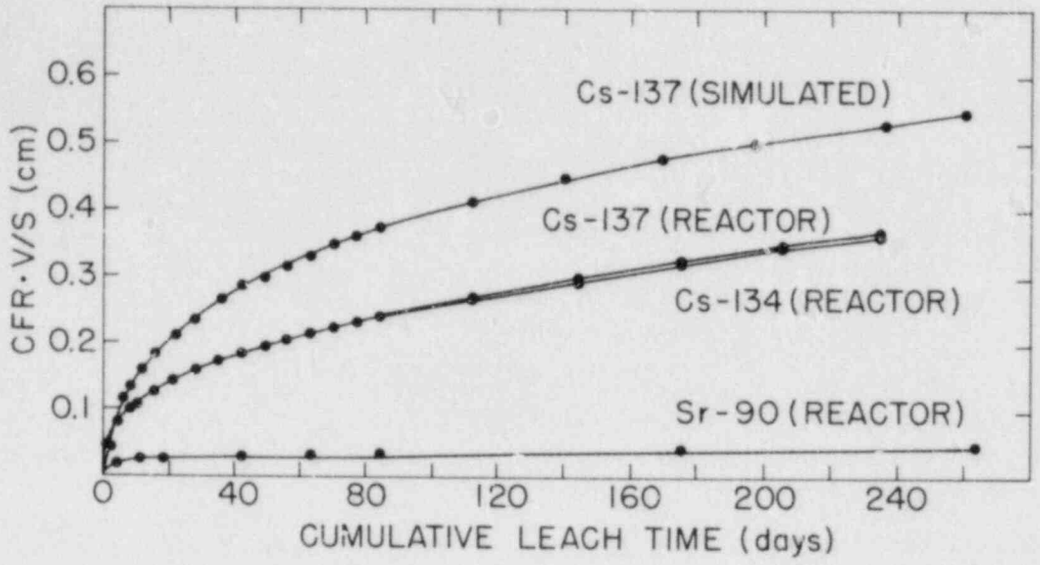

Figure 3.2 Normalized cumulative fractional release of radionuclides for BWR resin waste composites. Simulated waste form leach data from Dayal et al. (1983a).

Leach behavior of Sr-90 from actual reactor composites also exhibits faster initial releases followed by decreased levels with time for both types of wastes. A total of 8.8 and 4.8 percent of the initial Sr-90 is released in a total leach period of ~260 days for the PWR boric acid and BWR resin composites, respectively. It is important to note that, unlike Cs-137 and Cs-134 release, the concentration of Sr-90 in leachate samples is close to detection limits in many cases and thus, the data have large counting uncertainty.

The concentration of Co-60 in the BWR resin leachate is below the detection limit. Measurable levels of Co-60 release, however, are leached from the PWR boric acid composites. Only 1.2 percent of Co-60 is released upon a leach period of 389 days. Substantially low leachability of Co-60 for the two waste types is related to its chemical interaction within the cement matrix and the resultant formation of compounds of low solubility. Matsuzuru et al. (1977a) attributed low Co-60 release to cobalt hydrolyzation in the cement paste which forms macromolecules by polymerization and/or aggregation of hydroxides. Measurable releases of Co-60 have also been reported by other workers upon leaching of actual reactor waste immobilized in cement (Croney, 1984; Neilson et al., 1983; and Celeri et al., 1982). Because of the widespread use of chelating agents in decontamination operations at power reactor sites, we believe that Co-60 release is perhaps related to the presence of complexing agents in the PWR boric acid waste.

3.1.1 Radionuclide Leach Rate

To determine the rate of radionuclide release as a function of time, the incremental leach rate from the IFR data is determined as follows:

$$R_n = \frac{a_n}{A_o} \Big/ (S/V)(t_n - t_{n-1}) \qquad (3.5)$$

where

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

Use of incremental data for evaluating radionuclide leach behavior has been proposed to minimize the possibility of bias or error in a data point to be carried into subsequent data points, which occurs from coupling of the cumulative release data (American Nuclear Society, 1984; Godbee et al., 1980).

Incremental leach rate data as a function of cumulative leach time, t_n, for the reactor waste composites and their simulated counterparts are presented in Figures 3.3 and 3.4. A summary of mean incremental leach rate data for Cs, Sr, and Co isotopes, as influenced by leachant renewal frequency, is presented in Table 3.1. For the daily leachant renewal frequency region, only the range of R_n data are provided because of a rapid decline in these values upon progressive immersions. These data indicate that radionuclide leach rates vary in a relatively narrow range of 10^{-6} to 10^{-7} cm/s during the initial 100 minute immersion for the two reactor waste types. A rapid decline in incremental leach rate is observed during the daily leachant renewal frequency period. A moderate but progressive decline in the rate occurs when a weekly rather than daily leachant renewal frequency is observed and is followed by a tendency to level off upon extended leaching in the monthly leachant renewal frequency range.

The overall magnitude of drop in leach rates with time is radionuclide dependent. For example, the leach rates of Co-60 and Sr-90 for the PWR boric acid waste vary from an initially high value of $\sim 10^{-7}$ cm/s to $\sim 10^{-11}$ cm/s after extended leach periods. In comparison, the leach rate for Cs isotopes varies from an initally high value of $\sim 10^{-6}$ to $\sim 10^{-9}$ cm/s. For the BWR resin waste composites the leach rates vary from an initially high value of $\sim 10^{-6}$ to $\sim 10^{-8}$ cm/s for Cs isotopes and from $\sim 10^{-7}$ to 10^{-9} cm/s for Sr-90. For the two cesium isotopes in a given waste type, the incremental leach rates are very similar over the entire experimental leach period.

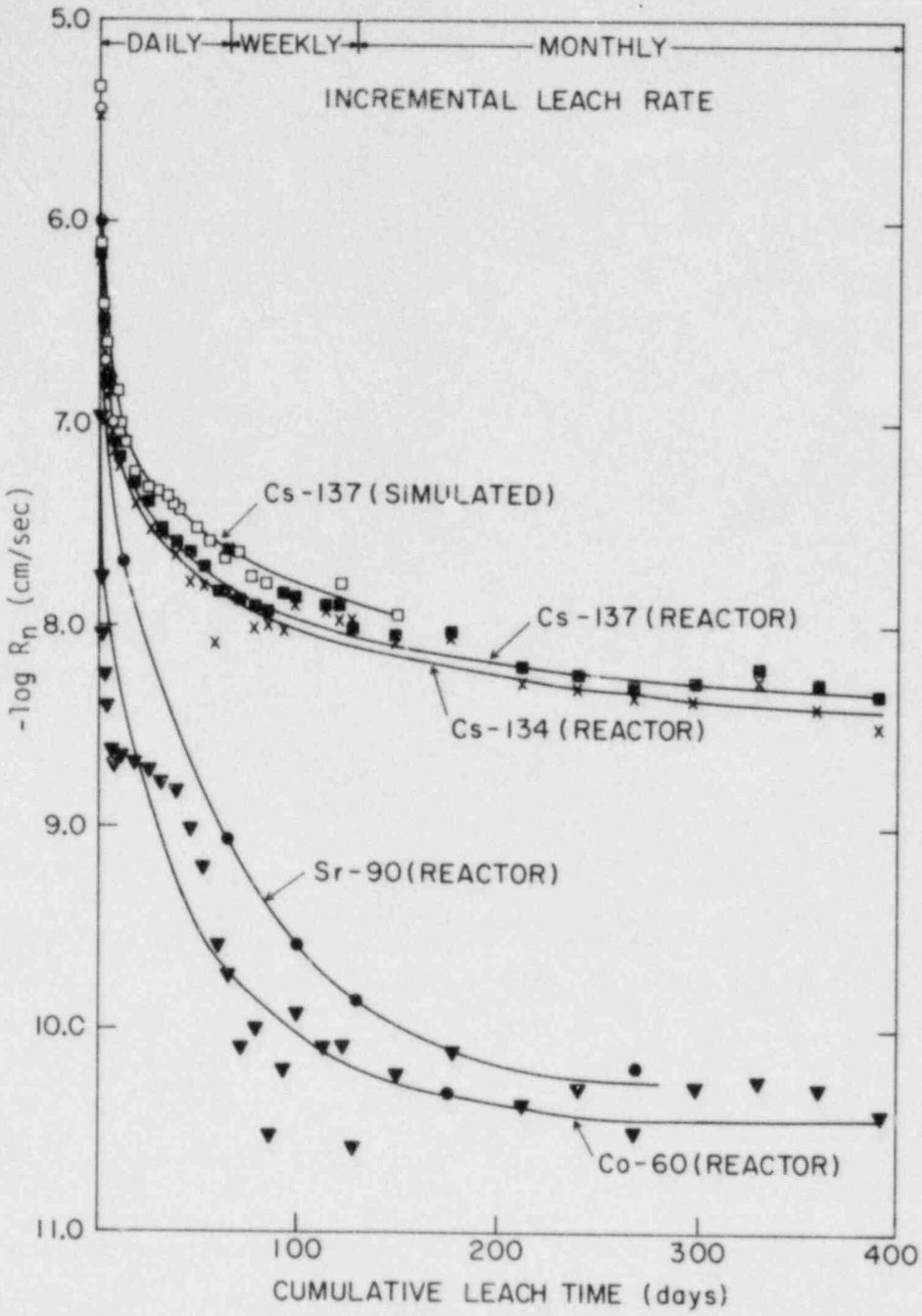

Figure 3.3 Incremental leach rate as a function of cumulative leach time for PWR boric acid waste composites. Simulated waste form leach data from Dayal et al. (1983a).

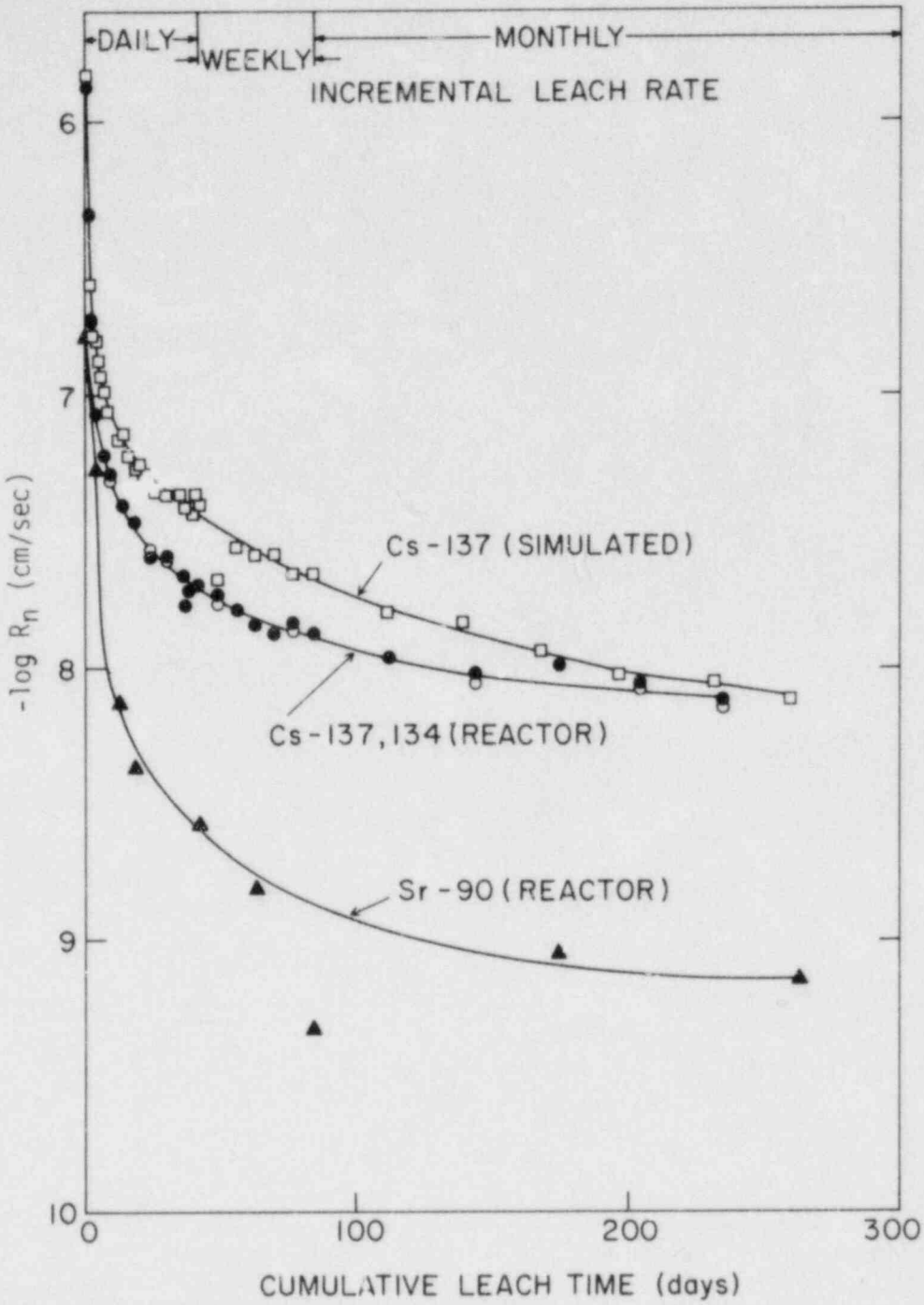

Figure 3.4 Incremental leach rate as a function of cumulative leach time for BWR resin waste composites. Simulated waste form leach data from Dayal et al. (1983a).

Table 3.1
Leach Rate Data for the PWR Boric Acid and BWR Resin Wastes as Influenced by Leachant Renewal Frequency

Radionuclide	Incremental Leach Rate (cm/s)			
	Initial 100 Minute Immersion	Daily[a] (range)	Weekly[a] (mean)	Monthly[a] (mean)
PWR Boric Acid Waste				
Cs-137	3.5×10^{-6}	$7 \times 10^{-7} - 2 \times 10^{-8}$	$1.2 (\pm 0.1) \times 10^{-8}$	$6.2 (\pm 1.6) \times 10^{-9}$
Cs-134	3.3×10^{-6}	$7 \times 10^{-7} - 1 \times 10^{-9}$	$1.1 (\pm 0.1) \times 10^{-8}$	$5.5 (\pm 2.0) \times 10^{-9}$
Co-60	1.1×10^{-7}	$2 \times 10^{-9} - 2 \times 10^{-10}$	$7.4 (\pm 3.3) \times 10^{-11}$	$5.2 (\pm 1.4) \times 10^{-11}$
Sr-90	9.8×10^{-7}	$2 \times 10^{-7} - 9 \times 10^{-10}$	2.0×10^{-10}[b]	5.7×10^{-11}[b]
BWR Resin Waste				
Cs-137	1.4×10^{-6}	$5 \times 10^{-7} - 2 \times 10^{-8}$	$1.5 (\pm 0.2) \times 10^{-8}$	$9.5 (\pm 0.1) \times 10^{-9}$
Cs-134	1.3×10^{-6}	$5 \times 10^{-7} - 2 \times 10^{-9}$	$1.5 (\pm 0.2) \times 10^{-8}$	$9.3 (\pm 0.1) \times 10^{-9}$
Sr-90	1.7×10^{-7}	$5 \times 10^{-8} - 3 \times 10^{-9}$	1.0×10^{-9}[b]	8.0×10^{-10}[b]

[a] Leachant renewal frequency intervals.
[b] Average of two values.

The incremental leach rates for the three radionuclides are consistent with the pattern of Cs-137 release as a function of leachant renewal frequency reported in our previous study (Dayal et al., 1983a). The Cs-137 release rate in that study was observed to be higher in the daily leachant renewal frequency region compared to those observed in the subsequent weekly and monthly leachant renewal intervals. Relatively low radionuclide release rates during the weekly and monthly leachant renewal periods were attributed to saturation effects resulting from the build-up of dissolution by-products.

3.1.2 Radionuclide Diffusivity

Interpretation of leach data in terms of radionuclide diffusivity for calculating a figure-of-merit parameter, Leachability Index (LI), has been recommended in the ANS 16.1 leach test proposed by the American Nuclear Society (1984). As discussed later, the NRC Technical Position on waste form has recommended the use of LI for demonstrating regulatory compliance with leachability criterion. Calculation of radionuclide diffusivity is also a prerequisite for predicting radionuclide release from full-size waste forms on the basis of leach data from small scale laboratory-size specimens and for extrapolation of these data to predict the long-term release behavior of radioisotopes (Dayal et al., 1983a). In addition, diffusivity data can also be used to monitor changes in radionuclide release mechanisms over a period of time (Dayal et al., 1983a). Radionuclide diffusivity can be calculated on the basis of either the incremental fractional release (IFR) or the cumulative fractional release (CFR) data.

3.1.2.1 Diffusivities Based on IFR Data

For isotopes of sufficiently long half-lives relative to the duration of the leach test, the American Nuclear Society (1984) recommends the calculation of effective diffusivity on the basis of incremental leach data. If less than 20% of the initially present radionuclide species is leached, D_e may be calculated on the basis of semi-infinite diffusion model by the expression

$$D_e = \pi \left(\frac{a_n/A_o}{t_n - t_{n-1}}\right)^2 \left(\frac{V}{S}\right)^2 \cdot T \qquad (3.6)$$

where D_e = effective diffusivity (cm^2/s), t_n = leaching time in seconds at end of leaching interval, and $T = [1/2\ (t_n^{1/2} + t_{n-1}^{1/2})]^2$ representing the "mean time" of the leaching interval in seconds. Other terms have been described previously.

Effective diffusivity on the basis of incremental fractional release data can also be calculated from the incremental leach rate (Equation 3.5), R_n, by the relationship

$$D_e = \pi\ (R_n)^2 \cdot T \qquad (3.7)$$

It is important to note that the term T in Equations 3.6 and 3.7 has also been defined as $T = t_n - \Delta t_{n/2}$ in the literature where Δt_n is the duration of a leachant renewal period. Our calculations show that the influence of these two definitions of T on D_e is significant for the initial 3 or 4 immersions only (up to a cumulative leach time of 4 days) in the present study. Consistent use of these definitions is important for comparing radionuclide leach data.

A summary of the mean radionculide effective diffusivities calculated on the basis of Equation 3.6 for the initial 100 minute immersion as well as for the daily, weekly, and monthly leachant renewal frequency ranges is presented in Table 3.2. These intervals correspond to the four regions identified previously in Table 3.1 on the basis of R_n vs cumulative leach time plots. The magnitude of Cs-137 and Cs-134 releases (CFR $\geq$ 0.2) require a correction factor to compensate for matrix depletion effects by employing the finite rather than the semi-infinite source model (American Nuclear Society, 1984). However, as discussed later, the D_e values calculated on the basis of semi-infinite model appear to be valid for the purposes of this study.

Table 3.2
Effective Diffusivities Calculated From Incremental Fractional Release Data.

	Effective Diffusivity (D_e, cm^2/s)			
Radionuclide	Initial 100 Minute Immersion	Daily[a]	Weekly[a]	Monthly[a]
Boric Acid--PWR				
Cs-137	1.2×10^{-7}	$1.7\ (+1.7) \times 10^{-8}$	$3.8\ (+0.9) \times 10^{-9}$	$2.5\ (+0.7) \times 10^{-9}$
Cs-134	1.0×10^{-7}	$1.3\ (+1.5) \times 10^{-8}$	$3.3\ (+1.0) \times 10^{-9}$	$1.9\ (+0.8) \times 10^{-9}$
Co-60	1.1×10^{-10}	$1.6\ (+1.1) \times 10^{-11}$	$1.6\ (+1.2) \times 10^{-13}$	$1.8\ (+0.8) \times 10^{-13}$
Sr-90	9.2×10^{-9}	4.2×10^{-9}[b]	1.0×10^{-12}[b]	1.7×10^{-13}[b]
Boric Acid--BWR				
Cs-137	1.7×10^{-8}	$6.5\ (+5.3) \times 10^{-9}$	$3.8\ (+0.4) \times 10^{-9}$	$3.7\ (+0.6) \times 10^{-9}$
Cs-134	1.7×10^{-8}	$6.4\ (+5.2) \times 10^{-9}$	$3.8\ (+0.3) \times 10^{-9}$	$3.6\ (+0.6) \times 10^{-9}$
Sr-90	2.8×10^{-10}	$4.6\ (+7.6) \times 10^{-10}$	1.9×10^{-11}[b]	2.9×10^{-11}[b]

[a] Leachant renewal frequency intervals.
[b] Average of two values.

3.1.2.2 Diffusivities Based on CFR Data

Diffusion of a stable isotope from a homogeneous, planar semi-infinite medium having a surface concentration of zero for t >0 is given by

$$(\Sigma a_n/A_o)\ (V/S) = 2\ (D_e/\pi)^{1/2}\ (\Sigma t_n)^{1/2} \qquad (3.8)$$

A more general relationship has been employed to describe the experimental leach data which have been observed to deviate from the relationship represented by Equation 3.8 especially for short leach periods (Dayal et al., 1983a; Christensen, 1982; Godbee et al., 1980; Matsuzuru and Ito, 1978; Anders et al., 1978)

$$(\Sigma a_n/A_o)\ (V/S) = 2\ (D_e/\pi)^{1/2}\ (\Sigma t_n)^{1/2} + \alpha \qquad (3.9)$$

where the term α represents non-diffusive release controlled by the surface of the test specimen while other terms have been described previously. Using Equation 3.9, a plot of $(\Sigma a_n/A_o)$ versus $(\Sigma t_n)^{1/2}$ yields a linear relationship with the slope, $[2.S/V\ (D_e/\pi)^{1/2}]$. Knowing the value of the slope, D_e is calculated from the relationship $D_e = (\text{slope} \cdot V/S)^2 \cdot \pi/4$. The magnitude of α is determined from the intercept of the line on the ordinate for $\Sigma t_n^{1/2} = 0$.

Cumulative fractional release data $(\Sigma a_n/A_o)$ for specific radionuclides versus $(\Sigma t_n)^{1/2}$ for the PWR boric acid and BWR resin waste composites are plotted in Figures 3.5 and 3.6. On the basis of previously reported results by Dayal et al. (1983a) and for comparing the results of Cs-137 release from the simulated and reactor wastes under identical conditions, we selected linear regions from these curves for calculating effective diffusivity values. A summary of effective diffusivities for selected regions calculated on the basis of CFR data and their comparison with those calculated on the basis of IFR data for the PWR boric acid and BWR resin wastes is provided in Table 3.3.

A comparison of effective diffusivity data presented in Tables 3.2 and 3.3 indicate that D_e values calculated on the basis of IFR data are consistently higher for each radionuclide studied in comparison with those calculated from the CFR data. The discrepancy occurs firstly because of a significant contribution of surface-controlled release which, as indicated earlier, is especially significant for short leach periods and is compensated for as the term α in Equation 3.9 for calculating CFR data-based D_e values. Such deviations are not compensated for in the IFR data-based D_e relationship represented by Equation 3.6. Secondly, higher diffusivity values calculated on the basis of CFR data may also result from the fact that Equation 3.6 employs elapsed time at the middle of a leachant renewal period, while CFR based D_e (Equation 3.9) employs cumulative leach time. As discussed in a later section, however, the magnitude of variations observed upon the use of incremental or cumulative leach data for calculating effective diffusivity values are not important for the purposes of this study and either the IFR or CFR data may be employed, provided a consistent approach is applied.

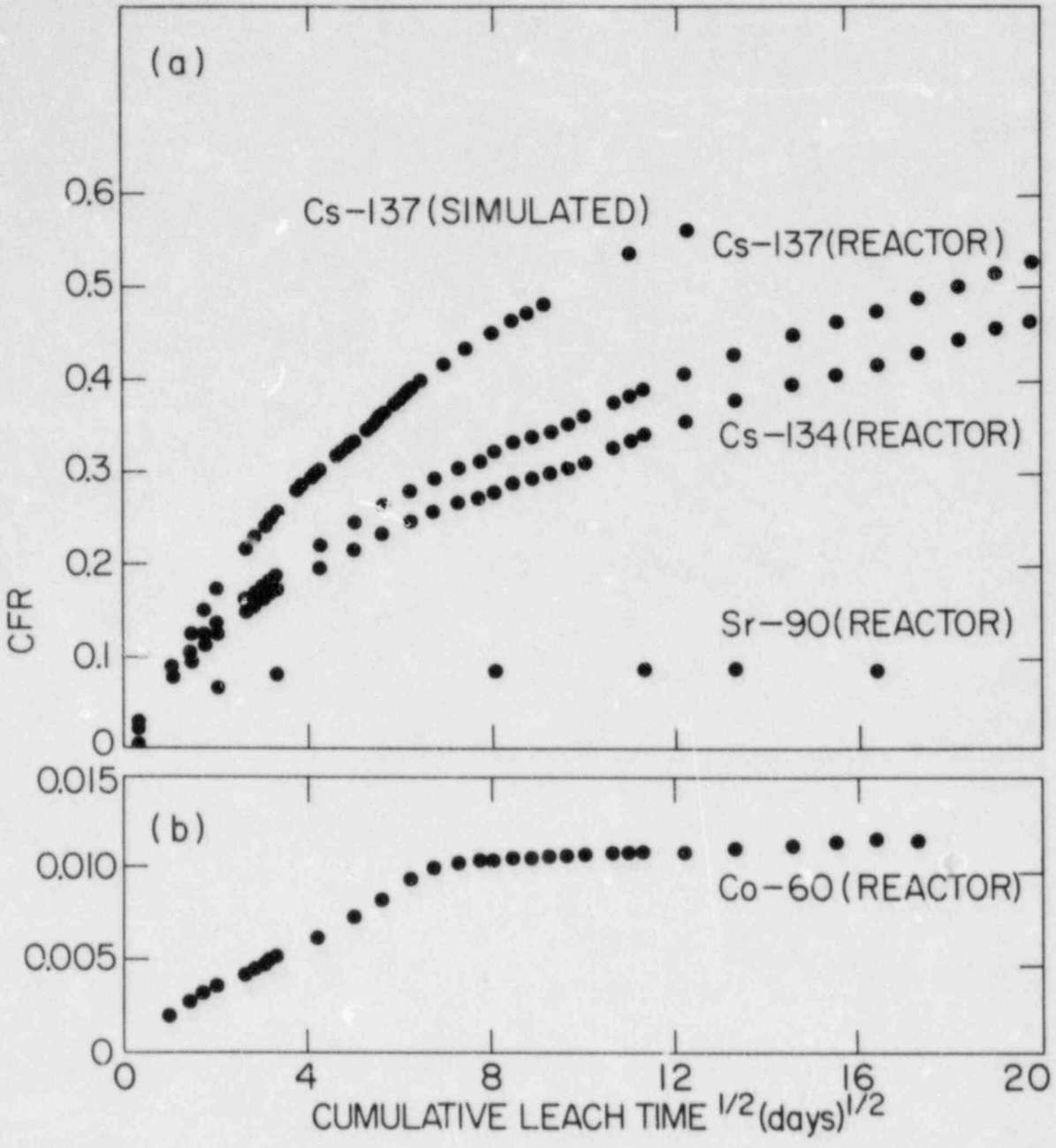

Figure 3.5 Cumulative fractional release of radionuclides as a function of the square root of cumulative leach time for PWR boric acid waste composites. Data for simulated waste CFR from Dayal et al. (1983a). Fewer data points for Sr-90 release reflect compositing of leachates from several immersions.

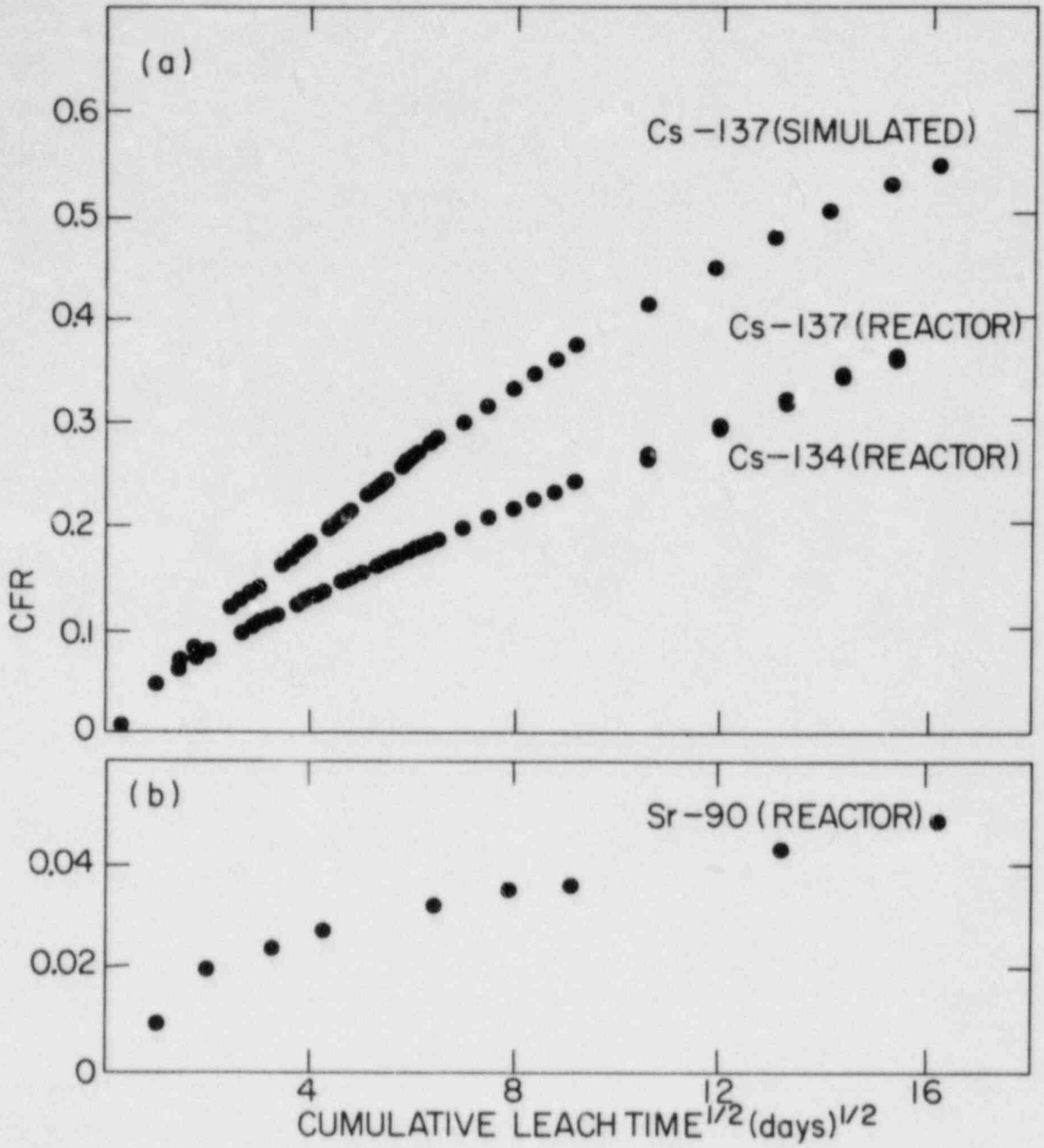

Figure 3.6 Cumulative fractional release of radionuclides as a function of the square root of cumulative leach time for BWR resin waste composites. Data for simulated waste CFR from Dayal et al. (1983a). Fewer data points for Sr-90 release reflect compositing of leachates from several immersions.

Table 3.3
Comparison of Effective Diffusivities Based on Cumulative and Incremental Fractional Release Data

Waste Type and Radionuclide	Linear Region (days)	Effective Diffusivity (D_e, cm^2/s)	
		CFR data[a]	IFR data[b]
Boric Acid--PWR			
Cs-137	7-60	7.1×10^{-9}	$9.7(\pm 0.4) \times 10^{-9}$
Cs-134	7-60	4.7×10^{-9}	$7.1(\pm 0.4) \times 10^{-9}$
Sr-90	11-268	1.5×10^{-12}	$1.9(\pm 3.1) \times 10^{-12}$
Co-60	53-298	1.4×10^{-13}	$2.4(+2.4) \times 10^{-13}$
Resin Beads--BWR			
Cs-137	7-42	4.5×10^{-9}	$5.0(\pm 0.8) \times 10^{-9}$
Cs-134	7-42	4.4×10^{-9}	$5.0(\pm 0.8) \times 10^{-9}$
Sr-90	4-263	6.4×10^{-11}	$8.2(\pm 2.7) \times 10^{-11}$

[a]Calculated on the basis of Equation 3.9. Uncertainties associated with these data are $< \pm 5\%$ except for Sr-90 from the PWR waste.

[b]Calculated on the basis of Equation 3.6.

Li and Gregory (1974) reported the self-diffusion coefficient values of a large number of tracers at 25°C at infinite dilution (Cs = 2.1×10^{-5} cm^2/s, Co = 7.0×10^{-6} cm^2/s, and Sr = 7.9×10^{-6} cm^2/s). A comparison of the self-diffusion coefficients and effective diffusion coefficients for the radionuclides investigated indicate that the cementitious matrix provides retardation up to four orders of magnitude for Cs-137 and up to six orders of magnitude for Co-60, attributable to the effects of tortuosity, sorption, and chemical interaction in the composite matrix for these radionuclides.

3.1.2.3 Influence of Finite Geometry Model on Leach Data

It is suggested in the literature that if >20% of the initially present radionuclide species is leached, matrix depletion effects become significant and the use of a finite geometry instead of the customary semi-infinite solution of the mass transport equation is recommended (American Nuclear Society, 1984). Correction factors are provided by the American Nuclear Society for evaluating effective diffusivity from a shape specific solution of the mass transport equation. Since greater than 20% of the initial amounts of Cs-137 and Cs-134 are observed from the two actual reactor waste types, we determined the variance in the diffusivity values using the semi-infinite medium approximation and the finite geometry model.

A comparison of effective diffusivity values of Cs-137 estimated for release of 30%, 39%, and 57% of the intial amount for the PWR boric acid waste at cumulative leach periods of 39, 100, and 389 days, respectively, shows that D_e values vary by less than a factor of two. Although the semi-infinite approximation tends to overpredict for cumulative relases of greater than 20%, we believe that D_e values based on semi-infinite medium approximation can be used for evaluating leach resistance of waste composites used in this study. Furthermore, considering other uncertainties in the diffusivity equations (American Nuclear Society, 1984; Dayal et al., 1983a), source term depletion corrections suggested by the ANS 16.1 test are not necessary under the conditions of this study.

3.2 Comparison of Radionuclide Leachability of Simulated and Actual Reactor Wastes

As indicated previously, only Cs-137 release data are presently available for simulants of boric acid and resin-bead waste composites. A comparison of these leach data from actual reactor waste forms and those prepared employing identical solidification formulations and leach test procedures are described below.

3.2.1 Boric Acid Type Waste

Cumulative fractional release data presented previously in Figure 3.1 depicted higher eachability of Cs-137 from simulated waste composites in comparison with that from the reactor waste counterpart (~56 percent vs 41 percent of the initial radiocesium leached upon 150 days of continuous leaching at which time the simulated waste leach experiment was discontinued). Corresponding D_e values calculated in the selected linear region during daily leachant renewal frequency intervals for the simulated and reactor wastes are ~2 x 10^{-8} and 0.7 x 10^{-8} cm^2/s, respectively (Table 3.4).

Table 3.4
Comparison of the Effective Diffusivity of Cs-137 for Reactor Waste Composites and Their Simulatants.

Waste Composite Type	Effective Diffusivity[a] (D_e, cm^2/s)
PWR Boric Acid Waste	0.7 x 10^{-8}
Simulated Boric Acid Waste[b]	1.9 x 10^{-8}
BWR Resin Bead Waste	0.5 x 10^{-8}
Simulated Resin Bead Waste[b]	1.6 x 10^{-8}

[a]Calculated on the basis of Equation 3.9 for selected linear regions. Uncertain associated with these data are $\leq$ + 6%.
[b]Data from Dayal et al. (1983a).

Since identical laboratory conditions were employed for collecting leach data (in terms of extrinsic factors such as immersion schedules, composite surface area to leachant ratio, temperature, etc.) in the two studies, higher rate of Cs-137 release from the simulated boric acid concentrate waste are primarily attributed to variability in the physical and chemical properties of the solidified matrix (intrinsic factors). The influence of most of the intrinsic parameters which have been identified in the literature to significantly influence radionuclide release (such as cement type, waste-to-cement ratio, etc.) was also kept experimentally identical as is evident from the fact that volumetric porosity of reactor wastes composites and simulated their counterparts varied by less than 3%.

The chemical nature of the waste itself appears to be the most obvious intrinsic variable influencing the release of Cs-137 in the two studies. As discussed previously, Croney (1984) presented data which show varying concentrations of a variety of stable elements in the PWR boric acid waste. Furthermore, we have reported that incorporation of this reactor waste in cement caused a significant delay in the time of setting of the paste as compared to the one observed for simulated boric acid waste. Although data are

not presented here, we found stable cesium to be present at concentration levels of <1 ppm which could inhibit the release of radiocesium. Presence of stable ions of similar chemistry in the waste form have been reported to inhibit the dissolution and release of radionuclides (Moore et al., 1977; Matsuzuru et al., 1977b).

Although higher releases of Cs-137 are observed for the simulated waste composites in comparison with those from reactor waste composites over similar leach intervals, the magnitude of variability is rather small. The leach behavior of both the reactor waste composites and their simulated counterparts exhibit considerable similarity, i.e. initially high surface-controlled releases of Cs-137 for both are followed by diffusion-controlled release. Furthermore, as discussed later, the observed variability does not appear to be important from regulatory compliance viewpoint. Thus, it appears reasonable to assume that a general correspondence exists in the leachability of Cs-137 from identically solidified and leached specimens of actual and simulated wastes employed in these investigations and that Cs-137 release data from testing of either the actual or simulated waste composites can be employed to evaluate and predict the leach behavior of boric acid type reactor waste composites.

3.2.2 Resin-Bead Type Waste

Cumulative fractional release data presented previously in Figure 3.2 also depicted higher release of Cs-137 from simulated waste in comparison with that from reactor waste over a given leach time span. Corresponding D_e values calculated in the selected linear region during daily leachant renewal frequency intervals for the simulated and reactor waste are 1.6×10^{-8} and $\sim 0.5 \times 10^{-8}$ cm^2/s, respectively (Table 3.4). Identical solidification formulations and procedures were employed for the simulated and actual reactor waste types as is evident from the fact that volumetric porosity of actual reactor waste composites and their simulated counterparts varied by less than 6%. Thus, variability in the rate of Cs-137 release in the resin-type waste composites also appears to be related to the presence of a variety of stable elements in the reactor waste which accumulate during demineralization operation. Stable cesium at concentration levels of <1 ppm was also detected in the BWR resin composite leachates which could inhibit the release of radiocesium.

As discussed above for the boric acid type waste composites, the magnitude of variability in the release of Cs-137 from the resin-bead type BWR waste composites and their simulated counterparts is also rather small. A similarity in the leach behavior of the two suggest that a general correspondence exists between the leachability of Cs-137 from of actual reactor waste and simulated waste composites employed in these investigations. Thus, the Cs-137 leach data derived from testing of simulated waste composites can also be employed to evaluate and predict the leach behavior of resin waste type reactor wastes.

3.3 Comparison of BNL and EG and G Leach Data

In a collaborative effort, samples of boric acid containing waste from the PWR were also solidified and leached at the EG and G, Idaho Falls laboratory. The solidification procedure for the EG and G study involved the mixing of waste (collected on September 24, 1981, a portion of which was sent to BNL) with Type M mortar mix - a proprietary mix consisting of cement and lime in a remotely controlled auger feeder system supplied by ATCOR. Addition of lime adjusted the pH of the waste and aided in the setting process. The waste was mixed in a batch mode with the contents mixed to fill one 210 L drum (56 cm diameter x 76 cm height) at a time. Two small samples (5 x 10 and 15 x 15) were also immediately taken from one of the drums and the paste allowed to set for a period of two months before the initiation of leaching. Additional details on in-plant solidification of waste are provided by Croney (1984).

A comparison of Cs-137, Sr-90, and Co-60 release data for the 5 cm x 10 cm test specimens as obtained by BNL and EG and G are presented in Figure 3.7. These two data sets for the same waste batch exhibit highly contrasting release behavior. Within a leach period of 25 days ~89% of Cs-137 is released for the EG and G data set. In comparison, only ~25 percent of Cs-137 is observed in the BNL study for a similar cumulative leach time. Significantly higher releases of Sr-90 and Co-60 are also observed in the EG and G study. The following appear to be the most plausible reasons for the observed differences in the magnitude of radionuclide releases from composites of similar dimensions:

Test specimens for boric acid-containing wastes in the BNL study are prepared by using Portland Type III cement as a solidification agent. Exact composition of the mix and process parameters for the in-plant EG and G solidification, on the other hand, being proprietary, are less well defined. Since radionuclide leachability has been shown to be strongly influenced by the cement type, presence of additives, and process parameters (Moore et al., 1977), wide differences in radionuclide release rates are possible.

Even more important a parameter in determining the magnitude of radionuclide releases appears to be the fact that boric acid-type waste composites at BNL are prepared with a waste-to-cement ratio of 0.7. In comparison, the EG and G test specimens are prepared with a waste-to-cement ratio of 1.0. Since a higher waste-to-cement ratio is known to produce a more porous solid product (Matsuzuru et el., 1977b) and the resultant composites would have a much higher reactive area exposed to the leachant, one would expect a higher rate of radionuclide release for these specimens. For example, the average volumetric porosity of BNL specimens is estimated at 34% in comparison with the calculated porosity of ~50% (determined on the basis of waste-to-cement ratio used) for the EG and G specimens. Thus the lower waste-to-cement ratio used in BNL formulation produces a less porous solid and consequently is less reactive. Matsuzuru et al. (1977b) observed similar decreases in the leachability of Cs-137 upon lowering the waste-to-cement ratio of composites.

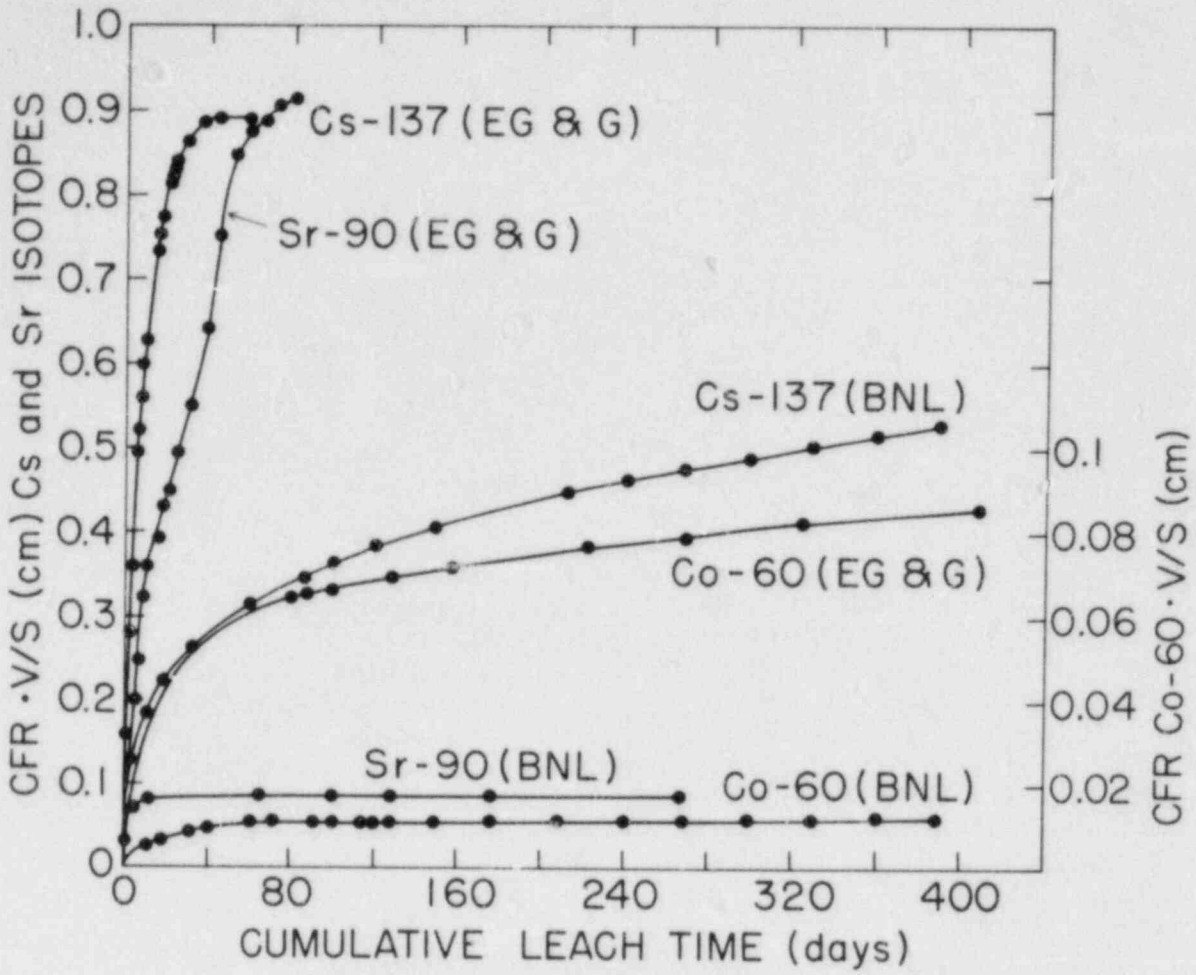

Figure 3.7 Comparison of radionuclide release from 5 x 10 cm PWR boric acid waste composites observed in the EG and G and BNL studies. EG and G data from Croney (1984).

The effect of variable waste-to-cement ratio on effective diffusion coefficient of Cs-137 from published data is shown in Figure 3.8. These data depict a significant correlation (r^2 = 0.9621) between the two parameters and indicate the significance of the waste-to-cement ratio in leachability investigations. In a recent study on the release of radionuclides from in-plant solidified full-scale specimens containing boric acid type reactor waste, Kalb and Colombo (1984) also reported effective diffusivity values of $\sim 10^{-7}$ cm^2/s for Cs-137, and $\sim 10^{-10}$ cm^2/s for Co-60 which closely approximate those reported for the EG and G study. The similarities in D_e values for the two studies can presumably be attributed to identical solidification processes employed in commercial waste management operations at the two reactor sites.

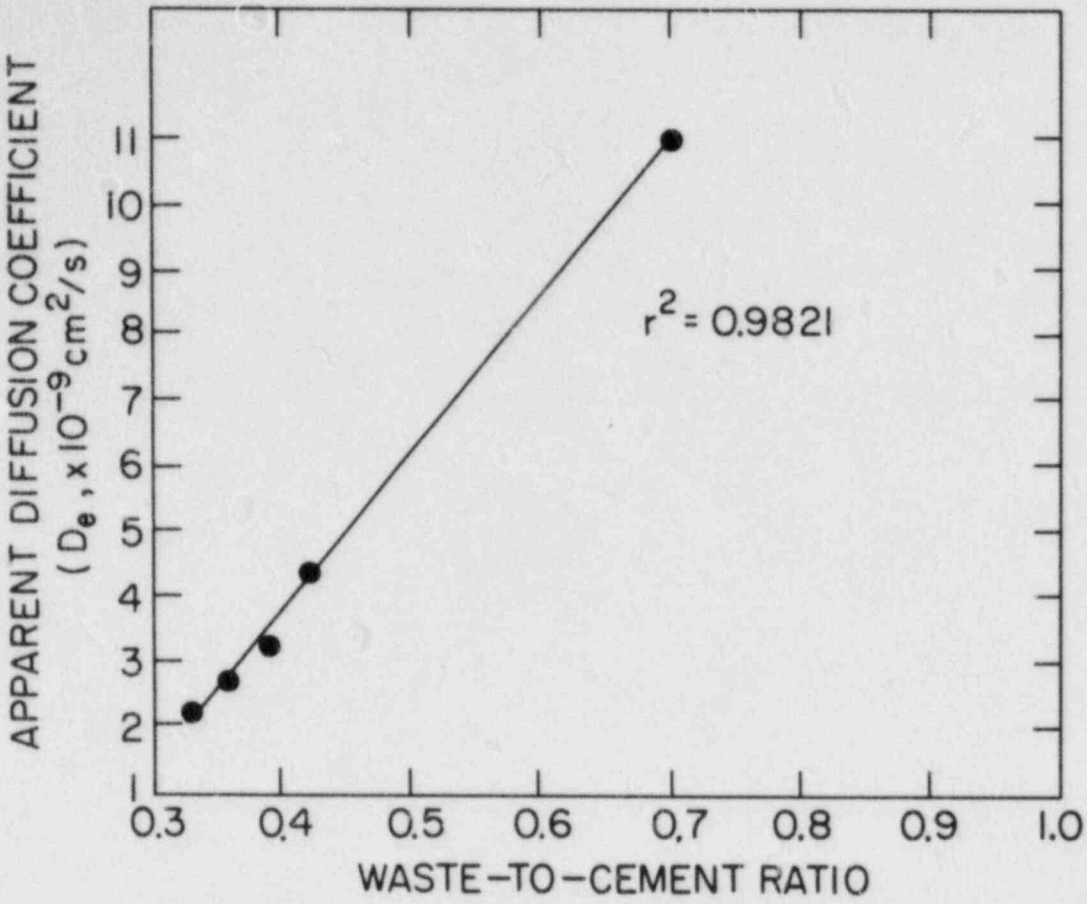

Figure 3.8 Influence of waste-to-cement ratio on the effective diffusion coefficient of Cs-137 (Dayal et al., 1983a; Matsuzuru et al., 1977b)

One of the preliminary objectives of our study was to evaluate the correspondence of BNL predicted releases (on the basis of laboratory leach data on small specimens) to the observed EG and G releases from full-size specimens. However, in view of the discrepancies observed in the release behavior of radionuclides in the two studies, predicted release from full-size specimens, based on our leach data, to those measured in the laboratory by Croney (1984) were not compared. A comparison of measured and predicted release on the basis of EG and G experimental data for the three waste form sizes (5 x 10, 15 x 15, 56 x 76, cm x cm) indicated that leach data derived from small-scale specimens could be extrapolated to estimate release from a full-size waste form for formulation used in the EC and G study (Croney, 1984).

4. RELEVANCE TO REGULATORY CRITERION IN TERMS OF LEACH RESISTANCE

The NRC Technical Position on waste form (Higginbotham, 1983), provides guidelines to waste generators for demonstrating compliance with 10 CFR Part 61 waste stability criteria. Certain minimum requirements (such as solidification of all liquid waste) must be met for the disposal of the three categories of waste (i.e. Class A waste, Class B waste, and Class C waste) designated to be suitable for land disposal. The high activity Class B and Class C wastes are also required to meet more rigorous requirements on waste stability such that the waste form maintains its structural integrity under the expected disposal environments. Specifically, the TP on waste forms recommends that waste specimens should maintain a minimum compressive strength of 50 psi as tested using ASTM C39 or ASTM D1074, following immersion for a minimum period of 90 days.

On the basis of our previous studies conducted at BNL and the fact that no visible deterioration of any of the five replicate specimens for either of the two reactor waste types was observed, it appears reasonable to assume that actual reactor waste forms would meet these structural stability guidelines.

In regard to the leach resistance upon contact with water, the TP recommends the use of the leach test proposed by the American Nuclear Society Standards Committee Working Group (ANS 16.1). The following recommendations on leach testing are provided:

> "Leach testing should be performed for a minimum of 90 days in accordance with the procedure in ANS 16.1. Specimen sizes should be consistent with the samples prepared for the ASTM C39 or ASTM D1074 compressive strength tests. In addition to the demineralized water test specified in ANS 16.1, additional testing using other leachants specified in ANS 16.1 should also be performed to confirm the solidification agents leach resistance in other leachant media. It is preferred that the synthesized seawater leachant also be tested. In addition, it is preferable that radioactive tracers be utilized in performing the leach tests. The leachability index, as calculated in accordance with ANS 16.1 should be greater than 6."

A recently distributed final draft of the test standard (American Nuclear Society, 1984) calls for a detailed set of test parameters emphasizing reproducile conditions that can be readily achieved and which can be related through generic studies to actual disposal site conditions. Accumulation of leach data upon ten leach intervals over a period of 90 days is proposed in the standard leach test while an "abbreviated"[a] test calls for accumulation of leach data upon seven leach intervals over a period of five days.

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[a]The "abbreviated test" may suffice for solidified materials of the types for which the results of extensive generic studies are available (American Nuclear Society, 1984).

The leach test data collected are analyzed to calculate a figure of merit parameter, termed "Leachability Index" (LI), for characterizing the release of radionuclides from the waste form. Analysis of leach data calls for the computation of apparent diffusivity values by employing semi-infinite plane source diffusion model to the IFR data (Equation 3.6). In the event that cumulative fractional release of the radionuclide under study exceeds 20% of the initial activity for leach intervals, the analysis method provides correction factors (tabular or graphical) to compensate for matrix depletion effects by employing the finite geometry source model. The LI for the standard leach test is calculated as follows:

$$LI = \frac{1}{10} \sum_{n=1}^{10} [\log (\beta/D_e)]_n \qquad (4.1)$$

Leachability index for the abbreviated test ($\overline{LI}$) is calculated from release data for the first seven leaching intervals as:

$$\overline{LI} = \frac{1}{7} \sum_{n=1}^{7} [\log (\beta/D_e)]_n \qquad (4.2)$$

The term β is a defined constant (1 cm^2/s) in Equations 4.1 and 4.2. The arithmetic average of the seven or ten determinations for each radionuclide is reported as its leachability index. American Nuclear Society (1984) recommends the handling of deviations in the data set as follows:

> "If the range of log (β/D_e) values in the data set exceeds 25% of the mean (LI or $\overline{LI}$), the spread of the data shall be considered excessive and another specimen shall be tested. If either the mean of the first four values of log (β/D_e) in a set, or the mean of the last four, differ from the LI (or $\overline{LI}$) found by more than $\pm$5%, the trend in the data shall be considered biased, and another specimen shall be tested. If the result from repeated specimens fail to fall within the above ranges, the bias of the material from which the specimens were taken must be reported with the Leachability Index (e.g., LI_{Co-60} = 7.5 - 15% shall mean that the average of the last four log (β/D_e) values in the set is 15% smaller than the average of the first four values). A + sign is to be used if the average of the last four data points exceeds the average of the first four. Deviations less than those specified need not be reported."

An evaluation of the approach and provisions of the ANS 16.1 leach test suggest that the procedure is a modification of the IAEA test proposed by Hespe (1971). Leach test conditions in the ANS test require the complete immersion of a test specimen in measured volume of leachant, which is periodically renewed on a prescribed schedule. Since the ANS test conditions generally correspond to the modified IAEA leach method employed in our studies except for the rigid immersion schedules, we used the present release data to calculate leachability index and for evaluating regulatory compliance.

A summary of leachability index values of radionuclides representing two immersion regions, corresponding approximately to the standard and abbreviated ANS 16.1 test, for the two reactor waste types and their simulants is presented in Table 4.1. Also presented in Table 4.1 are the LI values calculated from diffusivity data for the PWR boric acid waste reported by Croney (1984).

The results presented in Table 4.1 suggest that the LI values of radionuclides for the boric acid and resin bead type actual reactor wastes and their simulants surpass the numerical value of 6 specified in the TP for regulatory compliance. Although the cumulative release of radionuclides from the PWR boric acid waste and thus the LI values calculated from diffusivity data reported by Croney (1984) are significantly higher than those observed in the BNL study, it is interesting to note that the in-plant solidified EG and G composites are also acceptable to demonstrate compliance with the current regulatory provisions. However, data presented in Table 4.1 also indicate that the leachability index values are sensitive to leachant renewal frequency and other variables as described below.

Relatively low LI values of all radionuclides for the initial 7 or 10 immersions of both reactor waste types (Table 4.1), as discussed previously, reflect the dominance of surface-controlled release in the region. An increase in LI, reflecting lower diffusivity values, observed as the leachant renewal frequency is changed from daily to weekly and monthly renewals can be attributed to the saturation effect resulting from the build-up of dissolution by-products. Although these results indicate that LI values are sensitive to leachant renewal frequency, the spread in these data, however, when viewed in accordance with the procedure outlined in ANS 16.1 test, is not considered excessive.

The results presented in Table 4.1 indicate that the mean LI values are radionuclide dependent. For example, the LI values for Co-60 and Sr-90 for both waste types are much higher in comparison with those for Cs-137. These variations result from the fact that tortuosity of the diffusive path and solidification matrix interactions in terms of adsorption and ion exchange are radionuclide specific.

In regard to waste type and formulation, the data presented in Table 4.1 indicate that the mean LI values of a given radionuclide for the two Portland cement solidified waste types under study are largely similar. For example, the mean LI value of Cs-137 in the daily leachant renewal frequency regions for the PWR boric acid and BWR resin waste types are 7.9 and 8.2, respectively. In contrast, mean LI values of all radionuclides for the BNL data set of PWR boric acid waste are consistently lower in comparison with those for the EG and G data set. These differences, as discussed previously, are attributed to variability in formulations used, in particular, to the waste-to-cement ratios employed in the two studies.

Table 4.1
Leachability Index of Radionuclides for Varying Immersion Schedules of PWR Boric Acid and BWR Resin Waste Composites and Their Simulants.

Radionuclide	Leachability Index					
	BNL Data					EC and G Data[d]
	7 Immersions[a]	10 Immersions[b]	Daily[c]	Overall Data[c]	Overall Range	
Boric Acid Waste--PWR						
Cs-137	7.5	7.6	7.9 (± 4)	8.2 (± 6)	6.9 - 8.8	6.2
Cs-134	7.6	7.7	8.1 (± 5)	8.3 (± 6)	6.9 - 9.8	--
Co-60	10.6	10.7	11.0 (± 4)	11.9 (± 9)	10.0 - 14.3	10.4
Sr-90	NA	NA	9.3 (±18)	10.7 (±20)	8.0 - 12.2	6.8
Boric Acid--Simulated[e]						
Cs-137	7.2	7.3	7.6 (± 3)	7.7 (± 4)	6.7 - 8.3	--
Resin Bead Waste--BWR						
Cs-137	8.0	8.0	8.2 (± 2)	8.3 (± 2)	7.8 - 8.5	--
Cs-134	8.0	8.0	8.3 (± 2)	8.3 (± 2)	7.7 - 8.5	--
Sr-90	NA	NA	9.8 (± 7)	10.2 (± 7)	8.8 - 11.4	--
Resin Bead Waste--Simulated[e]						
Cs-137	7.6	7.7	7.8 (± 2)	7.9 (± 3)	7.7 - 8.4	--

[a]Approximately corresponds to the ANS 16.1 "abbreviated" test.
[b]Approximately corresponds to the ANS 16.1 immersion intervals for "standard" test.
[c]Arithmatic mean and percent standard deviation.
[d]Data from Croney (1984).
[e]Data from Dayal et al. (1983a)
NA = not available.

Analysis of leach data employed in the calculation of leachability index (such as the IFR vs CFR data-based D_e, semi-infinite vs finite source model-based D_e) described in this report or reported previously (Dayal et al., 1983a) suggest that LI values are sensitive to these data handling procedures. In addition, the results of our on-going studies on the influence of variable wet-dry cycles and leachant composition (Arora and Dayal, 1984) also suggest that LI values would be sensitive to these effects. However, from a regulatory compliance viewpoint, the influence of these variables on LI values of radionuclides for the two reactor waste types studied at BNL is not expected to be significant.

The ANS proposed leach test and data handling for calculating leachability index is an effort to standardize testing conditions such that the results obtained at different laboratories can be reproduced and compared to demonstrate compliance with the federal rule 10 CFR Part 61. In particular, the ANS test minimizes the role of extrinsic factors (such as leachant renewal frequency, chemical characteristics of the leachant, and temperature) which have been reported to influence radionuclide release. However, leachability index a figure-of-merit parameter, oversimplifies the complexity of radionuclide leaching from solidified waste forms and the limitations of the ANS recommended testing and data handling procedures need to be understood and considered for evaluating regualtory compliance. Some of the important limitations include: (1) The ANS test procedure provides no alternative in the event that the release of a particular radionuclide is not predominantly controlled by bulk diffusion such that force-fitting of data is necesary to calculate leachability index and (2) method of calculating and reporting LI is very broad such that the range of log (β/D_e) values in the data set can vary as much as 25% of the mean without being reported.

5. SUMMARY

Leach testing was conducted on two cement solidified reactor waste types (resin beads from a BWR and boric acid concentrate from a PWR). Radionuclide release behavior is characterized by initially rapid release, presumably a surface-controlled phenomenon, followed by predominantly diffusion-controlled release at a lower rate. At longer immersion intervals, however, the influence of saturation effects resulting from an accumulation of leached by-products further depressed the rate of radionuclide release. Effective diffusivity values of Cs-137 in the diffusion-controlled region were ~7 x 10^{-9} and ~5 x 10^{-9} cm^2/s for the PWR boric acid and BWR resin bead composites. For Sr-90 and Co-60, these values are two to four orders of magnitude lower than that for Cs-137, attributable to the effect of chemical interactions of these isotopes within the cement matrix.

A comparison of Cs-137 release behavior of the two reactor waste types and their simulated counterparts indicated lower release from reactor waste composites resulting in three to four fold reduction in their effective diffusivity values. However, since the leach behavior of both the reactor wastes and their simulated counterparts exhibited considerable similarity, it appears reasonable to asssume that Cs-137 leach rate derived from testing of simulated waste composites can be employed to evaluate and predict the release behavior from reactor wastes provided the specimens are prepared and leached under identical conditions.

In comparison with the release data observed at BNL, the EG and G release data on waste forms solidified from the same batch of PWR boric acid waste exhibit significantly higher releases of Cs-137, Sr-90 and Co-60 (approximately two to four orders of magnitude difference in effective diffusivity values). The results of two data sets are not directly comparable because of the higher waste-to-cement ratio employed at EG and G (0.7 for the BNL versus 1.0 for EG and G) and variance in the solidification agents used. A combination of these variables resulted in higher matrix porosity and consequently accelerated radionuclide releases from the EG and G composites.

Leachability index (LI) values were calculated in accordance with the ANS 16.1 test procedure for determining regulatory compliance. Both the BNL and EG and G release data meet the proposed NRC guidelines on leachability criteria ($LI \geq 6.0$). The leachability index values for a given radionuclide were found to be sensitive to a number of factors such as leachant renewal frequency, solidification formulation, and leachant composition, as well as the methodology employed in the calculation of LI (such as the IFR or CFR data based or the semi-infinite vs finite source model for calculating effective diffusivity). However, the influence of these variables for regulatory compliance for the two reactor waste types was found to be minimal.

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13. ABSTRACT (200 words or less)

Leach testing was conducted on two types of reactor wastes (resin beads from a BWR and boric acid concentrate from a PWR) solidified in cement. In these wastes, Cs-isotopes were the most mobile constituents followed by Sr-90. Co-60 was found to be the least mobile. Effective diffusivities of these radionuclides were $\approx 10^{-9}$ cm^2/s for Cs-isotopes, $\approx 10^{-11}$ cm^2/s for Sr-90, and $\approx 10^{-13}$ cm^2/s for Co-60. A comparison of the release of Cs-137 from these wastes and the results of our previous study in which simulants of these reactor wastes were solidified and leached under identical conditions shows a general correspondence in their release behavior, indicating the leach data derived from testing could be employed to evaluate and predict the release behavior for reactor wastes. Leachability index (LI) values were calculated for determining regulatory compliance of waste forms. The BNL release data meet the proposed NRC guidelines on leachability criteria (LI $\geq$ 6.0). Also summarized are the limitations in the use of LI values for demonstrating regulatory compliance.

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