FULL-SCALE LEACHING STUDY OF COMMERCIAL REACTOR WASTE FORMS *

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ABSTRACT

This paper describes a full-scale leaching experiment which has been conducted at Brookhaven National Laboratory (BNL) to study the release of radionuclides from actual commercial reactor waste forms. While many studies characterizing the leaching behavior of simulated laboratory scale waste forms have been performed, this program represents one of the first attempts in the United States to quantify activity releases for real, full-scale waste forms.

INTRODUCTION

Typical full-scale (55 gallon drum size) waste forms were acquired by BNL from an 800 MWe boiling water reactor (BWR) and an 830 MWe pressurized water (PWR). The waste streams included PWR evaporator concentrate (boric acid waste), BWR evaporator concentrate (sodium sulfate waste) and BWR evaporator concentrate plus ion exchange resins. These waste types were solidified in masonry cement, portland type III cement, and vinyl ester-styrene (Dow polymer). Four representative waste stream-solidification agent combinations were encompassed, as outlined in Table I.

Table I

Waste Type-Solidification Agent
Combinations Employed in Full-Scale
Leaching Experiment

	Solidification Agent		
Waste Type	Portland Type III Cement	Dow Polymer	Masonry Cement
Sodium Sulfate Concentrate	BWR[a]	BWR	--
Sodium Sulfate Concentrate + Ion Exchange Resins	BWR	BWR	--
Boric Acid Concentrate	--	--	PWR[b]

(a) 800 MWe Boiling Water Reactor
(b) 830 MWe Pressurized Water Reactor

Samples of the liquid waste stream were acquired at the time solidified specimens were formulated. These samples were analyzed by gamma spectroscopy for radionuclide concentration. The predominant isotopes revealed in these assays were Co-60 and Cs-137, with smaller concentrations of Cs-134, Mn-54, Ce-144, Sr-90, Zn-65, Co-58, Co-57, and Sb-125, identified.

Counting data, along with information relative to the quantity of waste contained in each specimen as provided by the participating utilities, were used to calculate the waste form activity inventory. This information, in turn, served as the source term for the full-scale leaching experiment. Additional information on liquid waste analysis and source term determination are included in Reference 1.

FACILITY

Radiation dose levels for the full-scale waste forms are sufficiently high as to present a potential exposure hazard to operating personnel. The full-scale leaching facility was designed therefore, to be operated and monitored remotely. Filling, sampling, and draining operations as well as the monitoring of liquid levels were conducted in a shielded control room adjacent to the leaching cell. An overall schematic view of the facility may be seen in Fig. 1.

Leaching Tanks

The leaching tanks are centrifugally cast reinforced fiberglass equipped with tight fitting covers to minimize evaporative losses. Each leach tank is fitted with a stainless steel support stand designed to raise the waste form off the bottom, thus exposing the majority of the waste form's bottom surface to leachant.

Leachant Supply System

In order to supply the large volumes of high quality water necessary for the leaching of full-scale waste forms, a water purification system was installed in the control room area. The system consists of a 5 micron filter, an activated carbon adsorption column (for removal of organics) and two mixed bed resin deionizers connected in series. The columns are replaced whenever the resistivity of the water falls below one megohm. In addition, an 850 liter leachant storage reservoir was installed to handle the volume necessary for one complete leachant renewal cycle in the event of a failure of the water purification system. Deionized water flows from the purification system through a paddle wheel flow transducer to a leachant distribution manifold. The volume of leachant delivered is displayed on a batch accumulator meter. Flow rates through the system average approximately 10 liters /minute.

Fig. 1   Layout of the Full-Scale Leaching Facility

Legend for figure:
1. Demineralizer System
2. Peristaltic Pump & Sampling Station
3. 3 in. Steel Doors
4. Brick Shielding (16 in.)
5. Control Panel
6. Leach Tank no. 4
7. Leach Tank no. 3
8. Leach Tank no. 2
9. Leach Tank no. 1
10. Sampling Station
11. Marine Window

Leachate Sampling System

Aliquots for leachate analysis are taken remotely by means of the leachate sampling system. This system consists of two dual channel variable speed peristaltic pumps, tygon tubing, and polypropylene three-way stopcock valves. Each tank has a separate sampling channel. Tubing is arranged in a closed loop to permit circulation of the leachate and thus promote homogeneity prior to sampling. The peristaltic pumps can be operated in reversa to allow purging and flushing of the sampling lines, minimizing the cross-contamination of samples with leachants from previous samples.

Leachate Discharge System

At the end of each leaching interval and after the leachate sample has been taken, the remaining leachate must be drained and fresh leachate supplied. The leachate discharge system was designed to drain the tanks quickly (less than 20 minutes on average), thus minimizing the time that the leaching specimens are exposed to air. Leachate is drawn from the tanks by a positive displacement flexible impeller pump. From the discharge side of the pump, leachate flows to two drain pits, a temporary hold up tank, and then on to the building's radioactive liquid waste system.

Safety Features

In the event that the operator fails to shut off the supply of fresh leachant, a liquid level sensor installed in each tank provides an audible warning signal prior to overflow of the tanks. Level sensors also alert the operator when tanks are empty. If a leak develops in one or more tanks, the leachate would flow down the slightly graded floor and empty into the drain pits located below. A stainless steel curb located along the perimeter of the experimental facility is designed to retain any liquid spill.

EXPERIMENTAL PROCEDURES AND RESULTS

The majority of existing experimental data characterizing the leaching properties of solidified radioactive waste has been generated through the study of simulated laboratory scale specimens. Attempts have been made to standardize the methods used in conducting these leaching experiments so that results obtained may be evaluated on a common basis. The ANS 16.1 proposed standard "Measurement of the Leachability of Solidified Low-Level Radioactive Wastes"[2] is one such attempt and thus, was selected for use in the full-scale leaching experiment. In their recently published Technical Position on Waste Form,[3]

clarifying waste form stability requirements outlined in 10 CFR 61, the Nuclear Regulatory Commission (NRC) also specifies this method for leachability testing.

Leachate samples were analyzed by gamma spectroscopy. Cumulative fraction activity releases $(\Sigma a_n/A_0)$ were calculated for each leaching interval as the sum of the individual incremental releases (Σa_n) divided by the initial activity present (A_0) in the waste form for each radionuclide under consideration. These data are plotted as a function of cumulative leaching time for a total of 127 days in Figs. 2-5.

Leach test results are also calculated in terms of "leachability index" as recommended in the ANS 16.1 method. This index is a dimensionless figure of merit which quantifies the relative leachability for a given waste type-solidification agent. It can thus be used as a basis for comparison of the radionuclide retention capabilities of various solidification matrix materials. In addition, as this parameter is a function of actual leaching behavior it can be applied for the modeling of isotope migration in shallow land burial. On a plant scale, the leachability index can be employed as a means of demonstrating that waste forms meet minimum quality assurance standards. As a result, the NRC has issued recommended minimum leachability index specifications in support of 10 CFR 61 waste form stability requirements[3].

The leachability index for a given radionuclide, I, is given by:

$$L_I = 1/7 \sum_{n=1}^{7} \left[\log (\beta/D_I) \right]_n \qquad \text{(Eq. 1)}$$

where:

β = 1 cm^2/sec (defined constant)

D_I = effective diffusivity

The effective diffusivity is calculated from the leach test data by application of the following expression:

$$D_I = \pi \left[\frac{a_n/A_0}{(\Delta t)_n} \right]^2 (V/S)^2 T \qquad \text{(Eq. 2)}$$

where:

D_I = effective diffusivity (cm^2/sec)
V = volume of specimen (cm^3)
S = geometric surface area of specimen (cm^2)
T = time at the middle of leaching interval (sec)
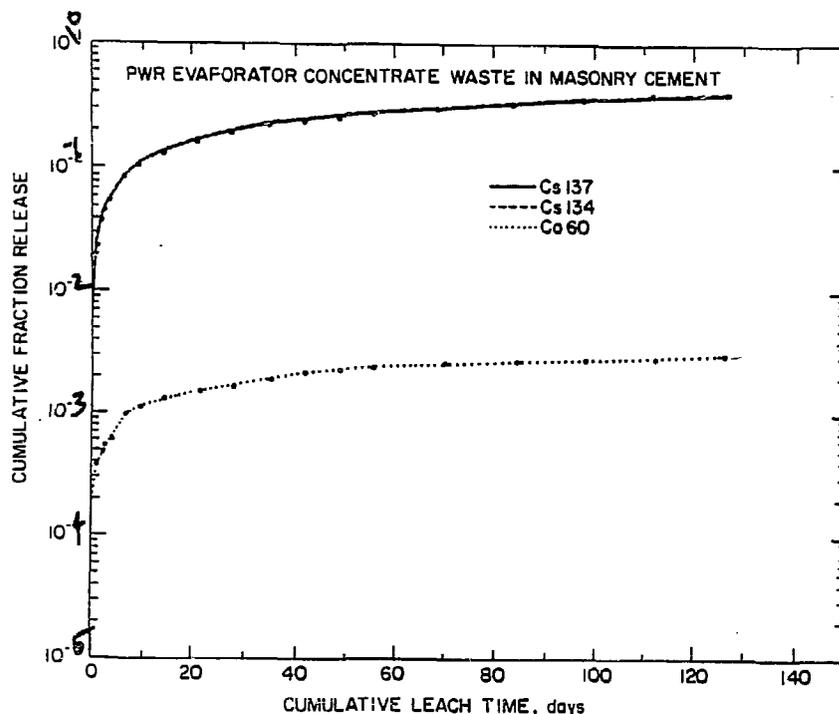$(\Delta t)_n$ = incremental leaching time (sec)

Fig. 2 Cumulative fraction release as a function of time for PWR evaporator concentrate waste in masonry cement (Leach Tank #1).
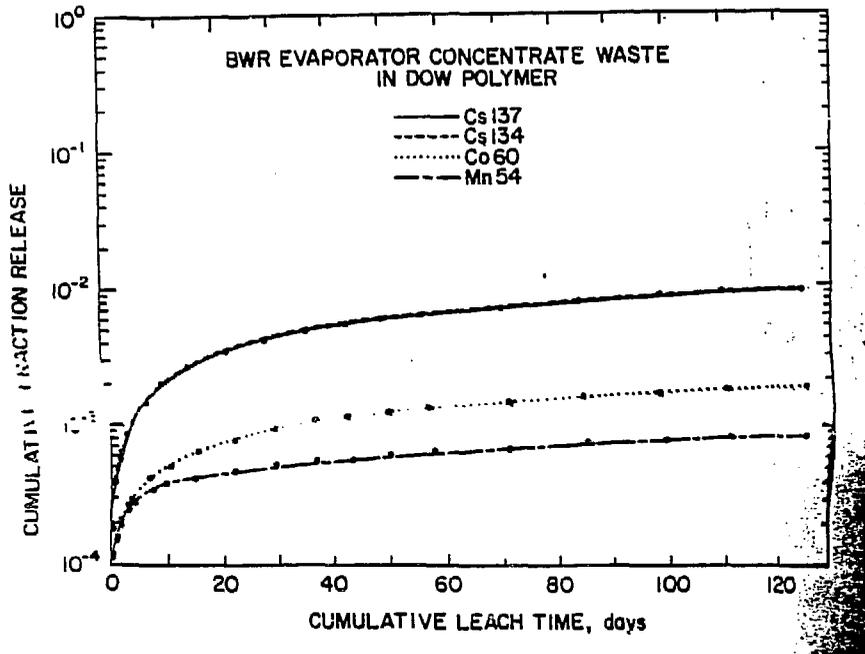
Fig. 3   Cumulative fraction release as a function of time for BWR evaporator concentrate waste in Dow polymer (Leach Tank #2).
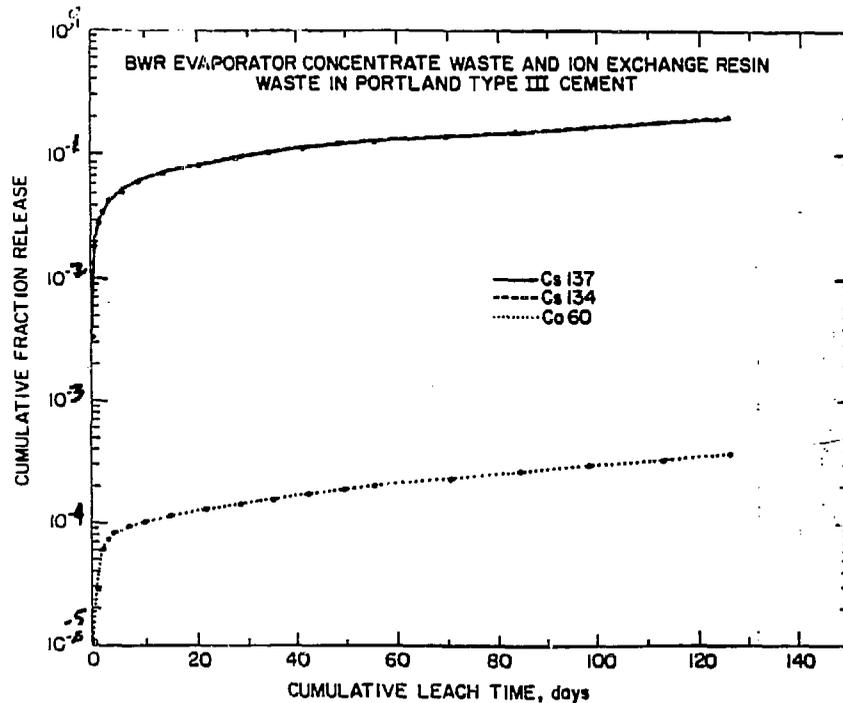

Fig. 4   Cumulative fraction release as a function of time for BWR evaporator concentrate + ion exchange resin waste in portland type III cement (Leach Tank #3).

Leachates from the BWR vinyl ester-styrene (Dow polymer) waste form contain the same isotopes as those present in cement leachates, with the addition of Mn-54. Leachability from the vinyl ester-styrene waste form was less element dependent than from cement waste forms, i.e., there was just over one order of magnitude difference separating isotopes displaying the greatest and least cumulative fraction release. This can be attributed to the fact that, unlike cement, the Dow polymer system does not chemically combine with the incorporated waste. During the solidification process, an emulsion is formed between the waste and binder which, upon curing, physically encapsulates the waste and retards leachability. Cumulative fractional releases of both cesium isotopes from the vinyl ester-styrene waste form were in the range of 10^{-2}, approximately one order of magnitude lower than those measured for an equivalent cement waste form. The Co-60 cumulatitive fraction release, however, was approximately 3 times greater for the Dow than for the equivalent cement waste form. Again, this difference is attributed to the different methods of waste encapsulation in the two waste forms.

Not all of the radionuclides present in each waste form are indicated in the leaching data. The radionuclides for which leaching data are not shown were not present in the leachate above detection limits (for reasonable counting times). This may be due to low leach rates, small initial concentration in the waste forms, or a combination of these factors.

REFERENCES

1. Neilson, R.M., Jr., P.D. Kalb, and P. Colombo, Lysimeter Study of Commercial Reactor Waste Forms: Waste Form Acquisition, Characterization and Full-Scale Leaching, BNL-51613, Brookhaven National Laboratory, Upton, NY, February 1983.

2. American Nuclear Society, Measurement of the Leachability of Solidified Low-Level Radioactive Wastes, Second Draft of a Standard, American Nuclear Society Standards Committee Working Group, ANS 16.1, April 1981.

3. U.S. NRC, "Technical Position Waste Forms," U.S. Nuclear Regulatory Commission, Washington, DC, May 1983.

4. Neilson, R.M., Jr., and P. Colombo, Waste Form Development Annual Progress Report, BNL-51614, Brookhaven National Laboratory, Upton, NY, September 1982.

5. Neilson, R.M., Jr., and P. Colombo, Solidification of Ion Exchange Resin Wastes, BNL-51615, Brookhaven National Laboratory, Upton, NY, August 1982.
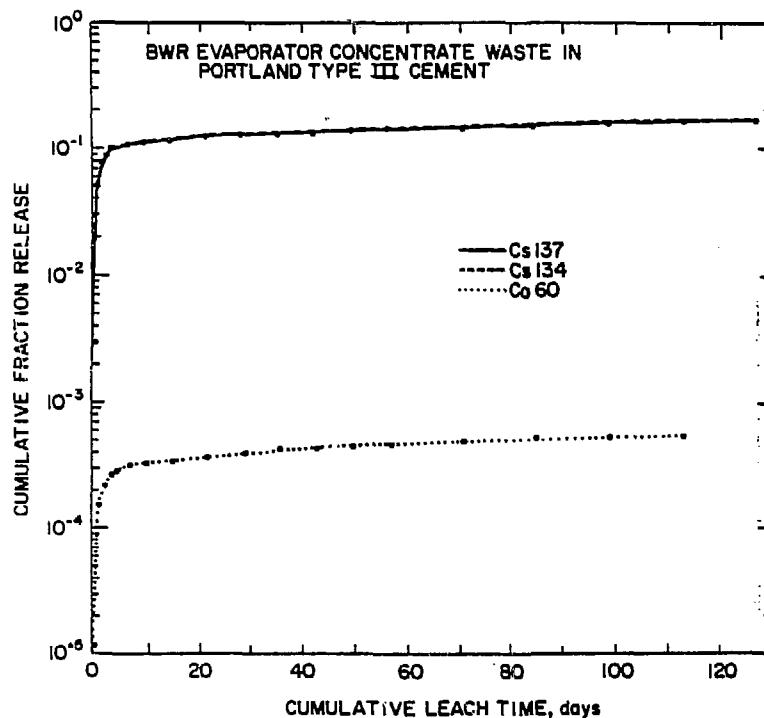
Fig. 5   Cumulative fraction release as a function of time for BWR evaporator concentrate waste in portland type type III cement (Leach Tank #4).

Values for the leachability index were calculated over the first seven leaching intervals as recommended[2] and are summarized in Table II. These data meet the proposed NRC minimum leachability index criteria ($\geq$ 6.0) within the limits of experimental error.

Table II

Full-Scale Leachability Index Values

Leaching Tank [a]	Leachability Index			
	L_{Co-60}	L_{Cs-137}	L_{Cs-134}	L_{Mn-54}
1	9.7	6.0	5.9	ND[b]
2	10.7	9.6	9.6	10.6
3	11.3	6.5	6.6	ND
4	11.1	6.2	6.2	ND

a) 1 = PWR concentrate waste in masonry cement
   2 = BWR concentrate waste in Dow polymer
   3 = BWR concentrate + ion exchange resin waste in portland type III cement
   4 = BWR concentrate waste in portland type III cement
b) ND = Mn-54 contained in waste form but not detected in leachates

CONCLUSIONS

Leachates from both BWR and PWR cement waste forms indicate measurable releases of Cs-137, Cs-134 and Co-60. In each case the cumulative fractional releases for both cesium isotopes were similar, as expected, and were between two and three orders of magnitude greater than that of cobalt. After 127 days of leaching, cumulative fractional activity releases of Cs-137 and Cs-134 for all cement waste forms tested was of the order of 10^{-1}. Cumulative fractional activity releases of Co-60 for these same waste forms ranged between 10^{-3} and 10^{-4}. The extremely low leachability of Co-60 is attributed to its chemical interaction within the cement matrix and the resultant formation of compounds of low solubility.

The full-scale data show that the relationship between cesium and cobalt leachability in cement is not closely tied to the waste composition (sodium sulfate or boric acid) in which the radionuclides are contained. Previous laboratory-scale studies involving the leaching of radioactive tracers from cement waste forms[4,5] have also shown similar relationships in the leachability of these isotopes. Thus, it is evident that the interactions between the radionuclides and matrix material predominate over the effects of waste composition in determining radionuclide leachability for cement waste forms.

DISCLAIMER