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by

Steven B. Oblath and Steven L. Hoeffner*

E. I. du Pont de Nemours and Company
Savannah River Laboratory
Aiken, South Carolina 29808

*ORAU Postdoctoral Participant

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E. I. du Pont de Nemours and Company
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ABSTRACT

The Savannah River Laboratory has been evaluating the leaching/migration behavior of commercial power reactor wasteforms by the use of lysimeters operated under field conditions at a humid site. These lysimeters model the conditions in actual burial trenches. Wasteforms comprising Portland cement, masonry cement, and vinyl ester-styrene polymer wasteforms were emplaced in the lysimeters in March 1982. Effluent water has been analyzed on a regular basis since that time. Cs-137, Sr-90, and/or Co-60 have been observed in the effluent water from the lysimeters, as well as in soil moisture samples collected from the unsaturated zone beneath the wasteforms. In March of 1984, horizontal cores were taken from one of the lysimeters containing a Portland cement wasteform to determine the vertical and radial profiles of radionuclides which might not have reached the lysimeter sump. Results from all of these sampling methods are discussed and interpreted.

INTRODUCTION

Lysimeter studies at the Savannah River Plant (SRP) are designed to measure radionuclide migration from well-characterized sources under actual burial ground conditions at a humid site. Three types of typical commercial power reactor low-level wasteforms were emplaced in lysimeters at SRP. The purpose of this program is to measure the leaching and migration rates of radionuclides from the wasteforms under shallow land burial conditions at a humid site. Use of lysimeters allows these studies to be carried out in the field under unsaturated conditions, while maintaining capability for a mass balance on the system.

The lysimeters, by acting as models of shallow land burial trenches, provide a technical basis for evaluating the performance of the wasteforms under actual burial conditions in a humid site. Identical wasteforms were subjected to immersion leach tests at Brookhaven National Laboratory (BNL). Comparison of these sets of data provides insight into how well saturated leach tests can predict actual behavior when buried.

STATUS AND ACCOMPLISHMENTS

The construction of the lysimeters was completed in October 1981, and ten wasteforms were emplaced in February and March 1982. An additional lysimeter, filled with soil but no waste, serves as a control. The ten wasteforms were acquired by Brookhaven National Laboratory (BNL) from power reactor sites. Source terms were determined and saturated leach tests were completed and are reported elsewhere.[1] Design, loading, operation, and sampling of the lysimeters has been described at the Fourth and Fifth DOE Low-Level Waste Management Program (LLWMP) Participants' Meetings.[2,3] Monitoring results through June 1984 were reported in the Sixth LLWMP Participants' Information Meeting.[4]

A full description of the wasteforms has been given elsewhere.[1] The three types of binders are Portland type III cement, masonry cement, and vinyl ester-styrene (VES) polymer. The Portland cement and polymer wasteforms contain sodium sulfate concentrate waste with or without spent ion exchange resin and are from a boiling water reactor. The masonry cement wasteforms are from a pressurized water reactor and contain boric acid wastes.

Analysis of both the effluent water and the water collected from the unsaturated zone immediately beneath the waste (using porous cup soil moisture samplers) has continued on a regular basis since January of 1983. Methods of analysis (including use of mixed-bed ion exchange resin columns) have been reported previously.[4] In the past year, Sr-90 concentrations in the effluent water have continued to increase. Cs-137 has been observed for the first time in effluent water samples, and showed a marked increase in the soil moisture samples from the lysimeters containing Portland cement wasteforms. Co-60, which has been observed in the effluent water since February 1983, was demonstrated to be largely anionic.

Analyses of soil samples collected in March 1984 from a horizontal coring of a lysimeter containing a Portland cement wasteform were completed. Both Co-60 and Cs-137 were observed in the cores. A similar coring was performed on a polymer-containing lysimeter in June 1985.

MONITORING RESULTS

Cobalt - 60

Effluent concentrations of Co-60 have increased to a maximum of 1030 pCi/L with the highest concentrations observed from the Portland cement wasteforms. By combining the observed concentrations (no correction for decay) with measured volumes of effluent water and source terms, annual fractional release rates have been calculated for each of the lysimeters. These values are given in Table 1. The values are obtained by counting the curies as they are released from the lysimeter over the stated time period, normalizing this to what would come out over a one year period, and dividing

by the original source term for the lysimeter.[4] It is important to point out that these values do not represent leaching of the wasteform, but are release rates from the entire waste/soil/water system of the lysimeter.

The two striking features of this table are the nearly constant release rates over the three year period and the differences in performance between the three types of wasteforms. The Portland and masonry cement wasteforms all show similar fractional release rates. The polymer wasteforms release about two orders of magnitude less cobalt to the sump. As will be discussed in a later section, this is quite different than what was observed by BNL in immersion leach tests.

By using cation and anion exchange resin beds in series rather than the mixed beds usually employed,[3] it has been determined that the cobalt which is released to the lysimeter sump is largely anionic in form. The data are given in Table 2. Switching the order of the resin beds indicates that the cobalt exists largely as a labile anionic complex. Other studies in our laboratory have shown that cationic cobalt should have an equilibrium soil/water distribution coefficient (K_d) greater than 1000 mL/g in the lysimeter system.[6] This large K_d for cationic cobalt indicates that unless all of the Co-60 leached from the wasteform to the soil/water system is anionic, only a portion of the cobalt is mobile.

The anionic cobalt is most likely in the form of an inorganic complex or chelated compound. The wastes are typical commercial power reactor wastes, so it is expected that organic chelating agents from decontamination reagents are present in the sodium sulfate concentrate wastes. Related studies involving Portland cement and VES polymer wasteforms have shown that most of the commonly used decontamination agents are leached from polymer wasteforms one to two orders of magnitude more slowly than from the cement wasteforms.[5] Although there is no data on the organic components of these particular wasteforms, this is a reasonable explanation for the difference in the Co-60 release rates.

Strontium - 90

Strontium has continued to be detected in low concentrations in the effluent water from three of the lysimeters containing polymer wasteforms. The Sr-90 first appeared between September 1983 and March 1984. Concentrations in the last year have increased to a maximum of 1.4 pCi/L. In addition, the lysimeters which contain cement wasteforms have sporadically shown concentrations as high as 2.4 pCi/L, but these have not been consistently observed and are believed to be false positives.

Release rates are more difficult to calculate for Sr-90 than for Co-60 as there are small amounts of Sr-90 observed in the control lysimeter effluent water. Measurements are also not made as often for Sr-90 as for Co-60. When corrected for this observed background, fractional release rates for the polymer wasteform lysimeters of 2-5 x 10^{-7} per year are

observed for the 17 month period for which there is data. If the spikes in the data for the Portland cement lysimeters are assumed to be real, then the release rates are approximately 10^{-8} per year. These lower values are expected, as strontium should substitute for calcium in the cement and would not be available for leaching.

The calculated release rates for Sr-90 of 10^{-7} per year for the polymer wasteform lysimeters are higher than the rate for Co-60. This is consistent with a lower K_d for strontium[6] and the fact that no complexation should be occurring. However, because Sr-90 is sorbed on the soil (unlike the anionic cobalt species observed in the sump) it is likely that the release rate will increase over time rather than remain constant as observed for Co-60. This is based on the the soil acting as a chromatographic column and the Sr-90 undergoing breakthrough.

Cesium - 137

Concentrations of Cs-137 were observed in the effluent water from one lysimeter for the first time in May 1985. This lysimeter contains a Portland cement wasteform comprising sodium sulfate concentrate waste, but with no spent resin. Concentrations up to 19 pCi/L have been observed. Elevated levels of Cs-137 had been observed in the soil moisture samples up to January 1984 when the samplers failed. Other Portland cement wasteform lysimeters showed significant increases in Cs-137 concentrations in the soil moisture samples in July 1984, so a breakthrough of Cs is not unexpected.

Based on such limited data, a fractional release rate for Cs cannot be calculated. However, based on the design of the lysimeter, the leading edge of the cesium has migrated at an average rate of one foot per year. With a high K_d for cesium in the native soil[6], it is surprising that the cesium has moved this fast. Channeling of the water/contaminant flow and/or settling of the wasteform are suspected causes for the cesium appearance.

COMPARISON TO BNL TESTS

During 1982 and 1983, BNL performed static, immersion leach tests on wasteforms identical to those in the SRL lysimeters.[3] These tests were carried out for 316 days on full scale wasteforms. The Portland and masonry cement wasteforms released cesium about 200 times faster than cobalt in these immersion tests. The polymer wasteforms released all of the species within a factor of 5 of the same rate when expressed as fraction per day.

The BNL results[1] are summarized in Table 3 as relative rates with the leach rate for each element from VES polymer defined as 1. The leach rates (fraction per day) for cobalt were within a factor of three for all three types of waste. Cesium leached at least an order of magnitude slower from the polymer wasteform than from either of the concrete wasteforms. No leach rates for strontium were determined, but based on the substitution of

strontium for calcium in the cement matrix, Sr is expected to be leached more slowly from the cement than from the polymer wasteforms.

For Co-60, the lysimeters show significantly different results than the immersion tests. Based on the concentrations observed in the effluent water, fractional releases from the lysimeters containing the polymer wasteforms are generally two orders of magnitude less than from the cement wasteforms. This cannot be predicted using the immersion test results alone, and may be due to anionic cobalt species migrating to the sump more rapidly than the cationic species. The leach rate of chelating agents from the wasteforms may also be a factor.[5]

The soil moisture samples from three of the polymer wasteform lysimeters indicate that the quantity of cobalt released from the polymer wasteforms is less than that from the Portland cement wasteforms by a factor of 10 to 30. The one polymer wasteform which contains resin shows a concentration only a factor of three less than the cement wasteforms, but it also has a factor of two higher Co-60 source term than any other wasteform. It appears that the relative release rates for Co-60 as measured in immersion leach tests may not accurately indicate what will happen when the waste is emplaced in the soil system.

Cesium does show the same trend in the lysimeters as in the immersion tests. Fractional release rates cannot be calculated since cesium has just recently been observed in the sumps. The soil moisture samples show cesium from only the cement wasteform lysimeters. This is consistent with the immersion leach test results (Table 3). Strontium release is observed only from the polymer wasteform lysimeters. This was expected due to incorporation of the strontium into the cement matrix in the cement wasteforms.

CORING RESULTS

In March of 1984, horizontal soil cores were collected beneath a Portland cement wasteform in one of the lysimeters. Cores were collected from both the upper and lower sampling ports across the entire six foot diameter of the lysimeter. The initial placement of the wasteform would have placed these cores 12 and 22 inches below the wasteforms, but settling appears to have reduced these two depths. The objective of this coring was to determine both a vertical and radial profile of the migrating radionuclides in the lysimeter after two years of operation.

Analyses were performed by drying the soil and obtaining a gamma PHA spectum for a known weight of the soil. Only Co-60 and Cs-137 were observed in the samples. Standards were prepared in about the same concentration by adding tracers to clean soil samples, drying them, and counting the standards in the same geometry used for the core samples. The calibration curves were linear.

Figures 1-3 show the concentration profiles of Cs-137 in the upper core, and Co-60 in both cores. Cesium is sufficiently retarded by the soil that only trace amounts are observed in the lower core. During the collection of the upper core, difficulties were encountered when the sampling device appeared to scrape the bottom of the wasteform. Inspection of the samples showed small pieces of concrete, which were removed from the samples prior to drying and counting the soils. Pieces of concrete should only be observed in the soil samples if the wasteform had settled 12 inches over the two year period, or if it were emplaced at the wrong depth. Either way, since only trace amounts of cesium were observed in the lower core, the data indicate that the leading edge of Cs-137 migrated about 10 inches in a two year period. The cesium profile also indicates an off-center placement of the waste, with the majority of the activity occuring in a 24 inch region. This agrees well with the 22 inch diameter of the wasteform.

Unlike cesium, significant concentrations of Co-60 are observed in both the upper and lower cores. The lower core shows a 22-24 inch band of high activity located at approximately the same distance into the lysimeter as was observed for cesium. The upper core shows elevated Co-60 activities at shorter distances into the lysimeter. This is believed to be due to contamination of one sample taken from 12 inches into the lysimeter during the coring process. Other than for this one sample, the results appear to be as expected.

The Co-60 concentrations in the lower core of up to 4 nCi/g are about a factor of 2 lower than in the upper core, but significantly below the 300 nCi/g maximum observed for cesium. This is consistent both with a greater mobility for the cobalt, and a lower fractional leach rate from the waste (as observed in the immersion leach tests). If the cobalt, which is present in the waste at a higher concentration, was leached at the same rate as the cesium, then the cobalt concentrations in the soil should be significantly higher.

CONCLUSIONS

The data collected during the first three years of this lysimeter experiment, summarized in this and previous papers,[3,4] have demonstrated that the wasteforms do release radionuclides under realistic burial conditions in a humid site. However, the low fractional release rates for all of the lysimeters indicate that the waste/soil systems are performing excellently.

In the short term, it appears that cement based wasteforms are preferable if one's goal is to minimize the release of Sr-90, however this will be at the expense of releasing greater amounts of cobalt and cesium. If one's purpose is to minimize the release of Co-60 and Cs-137, at the expense of Sr-90, than it may be preferable to use the VES polymer wasteforms. With the short half life of Co-60, it is probably more important to be concerned with strontium and cesium.

Probably the most important conclusion of the test is in the comparison of the immersion leach results to the leaching in the burial environment. The differences noted for Co-60 leaching indicate that what is observed in immersion leaching may not represent what is to be expected in the field. This is an area in which work is continuing to resolve the differences, and to understand the causes and their effects on release projections.

FUTURE WORK

Horizontal cores from a lysimeter containing a polymer waste form were collected in June 1985 and will be analyzed in the coming year. The results will help answer the lingering question of whether the polymer wasteforms release less cobalt than the cement based wasteforms, or if similar amounts are released, but the material is partitioned differently between the soil and water portions of the system. The monitoring of the soil moisture samples and the effluent water will continue.

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TABLE 1. Co-60 FROM SPECIAL WASTE FORM LYSIMETERS

Matrix	Lys #	Annual Fraction Released		
		Jan-June 83	Jul 83-Jun 84	Jul 84-May 85
Type III Cement	44	2×10^{-6}	3×10^{-6}	2×10^{-6}
bottoms	48	3×10^{-6}	2×10^{-6}	1×10^{-6}
Type III Cement	47	2×10^{-6}	6×10^{-6}	2×10^{-6}
bottoms + resin	49	8×10^{-8}	1×10^{-6}	2×10^{-6}
Masonry cement	51	7×10^{-6}	4×10^{-6}	5×10^{-7}
boric acid	52	1×10^{-5}	8×10^{-6}	2×10^{-6}
Polymer	42	2×10^{-8}	5×10^{-8}	4×10^{-9}
bottoms	46	2×10^{-7}	1×10^{-7}	4×10^{-8}
	43	----	4×10^{-8}	8×10^{-9}
Polymer	41	8×10^{-8}	7×10^{-8}	2×10^{-8}

TABLE 2. Co-60 SPECIATION STUDIES

	Polymer Wasteform	Portland Cement Wasteform			
Resin Bed Order	a/c	c/a	a/c	a/c/n	a/c/n
% Cationic	0	18	0	8	41
% Anionic	100	82	100	92	58
% Neutral	-	--	-	0	1

Resin beds were run in series in order indicated
a = anion exchange resin
c = cation exchange resin
n = alumina for sorbing neutral species

TABLE 3. RELATIVE LEACH RATES
IMMERSION TESTS AT BNL

	Cobalt	Cesium
VES Polymer	1 (defined)	1 (defined)
Masonry Cement	1.5	40
Portland Cement	0.5	10

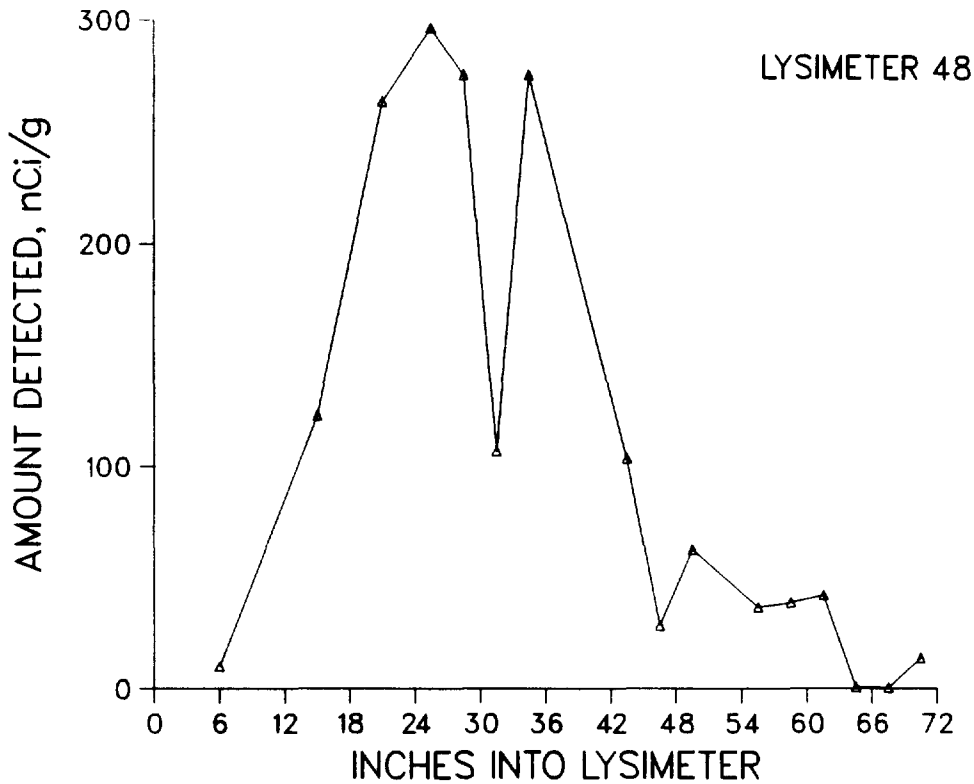

Figure 1. Cesium-137 concentration profile in the upper soil core.

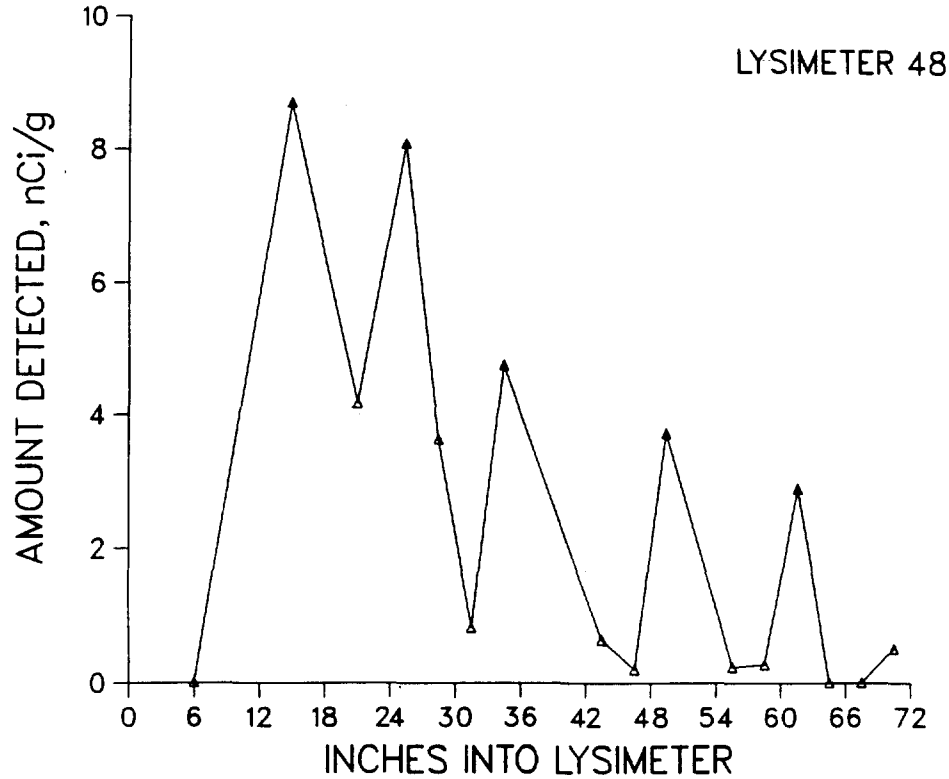

Figure 2. Cobalt-60 concentration profile in the upper soil core.

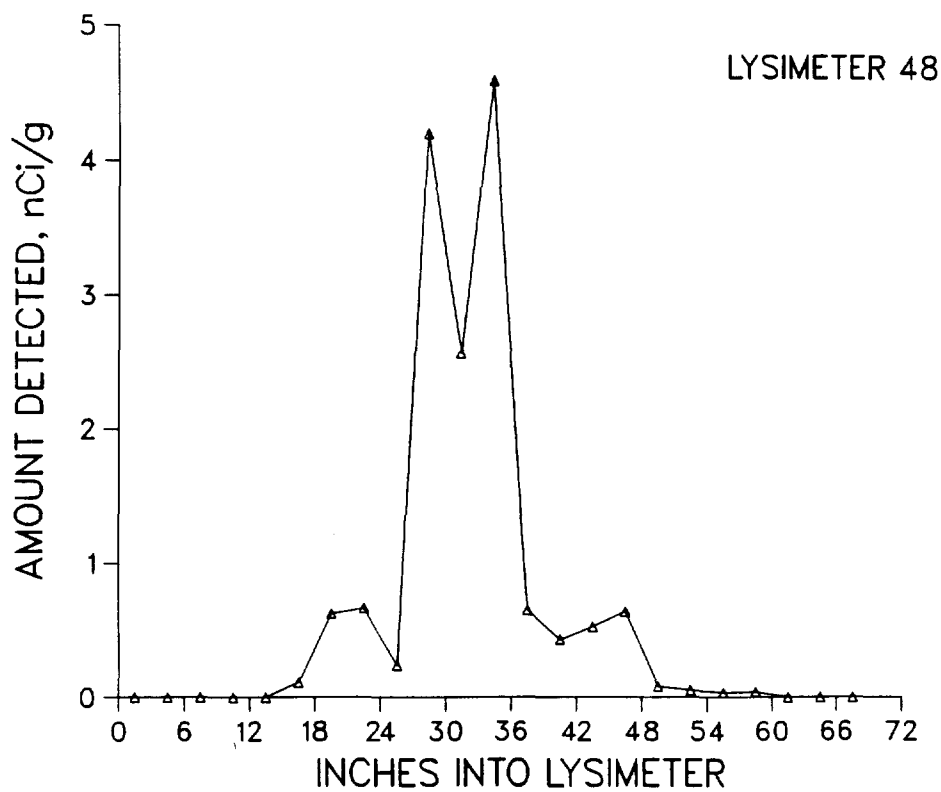

Figure 3. Cobalt-60 concentration profile in the lower soil core.