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RELEASE OF ORGANIC REAGENTS FROM SOLIDIFIED DECONTAMINATION WASTES*

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ABSTRACT

In order to provide technical information needed by the U.S. Nuclear Regulatory Commission to evaluate the adequacy of near-surface disposal of decontamination wastes, Brookhaven National Laboratory has measured the release of organic reagents from solidified simulated decontamination wastes. The waste streams consisted of either mixed-bed ion-exchange resins or anion exchange resins equilibrated with EDTA, oxalic acid, citric acid, picolinic acid or simulated LOMI decontamination reagent. These simulated resin wastes were solidified in either cement or vinyl ester-styrene. Samples were tested by a fixed interval leach procedure or according to the standard ANS 16.1 procedure. The leachability indices, which were calculated as prescribed in ANS 16.1, varied with leach period for some of the composites tested.

INTRODUCTION

Light water reactors may require one or more chemical decontaminations to achieve their designed lifetimes. Primary system decontamination is designed to lower radiation fields in areas where plant maintenance personnel must work. Commercially available chemical decontamination processes contain organic acids and chelates which will be present in the subsequent radwaste. In the past, the problem of enhanced migration of radionuclides away from trenches used to dispose of low-level radioactive waste, has been linked to the presence, at the disposal unit, of chelating or complexing agents such as those used in decontamination processes. Since the quantity of reagent employed in a full system decontamination is expected to be large (200-25,000 kg), the potential for enhanced migration of radionuclides needs to be addressed.

Brookhaven National Laboratory has been studying the release of organic reagents from solidified decontamination wastes in order to provide technical information needed by the U.S. Nuclear Regulatory Commission to evaluate the adequacy of near-surface disposal of decontamination wastes. Laboratory scale waste forms containing simulated dilute process decontamination wastes solidified in cement and vinyl ester-styrene were leach-tested, and a leachability index for the organic acid was calculated according to the procedure given in the standard test, ANS 16.1.[1]

MATERIALS AND METHODS

The following reagents were used in the testing: ethylenediaminetetraacetic acid (EDTA), oxalic acid (OA), citric acid (CA), EOC (an equimolar mixture of EDTA, OA and CA), picolinic acid (PA), formic acid (FA) and simulated LOMI reagent (an equimolar mixture of PA and FA was used). Two types of anion-exchange resins were used: IRN-78 (Rohm and Haas), a polystyrene strong base anion exchange resin in the ^-OH form and IONAC A-365 (Sybron), a polyacrylic weak based anion exchange resin with exchange groups in the free base and ^-OH form. Samples made with mixed bed resin had IRN-77 (Rohm and Haas) as the cation exchange resin used in the H^+ form. Enough IRN-77 was used to produce a weight ratio of two parts anion exchanger to one part cation exchanger. The anion exchange resins were equilibrated with an amount of acid that would exchange with 50% of the available sites.

Portland I cement was used to prepare laboratory scale waste forms of both mixed bed and anion exchange resin wastes. Prior to solidification of either the mixed bed or anion resin samples, the resin slurry was treated with sodium hydroxide as a means of adjusting the pH to 12. Samples containing LOMI reagent on IONAC A-365 resins were treated with hydrochloric acid to pH = 5.5 in order to produce a mixable cement/resin composite. Simulated decontamination wastes containing anion exchange resins were also solidified in vinyl ester-styrene (VES). Resins equilibrated with EDTA or EOC were treated with hydrochloric acid to adjust the pH to ≈9.5 prior to solidification. All of the forms prepared for leach testing were a nominal 2-in.-diameter by 4-in.-long right cylindrical solid. Details of the solidifications are given in Reference 2 and references therein.

Three different leach schedules were used in this work. Schedule A was a 90-day leach test in which all leach intervals were 7 days ±1 day. Schedule B followed the time table given in a draft (November, 1982) of ANS 16.1. Following a 30-second rinse, the leachate was changed after 2 h, 7 h, 24 h, 48 h, 72 h, and 96 h. (A leachate change after 120 h, as specified by ANS 16.1, was omitted.) Thereafter, the leachate was changed every 7 days for a total of 95 days. Schedule C followed the leach test described in the February, 1984 draft of ANS 16.1. Again, following a 30-second rinse, the leachate was changed after 2 h, 7 h, 24 h, 48 h, 72 h, 96 h, and 120 h. Three additional leachate changes are made after 19, 47, and 89 days, ±1 day, of immersion.

Procedures for determining the concentrations of organic acids in leachate solutions have been described elsewhere.[3] The quantity of organic acid in each leachate sample was used to determine the effective diffusivity. In all cases, the fraction leached from the samples was less than 20% of the quantity of organic acid initially present and thus the effective diffusivity, D (cm^2/s), was calculated using the equation given in ANS 16.1. A leachability index (L)

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was calculated as prescribed for each leach period by the ANS formulation:

$$L = \log (\beta/D)$$

where β is a constant (1 cm^2/s) and D is the effective diffusivity.

RESULTS AND DISCUSSION

The average leachability indices for the release of the organic acids from cement solidified resin samples are summarized in Table I. The average leach index is specific for the different reagents in the forms. Further, the measured values are reproducible among replicate samples. Only small differences in L and the bias on L are observed for samples having the same reagent but different resin types (or different leach test procedures). The percent bias given in the table indicates that the average of the first four leach indices is that percentage larger (+ sign) or smaller (- sign) than the average of the last four leach indices. The ranges of the leach indices are also given with the range percent in parentheses.

Figure 1 shows the cumulative fraction release (CFR) of EDTA and PA, both on mixed beds ion-exchange resins from cement forms. The plots of CFR vs the square root of leach time appear to follow a linear relation suggesting that the release of the acids are diffusion controlled.[3] The slopes of the two lines are different indicating different effective diffusivities of each acid. Differences in the diffusivities and corresponding leachability indices are most likely a consequence of the organic acid being leached from the forms since the samples were prepared using the same formulations, cured for about the same time and leach tested according to schedule A.

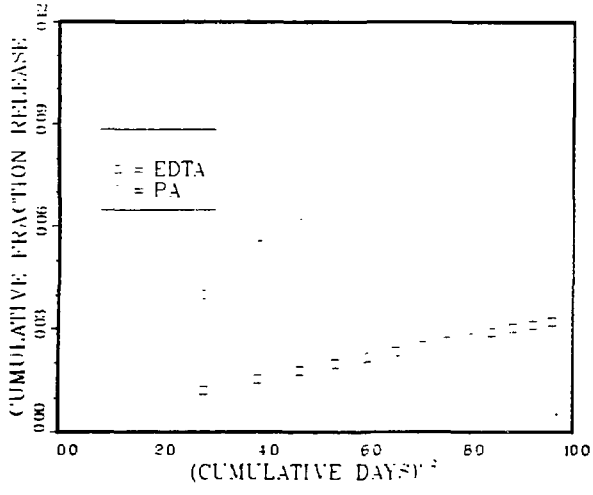

Figure 1. Plot of CFR vs the square root of time for the release of EDTA and PA. The samples tested were EDTA on mixed bed resins and PA on mixed bed resins each solidified in cement.

The leachability of EDTA was measured from cement solidified wastes containing either EDTA alone on mixed bed and anion exchange resins or a mixture of EDTA, oxalic acid and citric acid (EOC) on mixed bed resins and anion exchange resins. The average leach index for EDTA was not significantly affected by the presence of other acids in the waste form and varied from 10.1 for EDTA/mixed bed resins to 10.6 for EOC samples. Figure 2 is a plot of the cumulative fraction release for EDTA vs the square root of time for forms of EOC on mixed bed resin. The data are not linear as expected for diffusion-controlled release. The data indicate that the release of EDTA is decreasing as leach time progresses. This general trend was observed for other forms containing EDTA and leached according to the same schedule.

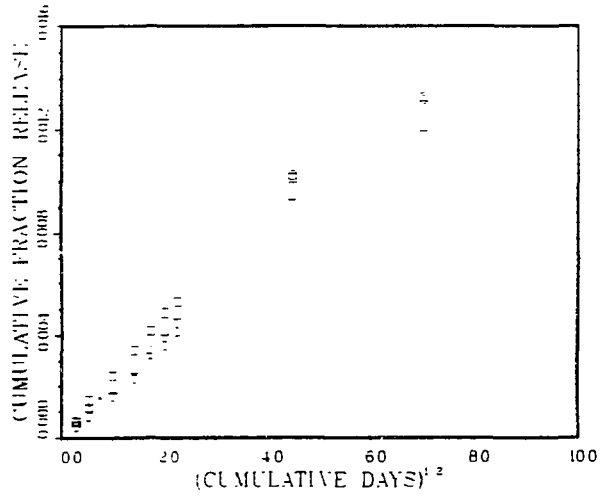

Figure 2. Plot of CFR vs square root of time for the release of EDTA from cement forms containing EOC on anion exchange resins. Data for three replicates are shown.

Oxalic acid and citric acid release were also measured from EOC forms (Table I). There appeared to be little affect on the release of either acid due to resin type. However, only limited data were available because the concentrations of the acids in the leachates were close to the detection limit for the analytical method. The citric acid release appears to be the same as that for EDTA whereas, oxalic acid appears to leach more slowly than EDTA.

Figure 3 is a plot of CFR vs square root of leach time for the release of picolinic acid from cement forms containing LOMI reagent on mixed bed resins and on anion exchangers. The data sets are similar but a small difference in the leach behavior can be seen in the data collected during the first five days of leaching. A difference is also found in the bias of the average leach index. For the release of PA from the LOMI mixed bed samples, L = 8.8, +8%; whereas, L = 8.7, +1% for the release of PA from LOMI on anion exchangers alone. The variation of CFR during the first week of the two tests is not attributed to differences in the leach schedules since they are the same during this period. Differences in the release of picolinic acid may be due to the differences in waste form compositions. Mixed bed resins were used in one form and only anion resins in the other. Also, the forms had cured for different periods before testing (mixed bed, 73 days; anion bed, 31 days). These factors may also have influenced the results.

TABLE I

Leach Test Data of Simulated Decontamination Wastes Solidified in Portland I Cement

Reagent[a]	Ion-Exchange Resins in Form	Leach Schedule[b]	Leach Index[c] Range[d]	Leach Index[c] Average[e]
EDTA	mixed bed	A	9.7 - 10.3 (6%)	10.1 +1%
			9.7 - 10.3 (6%)	10.1 +1%
EDTA	anion	C	9.9 - 11.1 (11%)	10.3 +5%
			10.0 - 11.0 (10%)	10.3 +5%
			10.1 - 10.9 (8%)	10.4 +4%
EDTA (EOC)	mixed bed	C	10.2 - 11.4 (12%)	10.6 +7%
			9.9 - 11.3 (13%)	10.5 +7%
			10.1 - 11.3 (11%)	10.5 +6%
EDTA (EOC)	anion	C	10.1 - 11.3 (12%)	10.5 +5%
			10.2 - 11.2 (9%)	10.6 +6%
			10.2 - 11.2 (9%)	10.6 +2%
OA (EOC)	mixed bed	C	11.6 - 12.4 (7%)	12.0
			10.2 - 12.4 (19%)	11.3
OA (EOC)	anion	C	10.9 - 11.0 (1%)	11.0
CA (EOC)	mixed bed	C	9.7 - 11.1 (14%)	10.3
			10.0 - 11.3 (3%)	10.2
			9.1 - 11.8 (27%)	10.1 +7%
CA (EOC)	anion	C	9.5 - 10.4 (10%)	9.8 +2%
			9.6 - 10.3 (6%)	9.9
			8.9 - 10.2 (13%)	9.8
PA	mixed bed	A	8.8 - 9.2 (4%)	9.1 +3%
			8.8 - 9.2 (4%)	9.2 +3%
PA	anion	C	8.9 - 9.6 (7%)	9.2 -1%
			8.9 - 9.6 (7%)	9.2 -1%
			8.9 - 9.6 (7%)	9.2 -1%
PA	anion	A	8.9 - 9.3 (4%)	9.1 +2%
			8.9 - 9.3 (4%)	9.1 +2%
PA (LOMI)	mixed bed	B	8.3 - 9.1 (9%)	8.8 +8%
			8.3 - 9.1 (9%)	8.8 +7%
			8.3 - 9.1 (9%)	8.8 +8%
PA (LOMI)	anion	C	8.6 - 9.0 (5%)	8.7 +1%
			8.6 - 9.0 (5%)	8.7 +0%

[a] Reagent indicates species measured in leach test. In parentheses is the reagent in form if more than one organic acid was present.
[b] See text for description of leach schedules.
[c] Leach index is calculated according to the method given in ANS 16.1. Data are listed for replicate tests.
[d] Value in parentheses is the leach index range relative to the average leach index.
[e] Values given are the average leach index and the bias. No bias is given when fewer than six test data were used for the average.

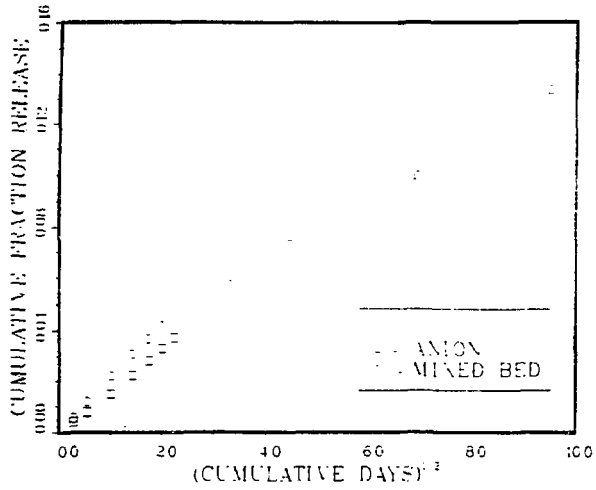

Figure 3. Plot of CFR vs square root time showing the release of picolinic acid from cement forms containing LOMI reagent on ion-exchange resins. o is for LOMI on mixed bed resins with leaching according to schedule B and □ is for LOMI on anion exchangers with leaching according to schedule C. Data from only one replicate of each composite tested are shown.

Although the average leach index is specific for the release of reagents solidified in cement, variations in L during the test appear to be influenced by the types of resins in the form. Figure 4 is a plot of the leach index for picolinic acid release from samples of LOMI reagent on mixed bed resins leached according to schedule B. During the first 20 days of the ANS 16.1 test, there is a gradual increase in the leach index, after 40 days, a constant value of the leach index is reached and maintained throughout the remainder of the 81-day test. A somewhat different behavior was observed for the release of picolinic acid from samples of PA on anion exchange resins and leached according to schedule C (Figure 5). The leach index decreased during the first week of leachate sampling and then increased during the remainder of the test. The temporal change in the leach index for the samples of LOMI reagents on anion exchange resins was similar to that of PA/anion exchangers although the values of L for the two samples were different.

The leachability of EDTA from simulated resin wastes solidified in vinyl ester-styrene (VES) was measured and the average leach indices are listed in Table II. The release of EDTA from VES samples is slower than from cement forms. Similarly, only about 0.02 to 0.03% of the EDTA was released from the VES forms compared to about 3% of the EDTA from the cement sample. The quantity of EDTA in the 30-second rinse solution at the start of the leach test, was more than twice that released over the remainder of the leach test. This acid is believed to be present in the surface moisture observed on the VES forms when they were removed from their containers. However, during the 88-day leach test, less than 1% of the EDTA in the form was released.

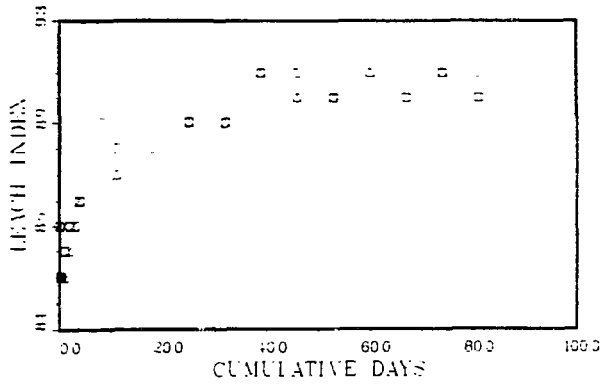

Figure 4. Leach index vs leach time for release of picolinic acid from forms containing the LOMI reagent on mixed bed resins of IRN-77 and IONAC A-365. Data for each of the three replicates are shown.

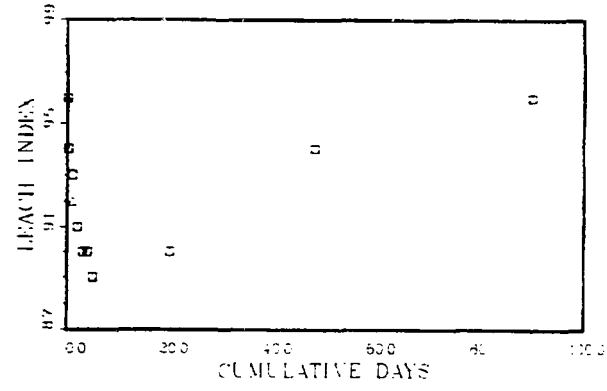

Figure 5. Leach index vs leach time. The leach index is for the release of picolinic acid from forms containing picolinic acid on IRN-78 anion exchange resins. Data for each of the three replicates are shown.

The average leach indices for PA from VES solidified LOMI reagent on anion exchange resins are 9.1+3%, 9.0+4% and 9.0+3% (Table II). Unlike EDTA, the leachability of PA from VES forms is similar to that from cement samples. A plot of CFR vs the square root of time for LOMI/VES samples is shown in Figure 6. Although there is some deviation from linearity, the data show a similar behavior to PA release from LOMI/cement samples (Figure 3).

TABLE II

Leach Test Data for Simulated Decontamination Wastes Solidified in VES

Reagent[a]	Ion-Exchange Resins in Form	Leach Schedule[b]	Leach Index[c] Range[d]	Average[e]
EDTA	anion	C	12.7 - 13.6 (7%)	13.1
			12.3 - 13.2 (7%)	12.9 +2%
			12.6 - 14.3 (13%)	13.4 -1%
PA (LOMI)	anion	C	8.7 - 9.4 (8%)	9.1 -3%
			8.6 - 9.3 (8%)	9.0 -4%
			8.5 - 9.3 (9%)	9.0 -3%

[a]Reagent indicates species measured in leach test. In parentheses is the reagent in form if more than one organic acid was present.
[b]See text for description of leach schedules.
[c]Leach index is calculated according to the method given in ANS 16.1. Data are listed for replicate tests.
[d]Value in parentheses is the leach index range relative to the average leach index.
[e]Values given are the average leach index and the bias. No bias is given when fewer than six test data were used for the average.

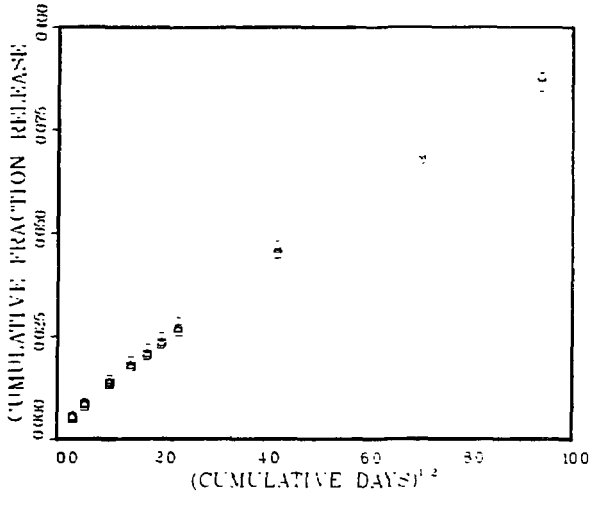

Figure 6. Plot of CFR vs square root of time for the release of picolinic acid from VES solidified wastes containing LOMI reagent on anion exchange resins. Three replicate data sets are shown.

CONCLUSIONS

The leachability indices measured for the release of organic acids from both cement and VES solidified wastes are specific for the reagent in the form. The leach index, which indicates the rate of release of an organic acid from a form, is not greatly affected by the resin type. However, changes in the leach index with leach period appear to be dependent on the resin type in the form. Based on individual leach test data, it was observed that, in general, the leach index increases with time (release of acid decreases), which may be a desirable behavior. Plots of CFR vs square root of leach time show ranges of data that may be approximated by a linear relation. Such an analysis suggests that the release of the organic reagents from the waste forms may be diffusion-controlled.[4]

The total amount of reagent released from the cement forms ranges from ≈3% for EDTA to ≈13% for PA from forms containing LOMI reagent. Assuming a homogeneous distribution of resin/reagent in the form, these quantities of reagent are present in a surface layer of the form that is only ≈0.3 mm to 1.5 mm thick. These results may not be indicative of the release of reagents from the entire form. Leach tests to longer times are believed necessary to help establish the mechanism for release of the acids from the forms. Uncertainty in the release mechanism can make an extrapolation of the leach index to large forms misleading. In turn, source terms calculated for modeling efforts may be poorly defined.

Releases of organic reagents from solidified waste forms appear too low. The apparent diffusivities are normally less than or equal to those observed for Cs releases from cement solidified forms. However, since the quantities of reagents that might be disposed of in a shallow land burial site in the future are large, even with solidification, site limits on total quantities may be desirable. At this time, the data base on releases, and their impact on potential sites, does not warrant a firm conclusion for or against such a site limit. The interplay of site and waste characteristics need to be examined to determine what, if any, further requirements are necessary.

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