

EFFECT OF LEACHANT CHEMICAL COMPOSITION AND PH ON LEACHABILITY OF CEMENT-SOLIDIFIED DECONTAMINATION ION-EXCHANGE RESIN WASTE*

Charles V. McIsaac
Idaho National Engineering Laboratory
P.O. Box 1625,
Idaho Falls, Idaho, 83415

ABSTRACT

This paper presents results of a leaching study conducted at the Idaho National Engineering Laboratory (INEL) on cement-solidified decontamination ion-exchange resin wastes collected from two operating commercial light water reactors (LWRs). Seventeen small-scale waste-form specimens collected during solidifications performed at the Brunswick Steam Electric Plant- Unit 1 and at the James A. FitzPatrick Nuclear Power Station were leach-tested following the ANS 16.1 procedure. Samples of untreated resin waste collected from the solidification vessels were analyzed for concentrations of radionuclides, selected transition metals, and chelating agents to determine the quantities of these species in the waste-form specimens. In order to assess the effect of leachant chemical composition and initial pH on leachability, the small-scale waste form specimens were leach-tested in deionized water, synthetic seawater, and three synthetic ground waters having pH between 4.2 and 10.4. Average incremental fraction release rates, cumulative fraction releases, and leachability indexes of radionuclides, metals, and chelating agents are presented.

INTRODUCTION

The U.S. Code of Federal Regulations 10 CFR Part 61, "Licensing Requirements for Land Disposal of Radioactive Waste," establishes a waste classification system based on the radionuclide concentrations in wastes. The regulation requires that higher-activity wastes, which are designated Class B and C wastes, be stabilized prior to disposal at a land burial site. Test procedures to demonstrate stability and leachability of waste forms are described in the Nuclear Regulatory Commission (NRC) Low-Level Waste Management Branch "Technical Position on Waste Form"(1). The Branch Technical Position specifies that small-scale waste-form specimens be prepared and tested to certify the stability and leachability of full-scale waste forms. It stipulates that these small-scale specimens should have compressive strengths of at least 3.4×10^5 Pa (50 psi) when tested in accordance with the American Society for Testing and Materials standard ASTM C39, "Compressive Strength of Cylindrical Concrete Specimens"(2) and leachability indexes greater than 6 when leach-tested for a minimum of 90 days in accordance with the American National Standard ANSI/ANS 16.1, "Measurement of the Leachability of Solidified Low-Level Radioactive Wastes by a Short-Term Procedure"(3).

The NRC Low-Level Radioactive Waste Research Program Plan (4) defines a strategy for conducting research on issues of concern to the NRC in its efforts to ensure the safe disposal of low-level radioactive waste. Leaching studies performed at the INEL have been conducted to help establish a data base on the stability and leachability of

waste forms representative of waste forms commonly generated at operating commercial power stations.

The present study is a continuation of studies (5,6) previously performed that determined the compressive strength and leachability of cement-solidified evaporator concentrates and decontamination ion-exchange resin beads leached in deionized water. During the current study, untreated resin wastes and small-scale waste-form specimens were collected from solidification vessels at the Brunswick-1 and FitzPatrick Stations, which had been decontaminated using the AP/Citrox and LOMI processes, respectively. Because cation and mixed-bed resin wastes generated at Brunswick-1 were solidified separately, both cation and mixed-bed resin waste and waste-form specimens were obtained from the power station. Only mixed-bed resin waste was solidified at the FitzPatrick Station. Ion-exchange bead resin wastes at both power stations were solidified in Portland type I cement. Two specimens collected from the FitzPatrick Station were baked for 4 h at 49°C to allow an assessment of whether or not the high temperatures associated with the cement hydration exotherm inside the full-scale liners affected the stability or leachability of the waste forms. In order to assess the effect of leachant chemical composition and pH on the stability and leachability of the waste forms, small-scale waste-form specimens were leached in deionized water, synthetic seawater with pH 6.4, synthetic Hanford ground water with pH 8.9, and synthetic Barnwell ground waters with pH 4.2 and 10.4.

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EXPERIMENTAL METHODS

The methods used to test the waste-form specimens were those recommended in the NRC Technical Position on Waste Form. Synthetic Hanford and Barnwell ground water leachants were prepared based on compositions of Hanford and Barnwell ground water reported in the literature.

Leach-Test Method

The test procedure used to measure the release of radionuclides, transition metals, and chelating agents from decontamination resin wastes solidified in portland cement was ANS 16.1. The standard is recommended by the NRC in the Branch Technical Position to measure the release of radionuclides from solidified low-level radioactive waste.

The seventeen solidified decontamination ion-exchange resin waste specimens that were leach-tested were right-cylindrical solids having nominal dimensions of 5 × 10 cm (diameter × height). The specimens obtained from Brunswick Plant- Unit 1 were cured at ambient temperature 254 days prior to the initiation of leach testing. Seven waste-form specimens obtained from James A. FitzPatrick Station were cured 119 days prior to leach testing. Two of the FitzPatrick specimens were baked at 49°C for 4 h during the first day of curing and the remaining 5 specimens were cured at ambient temperature. Waste-form specimens were leached in deionized water having a conductivity of less than 3 μ mho/cm at 25°C and in the four synthetic leachants previously described. Leachants were changed out at the intervals prescribed in ANS 16.1. The pH and conductivity of each leachate were measured at the end of each leaching interval.

The ANS 16.1 standard defines a material parameter of the leachability of diffusing species. This parameter is called the leachability index, L_i , and is defined as:

$$L_i = \frac{1}{k} \sum_{n=1}^k [\log(\beta/D_i)]_n \quad (\text{Eq. 1})$$

where, β = a defined constant (1.0 cm²/s), D_i = effective diffusivity of nuclide i (cm²/s), k = number of leaching intervals. Using Eq.(1), leachability indexes of selected radionuclides, transition metals, and chelating agents were calculated for each of the seventeen solidified resin waste specimens that were leach-tested. Leachability indexes were calculated so as to allow an evaluation of the performance of the waste forms based on the criterion specified in the NRC Branch Technical Position.

Compressive Strength Test Method

The test procedure used to measure the compressive strength of the waste-form specimens was ASTM C39. The standard is recommended by the NRC in the Branch Technical Position. The compressive strength criterion estab-

lished by the Branch Technical Position is 3.4×10^5 Pa (50 psi), although a value of 4.1×10^5 Pa (60 psi) is being considered to accommodate the maximum burial depth currently used at the Hanford disposal site, which is 16.8 m (55 ft). Only specimens that were not leach-tested were tested for compressive strength. One cation and one mixed-bed resin waste form obtained from Brunswick Plant- Unit 1 were tested after they had cured a total of 486 days. Two waste-form specimens collected from James A. FitzPatrick Station were cured a total of 212 days prior to testing. One of the FitzPatrick waste-form specimens tested for compressive strength had been baked for 4 h at 49°C during initial curing. Each specimen was fitted with epoxy end-caps to provide ends that were planar and perpendicular to the longitudinal axis of the specimen. Each specimen was placed in a hydraulic vice and the load on the specimen was gradually increased until the load gauge registered a decrease in load, which occurred when the specimen began to fail. The maximum load recorded for each specimen was used to compute the compressive strength of the specimen based on its cross-sectional area.

Resin and Leachate Analysis Methods

Ion-exchange bead resin wastes and leachate samples generated during leach-testing were analyzed for ⁵⁴Mn, ⁵⁵Fe, ⁶⁰Co, ⁶³Ni, ⁶⁵Zn, ⁹⁰Sr, ¹²⁵Sb, ¹³⁴Cs, ¹³⁷Cs, chromium, iron, nickel, cobalt, and chelating agents. Concentrations of gamma ray-emitting radionuclides were determined using hyper-pure germanium spectrometers. Concentrations of beta-emitting radionuclides were measured using radiochemical separation techniques followed by gas proportional or liquid scintillation counting. Samples of dissolved resin wastes and leachate solutions were analyzed for concentrations of chromium, iron, cobalt, and nickel using, respectively, atomic absorption spectroscopy and inductively coupled plasma-atomic emission spectroscopy. Concentrations of citric, oxalic, and picolinic acids in leachate samples were determined by ion chromatography.

EXPERIMENTAL RESULTS

Experimental results that are discussed include (1) waste form stability during leaching, (2) leachate final pH, (3) cumulative fraction releases of radionuclides, stable metals, and chelating agents, (4) leachability indexes of radionuclides, and (5) compressive strengths of the unleached waste-form specimens.

Waste Form Stability During Leaching

All of the Brunswick-1 waste-form specimens began to crack within minutes following immersion in the leachants. With the exception of the cation and mixed-bed resin waste forms leached in seawater, portions of all of the Brunswick-1 waste-form specimens crumbled into loose granular rubble during the first week of leaching. A photograph of a Brunswick-1 cation resin waste-form specimen taken prior

to leaching is shown in Fig. 1. A photograph of the same specimen after 200 days of leaching in deionized water is shown in Fig. 2. As shown in Fig. 2, the sample had crumbled and fallen to the bottom of the leaching vessel. The two specimens leached in seawater maintained their gross physical shapes through 200 days of leaching, but both cracked during the first day of leaching. Both of the specimens leached in seawater became coated with white mineral deposits. Although the material that coated the waste-forms leached in seawater was not analyzed, results reported in the literature (7,8) suggest that the precipitate was composed of the minerals brucite [$\text{Mg}(\text{OH})_2$], calcite (CaCO_3), and perhaps aragonite, which is another CaCO_3 mineral. These mineral deposits were likely responsible for the better stability of the specimens leached in seawater.

Within 2 hours of initial immersion, cracks appeared on the surfaces of all seven FitzPatrick waste-form specimens. The degree of cracking was more severe in the case of the two specimens that had been baked during the first day of curing. At the end of 24 h of leaching, several of the specimens slumped in their support nets as a result of relatively large cracks having formed in the bodies of the specimens. As was the case with the Brunswick-1 waste forms that were leached in seawater, the surface of the FitzPatrick waste form leached in seawater became covered with mineral deposits. Both of the samples that had been baked completely crumbled into loose rubble by the end of 98 days of leaching. With the exception of the waste form leached in Hanford ground water, the remaining five specimens remained more or less intact through 98 days of leaching. Less matrix material was lost from the specimen leached in seawater than from any of the other specimens, probably due to the fact that it became encased in calcium-based minerals.

Leachate pH

For each set of Brunswick-1 and FitzPatrick waste-form specimens, the pH of the deionized water, Hanford ground water, and acidic and basic Barnwell ground waters, which had initial pH of 7.0, 8.9, 4.2, and 10.4, respectively, were very similar following each leaching. The final pH of these leachates typically ranged between 11.5 and 12.5. The final pH of seawater leachates, which had an initial pH of 6.4, ranged between 9 and 9.7. The initial pH of a leachant had little effect on the final pH because of the large quantity of calcium hydroxide available in each waste form. Measurements performed as part of an ongoing leaching study showed that the pH of deionized water and seawater leachates changed dramatically within a few minutes following the immersion of waste forms. These results show that the pH of the deionized water and three ground water leachates were, for all practical purposes, identical except during the first few minutes following each leachant changeout.

The final pH of the seawater leachates exhibited the same general behavior as the final pH recorded for the other four leachants, but, as previously mentioned, the pH of the seawater leachates remained much lower than the pH of the other four leachates. This may, in part, be due to the formation of a reaction rim of calcite and other minerals on the surface of the waste forms leached in seawater, which may have inhibited the migration of calcium hydroxide from the waste forms. Also, buffers may have formed in the seawater leachates that would have suppressed increases in pH. Sulfate from the sodium sulfate used to prepare the seawater leachants could have reacted with dissolved carbon dioxide in an acid-base reaction to form bicarbonate and bisulfate, both of which could act as buffers.

Results of leaching studies reported by de Groot (9) showed that leachant pH was the main factor controlling the leaching of trace anionic elements, metals, and major elements from coal fly ash. However, as indicated from the previous discussion, the conditions of the experiments performed by de Groot were different from those that existed during this leaching study.

Releases of Radionuclides

Average incremental fraction release rates, incremental and cumulative release fractions, average incremental effective diffusivities, and leachability indexes of ^{54}Mn , ^{55}Fe , ^{58}Co , ^{60}Co , ^{63}Ni , ^{65}Zn , ^{90}Sr , ^{125}Sb , ^{134}Cs , and ^{137}Cs for three waste-form specimens that were leached in deionized water are presented in Tables I through III. Similar results for chromium, iron, cobalt, nickel, and oxalic, citric, and picolinic acids for the three waste-form specimens are also presented in these tables. Incremental release rates for radionuclides, stable metals, and chelating agents were calculated as quantity released per unit surface area per second ($\mu\text{Ci}/\text{cm}^2\cdot\text{s}$ or $\mu\text{g}/\text{cm}^2\cdot\text{s}$) and as fraction of initial inventory released per unit surface area per second ($\text{F}/\text{cm}^2\cdot\text{s}$). Leaching results for the fourteen specimens leached in the other four leachants are presented elsewhere (10).

Cumulative fraction releases (CFRs) of ^{60}Co from the five Brunswick-1 cation and the five Brunswick-1 mixed-bed resin waste forms in the five different leachants are plotted versus the square root of elapsed leaching time in Fig. 3 and 4, respectively. Similar results for the seven FitzPatrick mixed-bed resin waste forms in the same leachants are presented in Fig. 5.

The leaching results show that, after 91 days of leaching, releases of radionuclides from the Brunswick-1 cation resin waste forms were quite low. Maximum CFRs of ^{54}Mn , ^{55}Fe , ^{60}Co , ^{65}Zn , and ^{125}Sb were all well below 1%. Maximum CFRs of ^{63}Ni , ^{90}Sr , and ^{137}Cs were below 7%. The results also show that releases of radionuclides from the Brunswick-1 cation resin waste forms were generally highest in deionized water. The CFR of ^{137}Cs in seawater was about 30% higher than CFRs in other leachants. The slightly

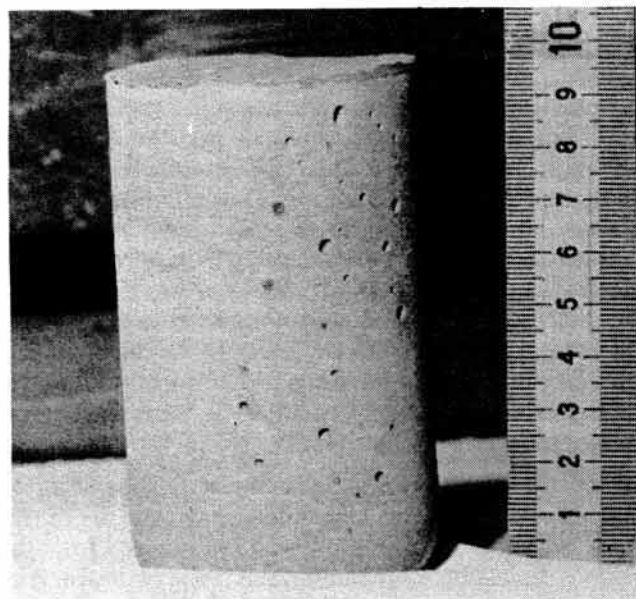


Fig. 1. Brunswick-1 cation resin waste-form specimen prior to leaching in deionized water.

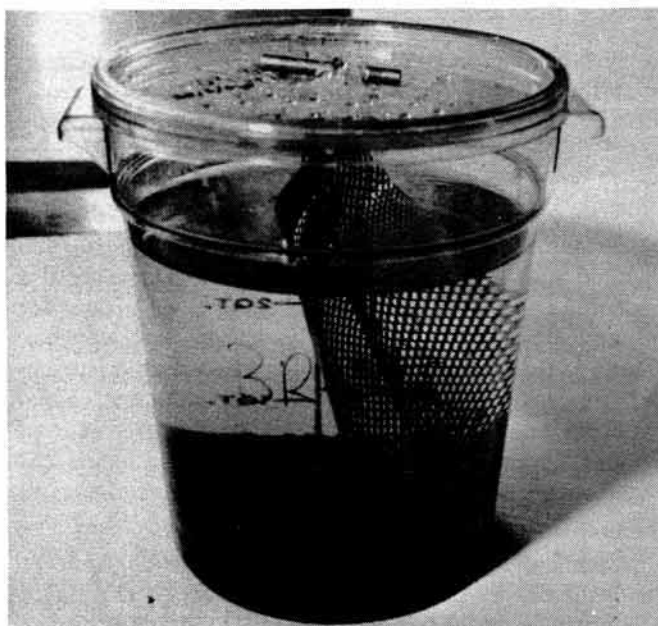


Fig. 2. Brunswick-1 cation resin waste-form specimen after leaching in deionized water for 200 days.

higher release of ^{137}Cs in seawater was likely due to the high ionic strength of the seawater, since as a monovalent cation, cesium attached to resin beads would readily exchange with cations in the seawater having higher oxidation states.

Releases of radionuclides from the Brunswick-1 mixed-bed resin waste forms were also generally quite low, but were usually much higher than releases of the same radionuclides from the cation resin waste forms leached in corresponding leachants. After 91 days of leaching, maximum CFRs of ^{54}Mn , ^{60}Co , and ^{125}Sb were well below 1%. Max-

imum CFRs of ^{55}Fe , ^{63}Ni , and ^{65}Zn were below 2% and CFRs of ^{90}Sr and ^{137}Cs were below 30%. The results show that releases of radionuclides from the Brunswick-1 mixed-bed resin waste forms were also generally highest in deionized water. CFRs of ^{60}Co and ^{63}Ni in Hanford ground water were each a factor of two or more higher than releases of these radionuclides in seawater or the Barnwell ground waters. Releases of ^{125}Sb in deionized water and in the ground water leachants were about the same and were about a factor of two higher than releases of ^{125}Sb in seawater.

The leaching results show that releases of radionuclides from the FitzPatrick mixed-bed resin waste forms were also generally quite low, but were significantly higher than releases of the same radionuclides from the Brunswick-1 waste forms leached in corresponding leachants. After 98 days of leaching, the maximum CFRs of ^{54}Mn , ^{65}Zn , and ^{125}Sb from the five unbaked waste forms were well below 1%. Maximum CFRs of ^{55}Fe , ^{60}Co , and ^{137}Cs from the unbaked specimens were, respectively, 1.7%, 2.0%, and 73% after 98 days. The leaching results for the unbaked FitzPatrick waste forms show that after 98 days of leaching, CFRs of ^{60}Co in deionized water, seawater, and in the Barnwell ground waters were essentially identical and were higher than the CFR of ^{60}Co in Hanford ground water. Releases of ^{55}Fe were highest in Barnwell ground water with pH 10.4 and were lowest in deionized water. After 98 days, the CFR of ^{137}Cs was 14% higher in seawater than in deionized water. CFRs of ^{137}Cs in deionized water, Hanford ground water, and in the acidic and basic Barnwell ground waters agreed to within 16%.

Releases of Stable Metals

In the case of the Brunswick-1 cation and mixed-bed resin waste forms, nickel and cobalt were not detected in any of the leachates analyzed for stable metals, chromium was detected only in seawater leachates, and iron was detected only in deionized water leachates (Tables I and II). In the case of the FitzPatrick mixed-bed resin waste form leachates, chromium and cobalt were not detected in any of the leachate samples that were analyzed for stable metals, iron was detected in only three deionized water leachates (Table III), but nickel was detected in almost all of the leachates. CFRs of nickel were essentially identical in deionized water, Hanford ground water, and in the acidic and basic Barnwell ground waters. Nickel was detected in only two of the five seawater leachates that were analyzed.

Releases of Chelating Agents

In the case of the Brunswick-1 mixed-bed resin waste forms, after 91 days of leaching, the CFR of citric acid in Barnwell ground water with pH 4.2 was 30% higher than in Hanford ground water with pH 8.9 and was a factor of two or more higher than the CFR of citric acid in deionized water, seawater, or Barnwell ground water with pH 10.4.

TABLE I

Leach Test Results for Brunswick-1 Cation Resin Waste-Form Specimen Leached in Deionized Water^a

Nuclide	CFR	Average Incremental Release Rate		Average Effective Diffusivity (cm ² /s)	Leachability Index
		($\mu\text{Ci}/\text{cm}^2 \cdot \text{s}$)	($\text{F}/\text{cm}^2 \cdot \text{s}$) ^b		
⁵⁴ Mn	1.2(-4)	6 ± 2 (-11)	6 ± 2 (-13)	4 ± 2 (-14)	14.8 ± 0.5
⁵⁵ Fe	1.2(-4) ^c	9 ± 9 (-10)	2 ± 2 (-12)	4 ± 4 (-14)	15.8 ± 0.9
⁵⁸ Co	< 3.0(-3)	< 2.2 (-10)	< 2.1 (-11)	< 1.0 (-11)	> 11.6
⁶⁰ Co	8.5(-5)	1.9 ± 0.5(-10)	4 ± 1 (-13)	2 ± 1 (-14)	15.1 ± 0.5
⁶³ Ni	1.2(-2) ^c	6 ± 5 (-10)	4 ± 4 (-11)	9 ± 9 (-10)	12 ± 1
⁶⁵ Zn	< 4.5(-4)	< 2.1 (-11)	< 3.2 (-12)	< 2.1 (-13)	> 13.2
⁹⁰ Sr	6.5(-2) ^c	3 ± 3 (-10)	1 ± 1 (-9)	1 ± 1 (-8)	11 ± 1
¹²⁵ Sb	< 5.8(-3)	< 1.2 (-11)	< 5.0 (-11)	< 2.5 (-11)	> 11.0
¹³⁴ Cs	< 2.1(-2)	< 1.0 (-11)	< 1.7 (-10)	< 3.8 (-10)	> 9.9
¹³⁷ Cs	1.2(-2)	1.8 ± 0.6(-10)	7 ± 2 (-11)	1.0 ± 0.3(-10)	10.5 ± 0.3
Metal		(μg/cm ² ·s)			
Chromium	< 4.1(-3) ^c	< 3.0 (-6)	< 3.5 (-11)	< 1.9 (-11)	> 11.2
Iron	1.8(-3) ^c	1.0 ± 0.4(-5)	9 ± 4 (-12)	7 ± 5 (-12)	12.2 ± 0.6
Cobalt	< 4.3(-2) ^c	< 1.5 (-5)	< 3.7 (-10)	< 1.6 (-9)	> 9.2
Nickel	< 9.8(-3) ^c	< 1.2 (-5)	< 8.5 (-11)	< 8.2 (-11)	> 10.4

a. Results are for only the first 91 days of leaching.

b. Fraction of initial inventory released per square centimeter of specimen surface area per second.

c. Not all leachate samples were analyzed for this radionuclide or metal. CFR value was estimated by interpolating measured incremental release rates.

TABLE II
Leach Test Results for Brunswick-1 Mixed-Bed Resin Waste-Form Specimen Leached in Deionized Water^a

Nuclide	CFR	Average Incremental Release Rate		Average Effective Diffusivity		Leachability Index
		($\mu\text{Ci}/\text{cm}^2 \cdot \text{s}$)	($\text{F}/\text{cm}^2 \cdot \text{s}$) ^b	(cm^2/s)	(cm^2/s)	
⁵⁴ Mn	< 1.7(-3)	< 8.0 (-11)	< 2.6 (-11)	< 5.1 (-12)	> 12.3	
⁵⁵ Fe	1.1(-2) ^c	1.3 ± 0.5(-9)	6 ± 3 (-11)	3 ± 2 (-10)	10.6 ± 0.6	
⁵⁸ Co	< 9.9(-2)	< 3.4 (-10)	< 8.6 (-10)	< 1.3 (-8)	> 8.2	
⁶⁰ Co	1.3(-3)	4 ± 2 (-10)	2 ± 1 (-11)	3 ± 2 (-12)	12.8 ± 0.4	
⁶³ Ni	1.8(-2) ^c	1.0 ± 0.6(-10)	1.2 ± 0.7(-10)	3 ± 1 (-10)	10.4 ± 0.9	
⁶⁵ Zn	< 1.0(-2)	< 2.8 (-11)	< 1.0 (-10)	< 1.2 (-10)	> 10.2	
⁹⁰ Sr	2.3(-1) ^c	1.6 ± 0.7(-10)	1.4 ± 0.6(-9)	2 ± 2 (-7)	9 ± 1	
¹²⁵ Sb	5.6(-3)	4 ± 2 (-11)	6 ± 3 (-11)	6 ± 2 (-11)	10.7 ± 0.3	
¹³⁴ Cs	< 1.2(-1)	< 1.5 (-11)	< 1.5 (-9)	< 2.0 (-8)	> 8.2	
¹³⁷ Cs	2.2(-1)	1.6 ± 0.9(-10)	3 ± 2 (-9)	6 ± 2 (-8)	7.5 ± 0.2	
Acid or Metal		($\mu\text{g}/\text{cm}^2 \cdot \text{s}$)				
Oxalic acid	6.3(-3)	1.6 ± 0.7(-4)	6 ± 2 (-11)	7 ± 3 (-11)	10.6 ± 0.2	
Citric acid	4.0(-3)	2 ± 1 (-4)	4 ± 2 (-11)	5 ± 3 (-11)	11.0 ± 0.3	
Chromium	< 1.9(-3) ^c	< 3.5 (-6)	< 1.6 (-11)	< 5.5 (-12)	> 11.9	
Iron	< 2.1(-2) ^c	< 1.6 (-5)	< 1.7 (-10)	< 5.2 (-10)	> 10.1	
Cobalt	< 4.3(-2) ^c	< 1.3 (-5)	< 3.0 (-10)	< 1.7 (-9)	> 9.2	
Nickel	< 1.6(-1) ^c	< 1.0 (-5)	< 1.1 (-9)	< 2.3 (-8)	> 8.1	

a. Results are for only the first 91 days of leaching.

b. Fraction of initial inventory released per square centimeter of specimen surface area per second.

c. Not all leachate samples were analyzed for this radionuclide or metal. CFR value was estimated by interpolating measured incremental release rates.

TABLE III
Leach Test Results for James A. FitzPatrick Mixed-Bed Resin Waste-Form
Specimen Leached in Deionized Water^a

Nuclide	CFR	Average Incremental Release Rate		Average Effective Diffusivity (cm ² /s)	Leachability Index
		($\mu\text{Ci}/\text{cm}^2 \cdot \text{s}$)	(F/cm ² ·s) ^b		
⁵⁴ Mn	5.6(-4)	1.0 ± 0.5(- 9)	6 ± 3 (-12)	3 ± 1 (-13)	13.3 ± 0.3
⁵⁵ Fe	7.6(-3) ^c	4 ± 3 (-10)	9 ± 7 (-11)	6 ± 4 (-11)	11.5 ± 0.8
⁵⁸ Co	1.2(-2)	9 ± 2 (- 9)	5 ± 1 (-11)	2.6 ± 0.7(-11)	10.8 ± 0.2
⁶⁰ Co	1.7(-2)	5 ± 1 (- 8)	7 ± 2 (-11)	5 ± 1 (-11)	10.5 ± 0.2
⁶³ Ni	---d	---d	---d	---d	---d
⁶⁵ Zn	2.3(-3)	4 ± 2 (-10)	1.0 ± 0.5(-11)	1.2 ± 0.4(-12)	12.3 ± 0.2
⁹⁰ Sr	---d	---d	---d	---d	---d
¹²⁵ Sb	< 7.7(-3)	< 7.9 (-11)	< 5.1 (-11)	< 3.6 (-11)	> 11.0
¹³⁴ Cs	7.3(-1)	8 ± 3 (- 9)	6 ± 2 (- 9)	3.6 ± 0.7(- 7)	6.6 ± 0.2
¹³⁷ Cs	6.4(-1)	1.5 ± 0.5(- 8)	5 ± 2 (- 9)	1.5 ± 0.5(- 7)	7.1 ± 0.2
Acid or Metal		($\mu\text{g}/\text{cm}^2 \cdot \text{s}$)			
Picolinic acid	5.4(-1)	8 ± 3 (- 3)	3 ± 1 (- 9)	1.4 ± 0.8(- 7)	7.5 ± 0.3
Chromium	< 6.6(-3) ^c	< 1.6 (- 6)	< 5.7 (-11)	< 2.4 (-11)	> 11.2
Iron	< 3.3(-3) ^c	< 1.0 (- 5)	< 2.6 (-11)	< 5.4 (-12)	> 12.0
Cobalt	< 2.5(-2) ^c	< 8.0 (- 6)	< 2.2 (-10)	< 3.5 (-10)	> 10.0
Nickel	5.0(-2) ^c	5 ± 2 (- 6)	3 ± 1 (-10)	1.1 ± 0.5(- 9)	9.4 ± 0.4

a. Results are for only the first 98 days of leaching.

b. Fraction of initial inventory released per square centimeter of specimen surface area per second.

c. Not all leachate samples were analyzed for this radionuclide or metal. CFR value was estimated by interpolating measured incremental release rates.

d. Concentrations of radionuclide in leachate samples were not determined.

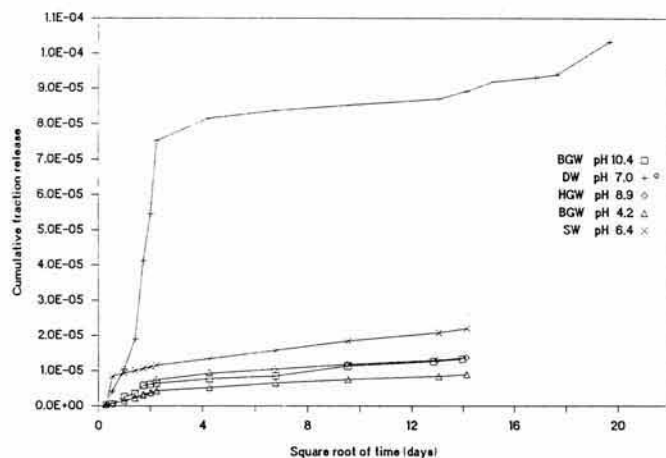


Fig. 3. Cumulative fraction release of ^{60}Co from five Brunswick-1 cation resin waste-form specimens leached in five different leachants.

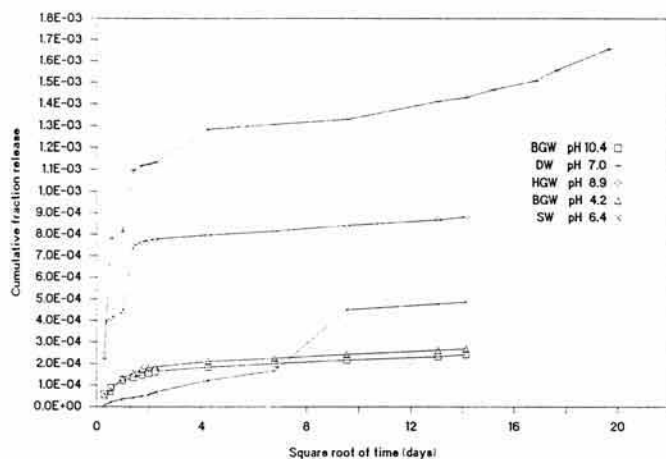


Fig. 4. Cumulative fraction release of ^{60}Co from five Brunswick-1 mixed-bed resin waste-form specimens leached in five different leachants.

Releases of citric acid were lowest in seawater. The CFR of oxalic acid in Hanford ground water with pH 8.9 was about 20% higher than in Barnwell ground water with pH 4.2 and was 50% or more higher than the CFR of oxalic acid in deionized water or Barnwell ground water with pH 10.4. Releases of oxalic acid in seawater were not determined.

In the case of the FitzPatrick waste forms, after 98 days of leaching, the CFR of picolinic acid was 39% higher in Barnwell ground water with pH 10.4 than in deionized water. CFRs of picolinic acid in deionized water, acidic Barnwell ground water, and Hanford ground water leachants agreed to within 29%. As was the case with citric

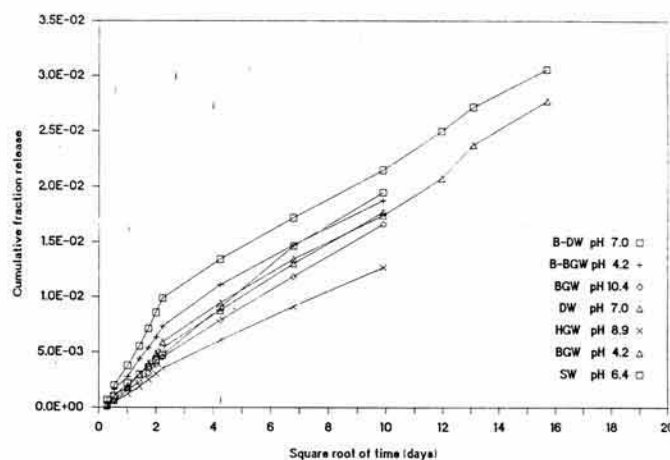


Fig. 5. Cumulative fraction release of ^{60}Co from seven FitzPatrick mixed-bed resin waste-form specimens leached in five different leachants.

acid, releases of picolinic acid were lowest in seawater. The CFR of picolinic acid in seawater was estimated to be 25% after 98 days.

Leachability Indexes of Radionuclides

Leachability indexes of radionuclides contained in the Brunswick-1 cation resin waste forms ranged from a low of 10.1 for ^{137}Cs in basic Barnwell ground water to a high of 16.7 for ^{60}Co in acidic Barnwell ground water and Hanford ground water. Leachability indexes of ^{54}Mn and ^{60}Co in deionized water were lower than leachability indexes of these radionuclides in other leachants, while leachability indexes of ^{55}Fe , ^{63}Ni , ^{90}Sr , and ^{137}Cs were similar for all leachants. In the case of the Brunswick-1 mixed-bed resin waste forms, leachability indexes ranged from a low of 7.2 for ^{137}Cs in acidic Barnwell ground water to a high of 14.1 for ^{55}Fe and ^{60}Co in, respectively, acidic Barnwell ground water and seawater.

For the FitzPatrick waste forms, leachability indexes ranged from a low of 6.4 for ^{137}Cs in a baked specimen leached in deionized water to a high of >15.4 for ^{54}Mn in an unbaked specimen leached in seawater. Thus, the leachability indexes of all eight radionuclides whose concentrations in leachate samples were measured were above the acceptable lower limit of 6.0 as defined by the NRC Branch Technical Position.

Compressive Strengths of Waste Forms

The compressive strengths of the Brunswick-1 cation and mixed-bed resin waste forms that were archived and not subjected to immersion in leachants were 392 and 505 psig, respectively. Similar results for the unbaked and baked waste forms collected from the FitzPatrick Station that were

archived and not leach-tested were 1857 and 1906 psig, respectively. Thus, all four of the waste form specimens easily exceeded the minimum acceptable compressive strength of 3.4×10^5 Pa (50 psi) specified in the NRC Branch Technical Position.

CONCLUSIONS

The leaching results show that loss of waste form physical stability did not result in significant releases of several classes of radionuclides. The low ^{60}Co CFR results for the Brunswick-1 waste forms are similar to those obtained for cement-solidified AP/Citrox bead resin waste forms that crumbled during a previous leaching study.(6) The low releases of ^{60}Co from waste forms that deteriorated during leaching indicates that a large fraction of the ^{60}Co in these waste forms was unavailable for leaching. The fraction unavailable for leaching would include ^{60}Co that was immobilized through irreversible reactions with materials in the waste form matrix. A possible mechanism for the immobilization of ^{60}Co and other transition metals in the cement matrix was reported by Komarneni, et al.(11) The implication of the results reported in Ref. 11, which is further supported by the results of this work, is that the leaching of transition metal radionuclides that constitute the majority of the activity in cement-solidified waste forms will, for all practical purposes, be unaffected by the physical state of the waste form.

The leaching results show that releases of radionuclides in deionized water were generally equal to or greater than releases in seawater, Hanford ground water, or Barnwell ground water. This implies that leaching studies performed using deionized water can be used to conservatively predict the leachability of decontamination ion-exchange resin waste forms immersed in seawater, Hanford ground water, or Barnwell ground water.

The fact that all seventeen Brunswick-1 and FitzPatrick waste-form specimens cracked or crumbled and consequently lost their physical stability during leach-testing indicates that the compressive strength of an unleached waste form is not a reliable parameter upon which to base expectations of waste form durability during leaching. The results also show that compressive strength may not be a good indicator of leachability. Releases of radionuclides from the FitzPatrick waste forms were significantly higher than releases of radionuclides from the Brunswick-1 waste forms even though the FitzPatrick waste-form specimens had much higher compressive strengths.

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