

LEACH STUDIES ON CEMENT-SOLIDIFIED ION EXCHANGE RESINS FROM DECONTAMINATION PROCESSES AT OPERATING NUCLEAR POWER STATIONS*

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ABSTRACT

The effects of varying pH and leachant compositions on the physical stability and leachability of radionuclides and chelating agents were determined for cement-solidified decontamination ion-exchange resin wastes collected from two operating commercial light water reactors. Small scale waste-form specimens were collected during waste solidifications performed at the Brunswick Steam Electric Plant Unit 1 and at the James A. FitzPatrick Nuclear Power Station. The collected specimens were leach tested, and their compressive strength was measured in accordance with the Nuclear Regulatory Commission's "Technical Position on Waste Form" (Revision 1), from the Low-Level Waste Management Branch. Leachates from these studies were analyzed for radionuclides, selected transition metals, and chelating agents to assess the leachability of these waste form constituents. Leachants used for the study were deionized water, simulated seawater, and groundwater compositions similar to those found at Barnwell, South Carolina and Hanford, Washington. Results of this study indicate that initial leachant pH does not affect leachate pH or releases from cement-solidified decontamination ion-exchange resin waste forms. However, differences in leachant composition and the presence of chelating agents may affect the releases of radionuclides and chelating agents. In addition, results from this study indicate that the cumulative releases of radionuclides and chelating agents observed for forms that disintegrated were similar to those for forms that maintained their general physical integrity.

INTRODUCTION

The U.S. Nuclear Regulatory Commission (NRC) is concerned with the safe disposal of low-level chemical decontamination wastes and has made provisions for their disposal in "Licensing Requirements for Land Disposal of Radioactive Waste" (U.S. Code of Federal Regulations Standard 10, Part 61). Section 61.56 provides requirements for the stability of waste forms, which must be met for the waste form to be acceptable for near-surface disposal. Low-level wastes from light water reactors (LWRs) are routinely solidified at LWR sites using hydraulic cement. Solidification of these wastes is intended to provide the needed structural stability to ensure that no subsidence of the disposal trench occurs and that the release of radionuclides via leaching is minimized.

The purpose of this research study is to evaluate the stability of actual low-level radioactive decontamination ion exchange resin wastes solidified in cement. The tests used in waste form performance assessment are specified in the NRC Low-Level Waste Management Branch's "Technical Position on Waste Form" (BTP), Revision 1 (1). In particular, the solidified waste was evaluated for immersion and leachability using ANS 16.1, "Measurement of the Leachability of Solidified Low-Level Radioactive Wastes by a Short-Term Test Procedure" (2), and for compressive strength using ASTM C39 (3). The release rates of radionuclides, chelating agents, and transition metals were determined for deionized, simulated ground water and simulated seawater.

Unsolidified decontamination ion exchange resin wastes and small-scale waste-form specimens were collected at the Brunswick Steam Electric Plant Unit 1 (Brunswick-1) and from the James A. FitzPatrick Nuclear Power Stations (FitzPatrick). Primary system piping at the two power stations

had been chemically decontaminated using the Citrox/AP/Citrox and LOMI/NP/LOMI processes, respectively. Citrox/AP/Citrox process reagents include citric acid, oxalic acid, and alkaline permanganate. The LOMI/NP/LOMI process reagents include picolinic acid and nitric acid permanganate. Ion exchange resin wastes were solidified in Portland Type I-pozzolanic (P) cement at both power stations. Cation and mixed bed resin wastes were solidified separately at Brunswick-1 while only mixed bed resin waste was solidified at the FitzPatrick Station. Three waste-form specimens collected from the FitzPatrick Station were prepared and then baked for 4 h at 49°C to assess the effects of elevated temperature on waste form leachability and physical stability. They were baked to simulate the high temperatures associated with the cement hydration exotherm during the curing process inside the full scale liner. This approximation of the exotherm is not expected to fully simulate the actual exotherm, which occurs in the solidification liner with respect to temperature or duration. The remaining specimens were cured at ambient temperature.

Samples of the waste forms were leached in deionized water, simulated ground waters for the Hanford and Barnwell waste sites, and simulated seawater. In addition, two FitzPatrick samples that were baked for 4 h at 49°C early in the curing process were also leached.

EXPERIMENTAL PROCEDURES

The experimental procedures used to collect the untreated resin waste and waste form samples are described together with those used to leach the waste-form specimens and perform compressive strength tests. In addition, standard analytical methods were used to determine the concentrations

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of radionuclides, metals, and chelating agents in the untreated resin waste and leachate samples.

Leach-Test Method

The ten waste-form specimens obtained from Brunswick-1 and the nine waste-form specimens from the FitzPatrick Station were right-cylindrical solids with nominal dimensions of 5 x 10 cm (2" x 4"). The Brunswick-1 samples were cured at ambient temperature for 254 days prior to the initiation of leach testing, and all FitzPatrick samples were cured at ambient temperature for 119 days prior to leach testing. This includes the three specimens which were initially baked for 4 h at 49°C. All samples were leached in cylindrical polyethylene containers with a capacity of about 3 L and filled with about 1.6 L of leachant. In all cases, the waste-form specimens were supported in the leach test vessel by coarse mesh plastic netting that was suspended by a wire from the container lid.

Five different leachants were used in this study to assess the effects of different ground waters and seawater on leachability. The leachants used were deionized water with a conductivity of less than 3 $\mu\text{mho/cm}$ at 298 K (25°C), synthetic seawater with pH 6.4, synthetic Hanford ground water with pH 8.9, and two different synthetic Barnwell ground waters with pH 4.2 and 10.4. The chemical compositions of the synthetic seawater and ground water leachants are presented in Ref. (4) along with the references for the formulations used.

Following the initial 90-day leaching period defined in ANS 16.1, leaching of both the Brunswick-1 and FitzPatrick samples was continued to assess the effects of long-term leaching.

The compressive strength of the waste-form specimens was measured in accordance with ASTM C39, "Compressive Strength of Cylindrical Concrete Specimens" (3), as recommended by the NRC's BTP (Revision 1). This position paper requires a minimum compressive strength for cement-solidified waste forms of 3.4×10^3 kPa (500 psi). This value is deemed necessary to ensure that cement-solidified waste forms maintain integrity and exhibit long-term stability as required by 10 CFR 61.

Data Analysis

The methods used to assess leachability (i.e., fractional release, cumulative fractional release, and leachability index) are based on the premise that internal bulk diffusion is the rate-determining process and are predicated on an intact waste form. However, because some of the Brunswick-1 and FitzPatrick samples either partially or totally disintegrated during the ANSI/ANS 16.1 leach period, the method used to determine the surface area of the disintegrated waste forms was modified.

Calculation of the surface area of the disintegrated waste forms considers the formation of a diffusion boundary between the layer of particulate debris on the bottom of the leaching vessel and the leachant. The surface of this diffusion boundary layer is estimated to be the surface area of the cross section of the leaching vessel. During the early stages of waste form disintegration, when a large portion of the waste form was intact, the total surface area of the waste form was considered to be the sum of the exterior surface area of the partial waste form (typically 180-230 cm^2 or 28-36 in^2 for the intact waste form) plus the surface area of the bottom of the leaching vessel over which the debris was spread (about 165 cm^2 or 25

in^2). As the waste forms continued to disintegrate, the surface area of the partial waste form decreased, but the surface area of the diffusion boundary on the bottom of the leaching vessel remained essentially constant, ranging from 163 to 172 cm^2 (25.3 to 26.7 in^2), depending on the shape of the walls of the leaching vessel. Consequently, the specimen surface areas ranged from about 220 cm^2 (34 in^2), with no degradation, to about 370 cm^2 (57.4 in^2) after waste form degradation began, to about 165 cm^2 (25 in^2) after complete decomposition has occurred. This approach allowed the determination of the relative leachability of waste-form specimens leached in different leachants.

Analytical Methods

Prior to analysis, leachate solutions were partitioned into volumetric samples to perform the various analyses. The analytical methods used to determine concentrations of radionuclides, transition metals, and chelating agents in leachate samples included high-resolution gamma ray spectrometry, liquid scintillation and gas proportional counting, inductively coupled plasma-atomic emission spectroscopy, and ion chromatography (IC). The detection of chelating agents in some leachate solutions required that the chelating agent be chemically separated from other components of the sample prior to IC analysis. Additional information on the analysis methods used and their associated uncertainties is presented in Ref. (5).

EXPERIMENTAL RESULTS

The experimental results presented include discussions of (a) the loss of waste form stability during leaching, (b) leach test results for five cation and five mixed-bed resin waste-form specimens from Brunswick-1, (c) leaching results for seven FitzPatrick mixed-bed resin waste-form specimens, and (d) compressive strengths of the waste-form specimens collected from Brunswick-1, and the FitzPatrick nuclear stations.

Loss of Waste Form Stability During Leaching

All of the Brunswick-1 waste-form specimens, except those that were leached in seawater, completely decomposed during leaching. All five FitzPatrick waste-form specimens that were cured at ambient temperature cracked during leach testing. The two specimens that were baked initially completely decomposed during leaching. Figure 1 shows typical decomposition of a waste-form specimen after 90 days of leaching. Decomposition of all waste-form specimens occurred early in the leaching program and suggests the presence of a gross physical effect that resulted in decomposition. Observations in this study suggest that loss of waste form stability after exposure to leachants may be due to swelling of the solidified resin beads.

Initial Components Inventory in Waste Streams

Leachates from the Brunswick and Fitzpatrick samples were measured for pH, conductivity, and concentrations of radionuclides, stable metals, and chelating agents. The initial radionuclide and organic complexing/chelating inventories were measured in the unsolidified resin waste stream samples obtained. This measurement provided the concentration of these species in the waste forms prior to leaching.

The total radionuclide concentration in the Brunswick-1 cation resin waste was 6.68 $\mu\text{Ci/g}$ resin (decay corrected to



Fig. 1. Brunswick-1 mixed-bed resin waste-form specimen after being leached for 90 days, showing the typical geometry of decomposition waste form.

December 18, 1987). The mixed-bed resin waste contained only a total of $0.38 \mu\text{Ci/g}$ resin. The major activities in the resins were ^{54}Mn , ^{55}Fe , ^{60}Co , and ^{63}Ni . These species constituted greater than 90% of the total activity in the cation and mixed-bed resin wastes. The dominant radionuclides, ^{60}Co and ^{55}Fe , constituted about 40% and 42%, respectively, of the total activity in the cation resin waste, and 36% and 39%, respectively, of the total activity in the mixed-bed resin waste. The measured fission products, ^{90}Sr and ^{137}Cs combined, constituted about 0.2% of the total activity in the cation resin and 0.3% of the total activity in the mixed-bed resin waste.

The total radionuclide concentration in the FitzPatrick mixed-bed resin waste was higher than the Brunswick-1 resin at $9.0 \mu\text{Ci/g}$ (decay corrected to September 18, 1988). ^{51}Cr , ^{54}Mn , ^{59}Fe , ^{58}Co , ^{60}Co , and ^{65}Zn were the major activities. Their combined activities constituted about 96% of the total activity. Cobalt-60 was the dominant radionuclide and represented 54% of the total resin activity. As was the case with the Brunswick-1 resin wastes, the fission products activities (^{90}Sr and ^{137}Cs) were as low as those in the Brunswick-1 waste resin. Their combined activities constituted 0.2% of the total FitzPatrick resin waste activity.

The total concentration of the transuranic (TRU) isotopes in the Brunswick-1 resins was $2.1 \times 10^{-3} \mu\text{Ci/g}$ for both the cation and mixed-bed resins. The total concentration of TRU isotopes in the FitzPatrick resin waste was about thirty times higher with a concentration of $6.7 \times 10^{-2} \mu\text{Ci/g}$. In all cases, ^{241}Pu constituted more than 90% of the TRU activity.

Stable iron concentration was the highest among the stable metals measured in the resin wastes. Its concentration was measured at 0.2 wt% in the Brunswick-1 cation resin waste and at 0.2 wt% in the FitzPatrick mixed-bed resin waste. Chromium had the highest concentration (about 0.2 wt%) in the mixed-bed resin waste obtained from Brunswick-1.

The concentrations of the chelating agents, citric and oxalic acids, in the Brunswick-1 mixed-bed resin waste were reported by the decontamination vendor to be 4.1 wt% and 2.0 wt%, respectively. The concentration of picolinic acid in the FitzPatrick Station resin waste was reported to be 1.0 wt%; however, the cumulative release data indicated that the actual concentration was at least 2.2 wt%. Consequently, a 2.2 wt% inventory of picolinic acid was used for calculational purposes.

Leachate pH and Conductivity

pH and conductivity were measured at the end of each leach period for leachates from Brunswick-1 cation and mixed-bed, and FitzPatrick mixed-bed resins waste forms to determine the effect of the waste form on the leachate pH. Initial leachants pH values were deionized water (pH 7.0), Barnwell ground water (pH 10.4 and 4.2), Hanford ground water (pH 8.9), and seawater (pH 6.4). The final pH of all leachates except seawater were comparable throughout the leach tests. At the end of the initial 2-h leaching interval, the pH of the leachates other than seawater ranged from 11.4 to 11.7. During the first three days of leaching, when leachates were changed after elapsed times of 2, 7, 24, 48, and 72 h, the final pH of these four leachates gradually increased, reaching maxima that ranged between 12.1 and 12.5. The conductivity measurement results follow similar patterns for the three types of waste forms with nominal values from 3-5 $\mu\text{mho/cm}$.

The data showed that the initial pH and conductivity of a leachant had little effect on their final values in leachates. This may be attributed to the large quantity of calcium hydroxide available in each waste form. The pH of leachates reached near-equilibrium values within minutes after waste-form specimen immersion, and the final pH of leachates other than seawater were essentially identical, generally ranging between 11 and 12.

In contrast to the early behavior of the specimens, when significant changes in the pH can be expected from exposure of fresh surfaces on the specimens during their decomposition, the pH of the deionized and ground water leachates decreased after several days as the leachant was replaced. The pH then rose to about pH 12, when leaching times were increased from 24 h to 13 days. Consequently, it can be concluded that the equilibrium pH for these waste forms was about pH 12. These data suggest that throughout the leaching period, the chemistry of the waste form would substantially control the pH of any leachant and that variations in initial leachant pH, except under special conditions that will be discussed, should not affect leachability.

Seawater leachates exhibited a lower final pH. This may be due to buffering effects of its chemical components. The formation of a reaction rim of calcite on the surface of the waste-form specimens leached in seawater may have also affected the release of calcium hydroxide in the waste-form specimen. No substantive differences in releases of radionuclides, transition metals, and chelating agents were observed that could be attributed to differences in initial or final leachate pH.

Radionuclide and Cumulative Fractional Releases

Release rates were measured for several radionuclides in Brunswick-1 and FitzPatrick waste form sample leachates. The radionuclides included ^{54}Mn , ^{55}Fe , ^{58}Co , ^{60}Co , ^{63}Ni ,

^{65}Zn , ^{90}Sr , ^{125}Sb , ^{134}Cs , ^{137}Cs , ^{241}Pu . In addition, release rates were also measured for stable metals. These included Chromium, Iron, Cobalt, and Nickel.

Release data indicate that only small fractions of the initial radionuclides inventories in the waste-form specimens were released. ^{137}Cs , a fission product, had the highest release rates. Measurements were made for ^{241}Pu . However, the results were near or below the detection limit for this radionuclide. The available data indicate that the leachability index of ^{241}Pu was well above that of other radionuclides such as ^{63}Ni . Furthermore, the release data indicate that the specimens that decomposed did not have substantially different release rates from the specimens that remained relatively intact.

The radionuclide absolute, fractional, and cumulative fractional release (CFR) rates obtained in this study indicate that the release rates of most the radionuclides are dependent on the chemistry of their respective elements. Only data related to decontamination radionuclides such as ^{60}Co , ^{63}Ni , and ^{55}Fe , and the characteristic fission product, ^{137}Cs , will be discussed. Cumulative fractional releases and leachability indexes will also be discussed with respect to BTP (Revision 1) performance.

Figure 2 shows a comparison of the CFRs observed for ^{60}Co , ^{63}Ni , and ^{55}Fe after 90 days of leaching in deionized water. The data shown were obtained from three waste-form specimens. The specimens are Brunswick-1 cation (BR-CR), Brunswick-1 mixed-bed (BR-MBR), and FitzPatrick mixed-bed decontamination resins (Fitz-MBR); and ^{60}Co from the Cooper Plant [Cooper mixed-bed resins (C-MBR) and Cooper cation resins (C-CR)] for comparison purposes (5). This figure indicates that the FitzPatrick samples had the highest CFR of all of the specimens shown.

Deionized water and simulated Hanford ground water at pH 8.9 leachants produced the highest releases from both types of Brunswick-1 waste-form specimens. Deionized water is practically ion-free, while the Hanford simulated ground water (pH 8.9) contains substantial amounts of calcium carbonate (2.6 g/l), sulfuric acid (1.65 g/l), and $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ (3.0 g/l). These constituents were not present to any extent in the other simulated ground waters. No comparable releases were observed for the cation resin waste-form specimen, which did

not contain any chelating agents. It is suggested that the presence of large amounts of Ca^{+2} and H^+ may enhance radionuclides releases from the ion exchange resins solidified in the waste-form specimen through ion exchange processes.

The low CFRs of ^{60}Co from the Brunswick-1 waste-form specimens that completely crumbled suggest that most of the ^{60}Co was immobilized through irreversible reactions with materials in the waste form matrix. The fact that there was no significant increase in the releases of transition metal radionuclides from the Brunswick-1 waste-form specimens which disintegrated indicates the potential for some irreversible reactions with the calcium in the cement.

Evaluation of the release results indicates that chelating agents can increase the release rate of all decontamination-produced radionuclides by one to two orders of magnitude. This may be due to the formation of complexed radionuclide species. It also appears that citric and oxalic acids (Citrox decontamination) are less effective (typically a factor of 10) than picolinic acid (LOMI decontamination) at increasing the leachability of most radionuclides from the waste form. Further work needs to be performed to evaluate the chemistry of these interactions and to fully confirm the mechanisms involved that appear to increase the leachability of the various radionuclides.

Radionuclide release data indicate that their leachabilities are species-dependent and may be a function of the specific elemental chemical behavior. This may be attributed to the prevalent oxidation state of the respective element and its solubility in the leaching environment. In fact, the leachability of ^{55}Fe is similar to that of ^{60}Co and both appear to be significantly affected by the presence of chelating agents. However, the release of ^{63}Ni appears to be less influenced by the presence of chelating agents. Other radionuclides, such as the fission products ^{137}Cs and ^{90}Sr , follow different release patterns than those for the activation products. Furthermore, their release patterns show little or no effective differences with changes in leachant composition.

Leachability Indexes

The leachability indexes for ^{60}Co , ^{63}Ni , and ^{55}Fe were compared for the three types of solidified waste-form specimens evaluated and for the Cooper mixed-bed and cation

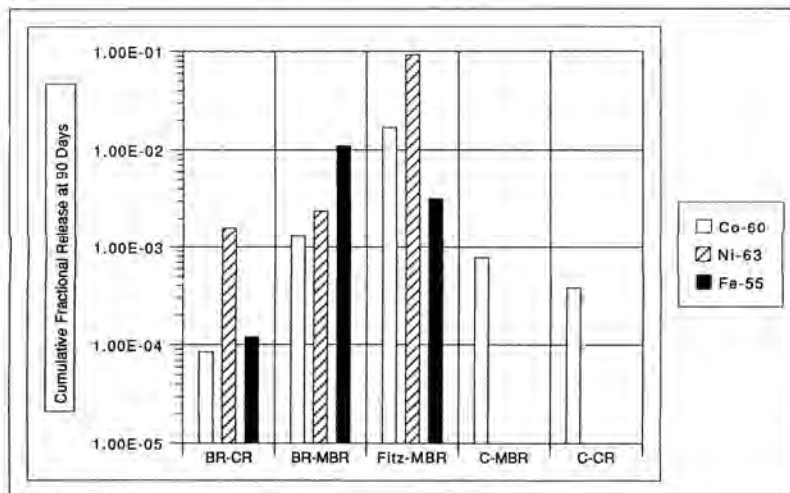


Fig. 2. Cumulative fractional releases for ^{60}Co , ^{63}Ni , and ^{55}Fe after 90 days of leaching in deionized water.

resin samples tested in a previous study at this laboratory. Figure 3 shows this comparison where the following nomenclature was used: Brunswick-1 cation resin (BR-CR), Brunswick-1 mixed-bed resin (BR-MBR), FitzPatrick mixed-bed resin (Fitz-MBR), Cooper mixed-bed resin (C-MBR), and Cooper cation resin (C-CR). The FitzPatrick waste forms exhibited the lowest ^{60}Co leachability indexes and were the only forms containing picolinic acid. The other waste forms contained citric and oxalic acids. These data suggest that the presence of picolinic acid may substantially reduce the leachability indexes for ^{60}Co . The leachability indexes for ^{63}Ni appeared to be similarly affected by the deionized water leachant only.

The leachability indexes of ^{55}Fe were similar for all waste forms. The data indicate a different leaching behavior for ^{55}Fe in the presence of anion resin and chelating agents. In particular, the release of ^{55}Fe is less affected by the presence of citric, oxalic, or picolinic acids. It may be primarily affected by the characteristic solubility of iron in specific pH aqueous solutions.

Release of Chelating Agents

Figure 4 compares CFRs of citric, oxalic, and picolinic acids from Brunswick-1 mixed-bed resin (BR-MBR), FitzPatrick mixed-bed resins (Fitz-MBR), and Cooper mixed-bed resins (C-MBR). The CFRs of chelating agents for deionized water indicate that only small fractions of their inventories were released. Picolinic acid exhibited the highest release under the leaching conditions used. Comparison of the CFRs of the decontamination radionuclides (Fig. 2) with the CFRs of the chelating agents shown in this figure suggests a correlation in which the higher release of the chelating agents corresponds to generally higher radionuclide releases. However, no explanation could be provided for the observation that the fractional releases for citric and oxalic acids from the waste forms that decomposed were lower than those calculated for the FitzPatrick waste form samples that did not disintegrate entirely.

The CFRs of the chelating agents from the Brunswick-1 and FitzPatrick mixed-bed resin waste-form specimens indicate that the CFRs of citric and oxalic acids for the various leachants are very similar and ranged from 3×10^{-3} to 9×10^{-3} . However, the FitzPatrick CFRs of picolinic acid are about a

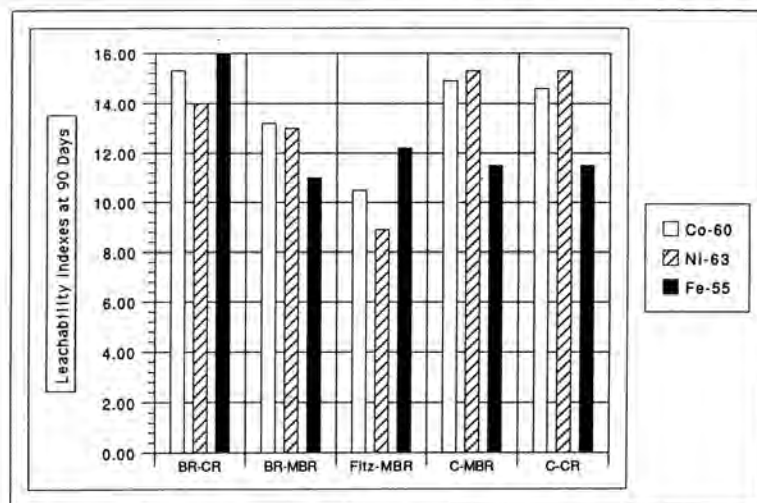


Fig. 3. Leachability indexes of ^{60}Co , ^{63}Ni , and ^{55}Fe in deionized water leachant.

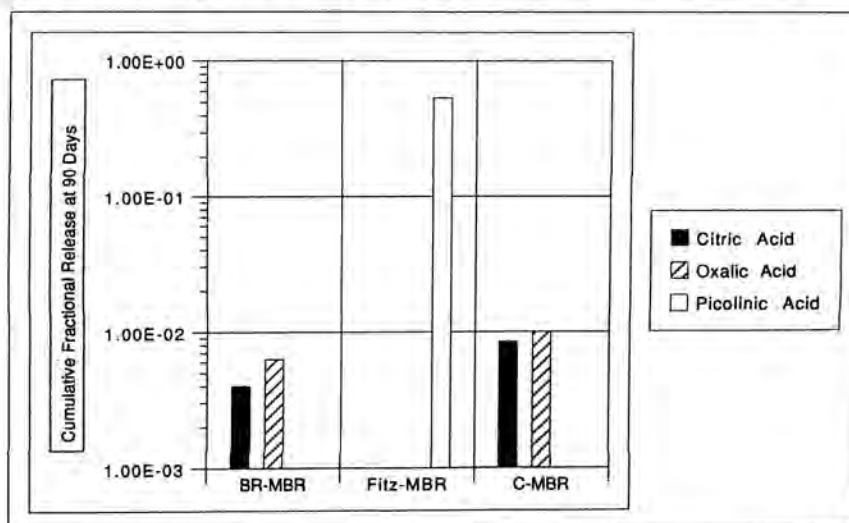


Fig. 4. Cumulative fraction releases for citric, oxalic, and picolinic acids in deionized water leachant.

factor of 10^2 higher. These data suggest that differences in the leachants used had no substantive effect on the CFRs of chelating agents from the various waste-form specimens. However, the magnitude of the release of picolinic acid suggests that it is more leachable than either citric or oxalic acid. In fact, the picolinic acid release rates were observed to be higher than any other species.

Releases of Stable Metals

The releases of stable metals into the leachates were below the detection limit for the instrumentation used except for nickel. The leachability of stable nickel is assumed to be similar to that of ^{63}Ni . The substantial release of nickel from the FitzPatrick waste forms may be due to formation of some complexes between this element and the chelating agent picolinic acid as with ^{63}Ni .

Compression Testing

Compression tests were performed only on unleached waste form samples. This is because all the leached Brunswick-1 and FitzPatrick samples lost their structural stability by the end of the leach test. Therefore, compressive strength measurements were performed to determine if the waste-form specimens met stability requirements before the leaching test. In addition to the Brunswick-1 and FitzPatrick samples, samples from Indian Point-3 and Pilgrim were also

measured for compressive strength. Testing of these samples does not fully satisfy BTP (Revision 1) requirements. These requirements stipulate that the compression test must be performed on both the as-cast and immersion-tested waste forms. The particular requirement of the BTP (Revision 1) indicates that the cement-solidified waste-form specimen must exhibit a compressive strength of 500 psi following the immersion testing.

The samples measured for compressive strength were unleached Brunswick-1 cation and mixed-bed resin waste-form specimens. They were cured for 486 days. The FitzPatrick (baked and unbaked) samples were cured for 212 days. The measured compressive strengths of the Brunswick-1 and FitzPatrick samples are shown in Table I and are expressed as kPa and psi. Relevant solidification parameters that include water-to-cement ratios, total cure times, specimen cross-sectional areas, and maximum loads achieved during compressive strength testing are also summarized in this table.

The FitzPatrick compressive strengths were factors of four to five times greater than the Brunswick-1 samples. This lower compressive strength for the Brunswick samples may have contributed to their rapid decomposition, or it may indicate an inherent problem in the formulations. Moreover, the Brunswick-1 cation resin waste form does not meet the

TABLE I

Compressive Strengths of Waste-Form Specimens

Waste Form	Decontamination Process	Water-to-Cement Ratio ^a	Cure Time of Unleached Specimens (days)	Cross-Sectional Area		Maximum Load		Compressive Strength	
				(cm ²)	(in ²)	(kg)	(lb)	(kPa)	(psi)
Brunswick-1 cation mixed-bed	Citrox	0.27	486	26.19	4.06	721	1590	2.70×10^3	392
		0.30	486	25.41	3.94	903	1990	3.48×10^3	505
FitzPatrick baked unbaked	LOMI	0.30	212	17.54	2.72	2291	5050	1.28×10^4	1857
		0.30	212	17.42	2.70	2331	5140	1.31×10^4	1906
Pilgrim unleached leached	DOW NS-1	0.37	1705	17.22	2.67	1120	2470	6.37×10^3	924
		0.37	<u>b</u>	17.54	2.72	2522	5560	1.41×10^4	2044
Indian Point-3 unleached leached	LOMI	0.38	1394	17.35	2.69	1075	2370	6.09×10^3	883
		0.38	<u>c</u>	18.00	2.79	295	650	1.61×10^3	233

a. Ratio of weight of free interstitial water to weight of cement and slaked lime or sodium hydroxide.

b. The leached waste form specimen was cured for 1.8 years prior leaching. It was leached subsequently in deionized water for a total of about 2.1 years. The sample had been removed from the leachate for about 90 days before compressive strength testing. The unleached specimen was cured for 3.8 years before leach testing. Curing and leach testing durations for this study do not meet the requirements of the Technical Position on Waste Form. However, they meet the compressive strength requirements.

c. The waste form specimen was cured for 1.5 years before leaching. It was subsequently leached in deionized water for a total of 2.1 years. The sample was removed from the leachant 90 days prior to performing the compressive strength measurement. The unleached specimen was cured for 4.7 years before performing the leach test. Curing and leach testing durations for this study do not meet the requirements of the Technical Position on Waste Form. However, they meet the compressive strength requirements.

BTP (Revision 1) requirement for compressive strength after leaching of 500 psi.

In the case of FitzPatrick, both the baked and unbaked waste-form specimens easily met the BTP (Revision 1) requirements with compressive strengths of approximately 1900 psi. These data suggest that the simulated exothermic temperature used in baking had little effect on the initial compressive strength of the waste-form specimens.

Waste form samples from the Indian Point-3 and Pilgrim reactors were also measured for compressive strength both before and after being leached. The waste-form specimen from Indian Point-3 contained decontamination resins from the LOMI process. The leached sample from Indian Point-3 Station was cured for 1.5 years and then was leached in deionized water for a total of 2.1 years prior to compression testing. The second specimen, which was compression tested without being leached, was cured at ambient temperature for a total of 3.8 years before compressive strength testing. Although the cure times and the leaching period substantially exceed the ASTM C39 standard requirements, these data indicate that the leaching of the waste-form specimen substantially reduced compressive strength.

The ion exchange resin waste stream from Pilgrim was derived from application of the NS-1 decontamination process developed by the Dow Chemical Company. Oxalic and citric acid, EDTA, and DTPA are used in the NS-1 process. The leached specimen that was compression-tested had been cured at ambient temperature 1.8 years and was then leached in deionized water for a total of 2.6 years. Compressive strength testing was performed on this specimen about 90 days after the specimen was removed from the leachant. The second specimen obtained from Pilgrim Station was cured at ambient temperature for a total of 4.7 years and not leached before being compression-tested. Examination of the compression test results indicates that the unleached specimen had a compressive strength about half that of the leached specimen. The results indicate that both waste-form specimens met the compressive strength requirements of Revision 1 of the BTP.

CONCLUSIONS

Leachate pH and conductivity measurements of the Brunswick-1 and FitzPatrick waste form samples indicate that the chemistry of the waste form quickly affects (within several minutes) the leachant pH. Thus, the leachant quickly reaches an equilibrium pH. The data obtained indicate that variations in the initial leachant pH does not affect the CFRs or release rates of components of the waste form, such as radionuclides and chelating agents in cement-solidified wastes. An exception to this behavior is when the leachant has a high ionic strength (e.g., seawater). No substantive differences in radionuclide and chelating agent release were observed as a result of the use of a low pH leachant. Examination of the absolute and fractional release rate data indicates that there are significant (1-2 orders of magnitude) leachant- and radionuclide-specific effects on releases from the waste form.

In this study, all of the Brunswick-1 (Citrox decontamination) waste-form specimens, except those leached in seawater, and the FitzPatrick (LOMI decontamination) samples that were baked decomposed during the leach test. The FitzPatrick samples that were not baked developed severe cracks early in the leach-testing program and were considered

to have lost any form of physical stability. Decomposition occurred rapidly and early in the leach test, indicating a gross physical effect.

Specimens that were leached in seawater may have maintained their general physical form because of the formation of an osmotic condition between the resin beads and the high ionic strength leachant. The ensuing decrease in resin bead uptake of water from the leachant will tend to reduce their swelling.

Calculated release rates appear to be radionuclide-specific. Typically, the magnitude of the leachability of a radionuclide is a function of the solubility of its prevalent chemical species.

The release of radionuclides from the specimens evaluated appeared to be unaffected by the waste form physical integrity. The leachability indexes of all waste forms were above the recommended minimum of 6.

The presence of picolinic acid has a substantial effect on the leachability indexes of ^{60}Co , ^{63}Ni , and ^{55}Fe . It tends to reduce the leachability index by a factor of four to five, when compared to resin waste forms containing citric and oxalic acid, or to waste forms without chelating agents. The LOMI process, picolinic acid, increases the leachability of most radionuclides more effectively than the Citrox process, citric and oxalic acids, by a factor of 10. Measurements were made for ^{241}Pu . However, the results of these measurements were near or below the detection limit for this radionuclide.

Picolinic acid is released at much higher absolute and fractional release rates than are citric and oxalic acids, and at higher levels than any other species. It is suggested that picolinic acid forms complexes with some radionuclides and causes substantial increases in releases from the waste form.

The releases of stable metals into the leachates were basically below the detection limit for the instrumentation used except for nickel. It was concluded that the leachability of stable nickel was very similar to that of ^{63}Ni .

Compression testing of unleached samples does not provide information on the stability of the waste form after immersion or leaching because the Brunswick-1 and FitzPatrick waste-form specimens met the BTP (Revision 1) compression test requirements before leaching began but quickly decomposed upon immersion in leachants.

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