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by

M. John Plodinec, Paul D. Soper,
Ned E. Bibler, and John L. Kessler

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

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SRP RADIOACTIVE GLASS STUDIES: SMALL-SCALE PROCESS DEVELOPMENT AND PRODUCT PERFORMANCE*

M. John Plodinec, Paul D. Soper,
Ned E. Bibler, and John L. Kessler
E. I. du Pont de Nemours & Co.
Savannah River Laboratory
Aiken, South Carolina 29808

INTRODUCTION

The Savannah River Plant has been producing defense nuclear materials for over 25 years. Radioactive wastes from chemical separation processes have accumulated during this time and now amount to approximately 28 million gallons. This high-level liquid waste is stored in underground tanks on the plant site. The Savannah River Laboratory (SRL) has been actively investigating methods of immobilization of these wastes.

The alkaline waste consists of three fractions: an insoluble sludge consisting primarily of hydroxides and hydrous oxides of aluminum, iron, and manganese, a crystalline salt cake, and a saturated supernatant solution. The sludge fraction contains approximately 60% of the total radioactivity of the waste and virtually all of the long-lived actinides. The most important radionuclide in the supernatant solution is Cs-137, only 5% of which is trapped in the sludge.

Current plans are first to immobilize the sludge fraction, and later to decontaminate and solidify the salt and dissolved solids in the supernatant solution. This two-stage approach reduces the initial capital investment and also allows for a more efficient allocation of resources.

The reference process for immobilizing the sludge fraction is vitrification. Before being fed to the melter, the waste sludge is washed with hot caustic to remove excess aluminum and rinsed with water to remove soluble salts. Glass-forming chemicals (in the form of premelted borosilicate glass frit) are then added to the waste, and the waste/frit slurry fed to a Joule-heated ceramic melter. This process has been successfully demonstrated on actual wastes with both calcine and slurry feeding of the melter, with two different glass frit compositions, and with a range of waste compositions.

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These demonstrations took place in a small-scale melter in a shielded cell facility. Another melter of the same design is run using nonradioactive simulated waste sludge. In a companion program, the vitrification process is being demonstrated on a large scale with simulated sludge.

In this report, recent results are reviewed. These show that the slurry-fed melting process is able to immobilize a wide range of waste compositions with minimal effluents, at an acceptable rate. The actual waste glass produced by the small continuous melter is at least as durable as simulated waste glass made in the laboratory, in standard (MCC) leach tests.

VOLATILITY FROM THE GLASS MELT

A schematic of the slurry-fed melter used in these studies appears in Figure 1. The off-gas treatment system consisted of a series of units, each of which was designed to answer certain questions. Any volatilized or entrained material first passed through a semivolatiles trap. This consisted of a tube lined with removable rings. The temperature along the trap dropped from about 800°C at the end nearest the melt surface to 350°C where the trap was connected to the transfer line. By chemical and radiochemical analysis of deposits on the rings, whose temperatures during operation were known, it was possible to deduce the chemical and physical behavior of many components of the off-gas stream, including the most important radionuclides.

The semivolatiles trap was connected to a packed-bed scrubber by a transfer line held at 350°C. This is approximately the off-gas exit temperature which will be present in the full-scale Defense Waste Processing Facility (DWPF). The scrubber removed water--70% of the slurry fed to the melter--and entrained particulate material. This was followed by two backup absorption beds, one for ruthenium and one for iodine. The entire system was run under a slight vacuum. In none of the studies were any radionuclides detected downstream of the scrubber.

Table 1 shows the feed composition for the volatility tests. Table 2 lists the relative amounts of the radionuclides found in the off-gas system. When waste is fed alone, significantly greater amounts of cesium and ruthenium are found in the semivolatiles trap and transfer line, but the amounts of strontium and technetium found are roughly the same. This suggests that cesium and ruthenium are lost by volatilization, and strontium and technetium by entrainment.

Entrainment is strongly dependent on the geometry of the melter plenum and on air in-leakage rates. Although the results reported here are conservative upper limits on volatile losses for cesium and ruthenium, entrainment can differ significantly with scale-up.

MELTING RATE STUDIES

These studies were performed on simulated waste sludge using a melter identical to the one described above except for a simpler off-gas system. Waste/frit slurries of differing weight percent solids were fed to the melter. Addition of formic acid to the feed was required on all slurries over 40 wt % solids. At these high solids loadings, circulation of slurry in the feed loop cannot be maintained without the improvement in rheology afforded by formic acid treatment. These studies clearly show that removing water from the slurry, rather than melting of solids, is the limiting factor determining melt rate. As may be seen in Table 3, the rate at which water is removed is roughly constant. Therefore, slurries that contain more solids for a given amount of water produce higher melt rates. This result, shown graphically in Figure 2, is consistent with a theory developed by K. R. Routt, which will be published soon.

MCC-1 LEACHABILITY STUDIES

To measure the durability of the radioactive glass prepared with the melter in the shielded cells, leach rates at 40°C in deionized water were measured for Cs-137, Sr-90, and alpha activity (predominantly Pu). Procedures for the MCC-1 static leach test were followed as much as possible.[1] Feed for the melter for this glass was a mixture of Frit 21 and radioactive sludge from SRP storage Tank 13. Compositions are shown in Table 4. Also, a small amount of zeolite loaded with Cs-137 was present. The zeolite resulted from a demonstration test for removal of Cs-137 from the supernate by ion exchange. Results of the leach tests (Table 5 and Figure 3) agree with the data[2] available for MCC-1 tests for non-radioactive glasses at 40°C. This agreement indicates similar durabilities. Also, the rates in Table 5 decrease with increasing leach time, in agreement with observations in tests with both non-radioactive and radioactive glass.[3]

The three "elemental" leach rates - Cs-137, Sr-90 and gross alpha - are equal within experimental error after 36 days. The leach rate at this time of 0.01 g/m^2-day, when multiplied by

365 days/year and the 3 x 10^{-6} m^2/g specific surface area of the glass monolith, gives a fractural relesse rate of 1 x 10^{-5}/yr. The actual release would be even lower than this, since the leach rates will continue to decrease with time.

A significant result in Table 5 is that the pH does not decrease in the 28- and 36-day tests as a result of radiolysis of dissolved air in the water. Dose rate to the leachant is approximately 5 x 10^5 rad/hr from the beta particles and gamma rays of the glass. A pH decrease would result if the radiolysis formed nitric acid. This effect has been observed in Co-60 radiation tests.[4] This apparent lack of an effect of radiolysis on leachant pH supports the proposal that radiolytic nitric acid formation will not be significant during geologic storage of the glass.[5] The reason that a pH decrease was not observed with these radioactive glass samples is currently being investigated. Possibly, the dose rate is a factor.

Because of the intense radioactivity of the glass (approximately 5 X 10^5 rad/hr at contact), four procedures prescribed in MCC-1 were changed. First, polyethylene leach containers rather than Teflon (Du Pont) were used because of the relatively low radiation stability of Teflon and the possibility of radiolysis producing HF from the Teflon . Second, the radioactive glass was placed in stainless steel baskets for leaching. Plastic could not be used adjacent to the glass because they would quickly degrade from the intense beta radiation from the glass. Third, the vigorous cleaning procedure to remove contaminants from the leach vessels was not necessary because only radioactivity was used to measure leach rates. Lastly, samples for leaching were obtained by fracturing the glass rather than by core drilling. Also, the fractured surfaces were not polished before leaching. Because fractured samples were used, the surface area had to be estimated. This was done by placing each surface against a calibrated grid and estimating its area. The error introduced by this procedure was <20%. As prescribed in MCC-1, the glass was washed in an ultrasonic cleaner in water and alcohol prior to leaching. Control experiments indicated that radioactive contamination was not a problem in the shielded cells. During leaching, the sample bottles were placed in a 40° ±2°C oven. When a test was completed, the glass was removed, the leachate in the container acidified, and then sampled after standing another day. The Cs-137, Sr-90, and gross alpha activities of the leachate were then determined by standard counting techniques.

The specific activities of the glass were determined by dissolving a known amount by Na_2O_2 fusion, followed by HNO_3 dissolution. The solution containing the dissolved glass was then counted. The specific activities for Sr-90 and gross alpha

(Table 5) were in reasonable agreement with those expected from analysis of the sludge. The Cs-137 activity was approximately 100X higher because of the addition of the Cs-loaded zeolite.

SUMMARY

Tests using actual Savannah River Plant radioactive waste sludge in a small-scale joule-heated ceramic melter contained in the Shielded Cells Facility have demonstrated that losses of radionuclides due to volatility are low and easily treated, and that the glass produced is of comparable quality to laboratory-prepared simulated glass.

Future work will include studies with wastes from other tanks, using new frit compositions. Leaching tests will continue, with emphasis being placed on long-term tests under anticipated repository conditions.

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TABLE 1

Compositions For Volatility Tests[a]

Frit 131		Tank 15 Sludge Composition as Oxides		Radionuclide Composition	
Component	Wt %	Oxide	Wt %	Isotope	mCi/g
SiO_2	57.9	Al_2O_3	53.3	Cs-137	0.95
Na_2O	17.7	Fe_2O_3	8.1	Sr-90	0.37
B_2O_3	14.7	MgO	7.6	Ru-106	0.017
Li_2O	5.7	U_3O_8	2.7	Tc-99	0.0025
MgO	2.0	Na_2O	2.4		
TiO_2	1.0	MnO_2	2.5		
ZrO_2	0.5	SiO_2	3.4		
La_2O_3	0.5	ThO_2	1.6		
		Other	18.4		

[a] The 30 wt % solids in the slurry consisted of 70 wt % Frit 131 and 30 wt % Tank 15 sludge.

TABLE 2

Radionuclides in the Off-Gas System

Radionuclide	% in Off-Gas System	Distribution, %		
		Trap	Line	Scrubber
Cs-137	1	0.2	0.8	Approx. 0
Ru-106	5	1	4	Approx. 0
Tc-99	2	0.05	2.0	Approx. 0
Sr-90	5	5	Approx. 0	Approx. 0

TABLE 3

Effect of Solids Loading of Slurry on Melt Rate

Wt % Solids	Water Removal Rate (lb/hr-ft^2)	Melt Rate (lb/hr-ft^2)
30	8.3	3.6
40	8.3	5.5
40[a]	8.0	5.3
45[a]	7.8	6.5
50[a]	9.2	9.2
60[a]	7.1	10.7

[a] Formic-acid-treated slurries.

TABLE 4

Compositions Used in Leaching Tests[a]

Frit 21[b]		Tank 13 Sludge[c] Composition as Oxides		Radionuclide Composition	
Component	Wt %	Oxide	Wt %	Isotope	mCi/g
SiO_2	52.5	Fe_2O_3	39.9	Sr-90	15.5
Na_2O	18.5	MnO_2	13.9	Ce-144	2.0
TiO_2	10.0	Al_2O_3	13.4	Ru-106	0.40
B_2O_3	10.0	U_3O_8	4.7	Eu-154	0.30
Li_2O	4.0	Na_2O	4.2	Cs-137	0.30
CaO	5.0	CaO	3.2	Pu-238, 239; Cm-244	0.28
		Others	20.7		

[a] Glass leached is 65 wt % Frit 21, 34 wt % Tank 13 sludge, and 1 wt % Cs-137 loaded zeolite.

[b] Reference 3.

[c] Reference 6.

TABLE 5

Leach Rates of Actual Waste Glass in MCC-1
Tests at 40°C in Deionized Water[a]

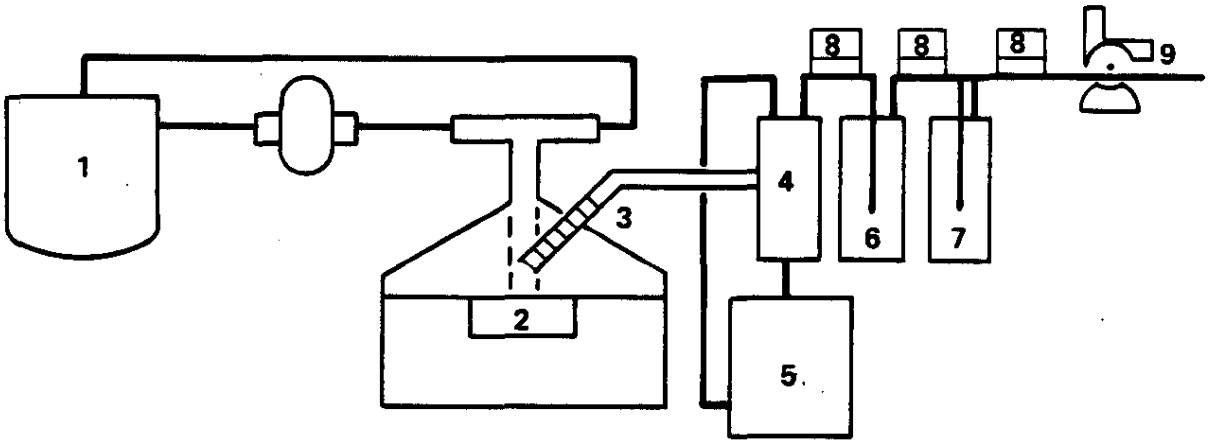
Time (days)	Leach Rates (g/m^2-day)[b]			pH Change: Initial/Final
	^{137}Cs	^{90}Sr	Gross Alpha[c]	
3	0.030	0.041	0.18	Not determined
7	0.041	0.050	0.21	Not determined
28	0.012	0.016	0.05	6.5/7.7
36	0.006[d]	0.005[d]	0.01[d]	7.4/8.2[d]

[a] Glass is 65% Frit 21, 34% Tank 13 sludge and 1% Cs-137 loaded zeolite. Specific activity of the glass (dpm/g glass): Cs-137, 1.2×10^{10}; Sr-90, 7.9×10^{9}; gross alpha, 1.0×10^{8}.

[b] SA/V = approximately 0.1 cm^{-1}, approximately 10 grams leached in 200 mL water. Results based on acidified leachates.

[c] Activity was 23% Pu-239, 44% Pu-238, and 33% Cm-244.

[d] Based on 5 separate tests. Relative standard deviation is approximately 30%.



1. Feed Slurry Tank
2. Melt Chamber
3. Semivolatiles Trap
4. Scrubber
5. Scrub Liquid Tank
6. Ru Trap
7. I_2 Trap
8. NaOH Solution Traps
9. Exhaust Fan

FIGURE 1. Schematic of the Small Slurry-Fed Joule-Heated Ceramic Melter and Off-Gas Treatment System Used in this Study. No Radionuclides Were Ever Detected Downstream of the Scrubber.

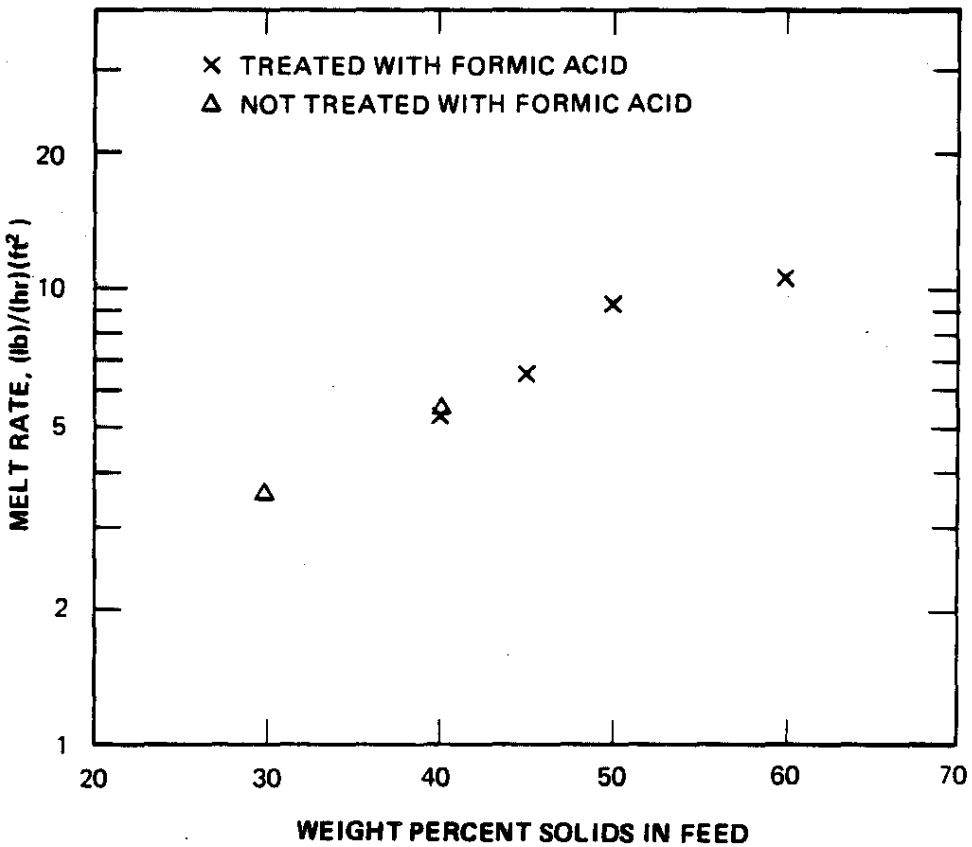


FIGURE 2. Melt Rate vs. Weight Percent Solids in The Slurry Fed to the Melter Shown in Figure 1. Since the Water Removal Rate is Constant (See Table 3), Slurries of Higher Solids Loadings Give Higher Melt Rates.

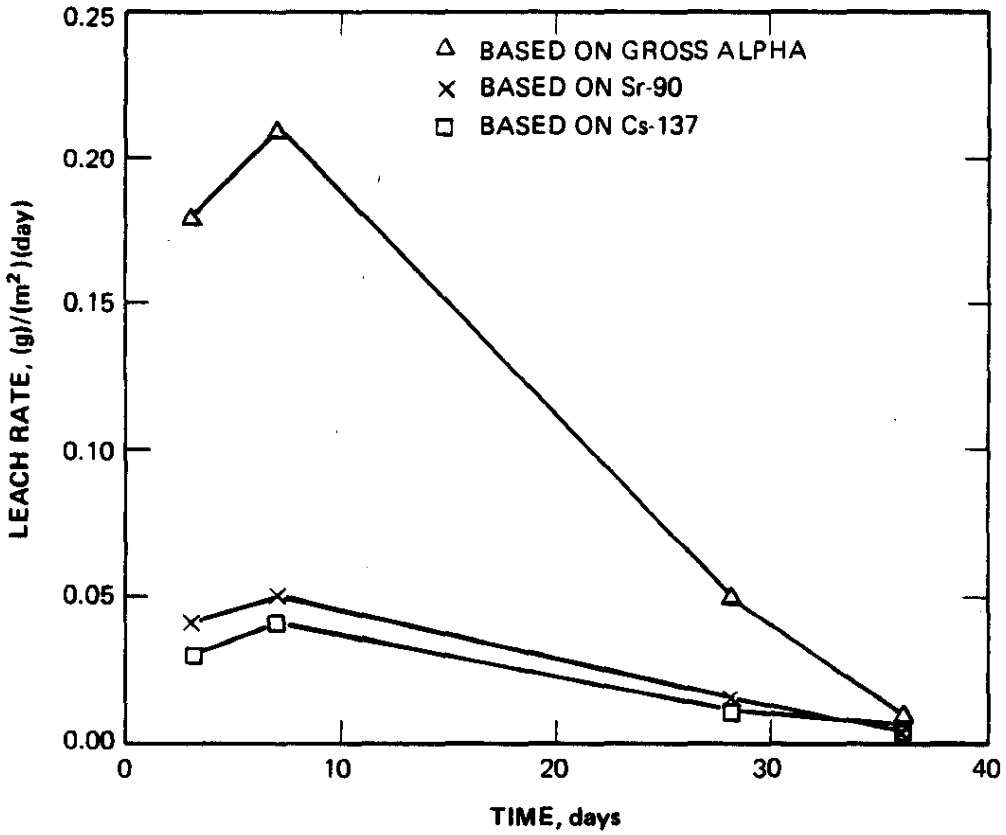


FIGURE 3. Time Dependence of "Elemental" Leach Rates of Actual SRP Waste Glass. All Three Rates are Equal to About 0.01 g/m^2-day after 36 days, Corresponding to an Annual Fractional Release of 1×10^{-5}/yr.