DP-1397

663124

EVALUATION OF GLASS AS A MATRIX FOR SOLIDIFICATION OF SAVANNAH RIVER PLANT WASTE

RADIOACTIVE STUDIES

J. A. KELLEY

SAVANNAH RIVER LABORATORY
AIKEN, SOUTH CAROLINA 29801

PREPARED FOR THE U.S. ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION UNDER CONTRACT AT(07-2)-1

Printed in the United States of America

Available from
National Technical Information Service
U. S. Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22161

Price: Printed Copy $4.00; Microfiche $2.25

66264

DP-1397

Distribution Category: UC-70

EVALUATION OF GLASS AS A MATRIX FOR SOLIDIFICATION OF SAVANNAH RIVER PLANT WASTE

RADIOACTIVE STUDIES

by

J. A. KELLEY

Approved by

W. H. Hale, Jr., Research Manager
Separations Chemistry Division

Publication Date: October 1975

E. I. DU PONT DE NEMOURS AND COMPANY
SAVANNAH RIVER LABORATORY
AIKEN, SOUTH CAROLINA 29801

PREPARED FOR THE U. S. ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION UNDER CONTRACT AT(07-2)-1

ABSTRACT

Laboratory tests using actual sludges collected from Savannah River Plant (SRP) waste tanks were performed to evaluate glass as a waste solidification matrix. Sludge was collected from three SRP waste tanks, washed to remove soluble salts, and then ground to a fine powder. From 25 to 40 wt % of these sludges was vitrified into a borosilicate glass by melting at 1150°C. Substitution of 4 wt % Li_2O for 4 wt % Na_2O in the glass mix allowed higher loading of a high-aluminum sludge. No problems with phase separation were encountered, and all sludge components, except mercury which volatilized, appeared to dissolve completely in the glass melt. Volatilization of radionuclides during melting was 0.3% for ^{137}Cs, 2.9% for ^{106}Ru, and $\leq$0.01% for other nuclides.

Initial leachabilities of glass products were low: 10^{-6} to 10^{-5} g/(cm^2-day) for ^{137}Cs, ^{90}Sr, and alpha activity. Leachabilities decreased to 10^{-8} to 10^{-7} g/(cm^2-day) in ∿2 weeks. Heating the glasses at 600°C for 1 month caused devitrification which increased leachability, but durable waste forms still remained.

This work showed that vitrification of SRP high-level waste sludges in borosilicate glass is feasible. Further investigation of melting concepts, scale-up, cost, long-term stability, and other factors are planned as a part of the development program for long-term waste management.

CONTENTS

LIST OF FIGURES

LIST OF TABLES

EVALUATION OF GLASS AS A MATRIX FOR SOLIDIFICATION OF SAVANNAH RIVER PLANT WASTE. RADIOACTIVE STUDIES

INTRODUCTION

Borosilicate glass is being considered as a possible solidification matrix for Savannah River Plant (SRP) high-level waste sludge. In a previous report,[1] the overall waste processing study, preliminary evaluation of glass compositions, glass characterization by leaching and differential thermal analysis, and data for volatilization of radionuclides during melting were presented. Based on the work with simulated sludges and tracers, an optimum glass composition was chosen for further study. This glass mix could incorporate from 35 to 45 wt % simulated SRP sludges by melting at 1150°C. Initial leachabilities of glass products were about 10^{-6} g/(cm^2-day) decreasing to 10^{-8} g/(cm^2-day) in about six weeks. The glass mix contains TiO_2 which limits ^{137}Cs volatility to <0.5%. Ruthenium volatility with simulated sludges was from 10 to 50% depending on the nitrate and MnO_2 content of the sludge. Also, substitution of a small amount of Li_2O for Na_2O in the glass mix reduced melt viscosity and allowed higher loading of high-aluminum sludges. Sulfate solubility in the glass was 0.8 to 1.0 wt %. With more sulfate, a water-soluble, ^{137}Cs-rich phase separated on the glass surface.

This report presents results of a follow-up study of vitrification of actual SRP waste sludges. This work was done to determine whether unexpected problems would be encountered with actual wastes and to determine maximum sludge loading, volatilization during melting, product leachability, and the effects of devitrification.

SLUDGE DESCRIPTION

Twelve 3-ℓ samples of high-level waste sludge were collected from four SRP waste tanks. The sludges were washed to remove soluble salts and ground to obtain a free-flowing powder. The major elemental components of three of these sludges are shown in Table 1. Sludge from Tank 7 was found to be mainly sand and coal from reactor-area filter backwashes and was not used in this work. The major radionuclides found in the sludges are shown in Table 2. A detailed description of sludge collection, processing, and characterization is presented in another report.[2]

TABLE 1

Chemical Composition of Washed, Dried Sludges, wt % (mole %)[a]

	Tank 5		*Tank 13*		*Tank 15*	
Fe	27.5	(39.6)	27.9	(40.0)	3.1	(3.9)
Mn	10.8	(15.9)	8.8	(12.8)	2.3	(2.9)
Al	1.5	(4.6)	7.1	(20.9)	33.5	(86.1)
U	15.4	(5.2)	4.0	(1.3)	0.9	(0.3)
Na	6.1	(21.6)	3.1	(10.6)	1.2	(3.6)
Ca	0.6	(1.3)	2.3	(4.7)	0.2	(0.4)
Hg	0.1	(-)	2.1	(0.8)	0.9	(0.3)
Ni	5.1	(7.1)	0.5	(0.7)	0.5	(0.6)

a. Major elements only.

TABLE 2

Radionuclides in Washed, Dried Sludges, mCi/g

	Tank 5	*Tank 13*	*Tank 15*
^{90}Sr	74.7	15.5	25.6
^{144}Ce	4.8	2.0	16.9
^{106}Ru	2.7	0.4	1.7
^{154}Eu	0.5	0.3	1.2
^{137}Cs	1.3	0.3	0.1
^{125}Sb	0.4	0.1	1.3
Total α	0.1	0.3	0.1

The sludges had diverse chemical compositions, with iron, manganese, aluminum, and uranium the principal elements found. ^{90}Sr was the predominant radionuclide in each sludge product.

VITRIFICATION OF SLUDGES AND ZEOLITE

Glasses were made with washed, dried sludges from Waste Tanks 5, 13, and 15. From 20 to 45 wt % sludge was melted with Mix 18 frit (Table 3). The frit was prepared by pouring molten glass into water; the broken glass was then ground to a fine powder. The frit minimized melt frothing which occurs when metal carbonates are used in glassmaking. Tests were made in a muffle furnace to determine the maximum sludge loading that gave a homogeneous, pourable product. With Tank 5 and 13 sludges, 40 wt % sludge was the optimum loading. With 45 wt % sludge, the glass was pourable, but the product was grainy, indicating undissolved sludge particles were in the glass. Because Tank 15 sludge is rich in aluminum, only 25 wt % of this sludge could be incorporated. Higher loadings caused crusty or nonpourable products.

TABLE 3

Composition of Mix 18 Glass Frit, wt %

SiO_2	52.5
Na_2O	22.5
B_2O_3	10.0
TiO_2	10.0
CaO	5.0

One test was made in which 4 wt % Li_2O was substituted for 4 wt % Na_2O in Mix 18. Previous studies[1] showed that this significantly reduced melt viscosity. With this change in the glass composition, 35 wt % Tank 15 sludge could be incorporated. The viscosity of this melt was less than the melt with 25 wt % Tank 15 sludge that contained no Li_2O. Li_2O is not needed with all plant sludges, but it could be used with high-aluminum sludges.

No problems were encountered during melting. No separate sulfate phase was observed even with 40 wt % sludge loading. All sludge components appeared to dissolve completely in the glass with $\leq$40 wt % loading. Black, shiny glasses were formed with all sludges.

VOLATILIZATION OF RADIONUCLIDES DURING MELTING

In further tests with plant sludges, volatilization of radioactivity during glass melting was determined. A tilt-pour furnace shown schematically in Figure 1 was used. Glass frit and sludge were mixed and then melted in a ceramic crucible. An *Inconel* (Registered trademark of International Nickel Co.) funnel fitted over the crucible and attached to vacuum, collected radioactivity volatilized during melting. A scrubber containing 2M NaOH collected radioactivity not deposited on the funnel. After the melt was heated for 3 hr at 1150°C, the funnel was removed and a graphite crucible was inserted into the furnace. The furnace was then inverted and the molten glass was poured into the graphite crucible. The glass was annealed at 500°C for 1 hr in another furnace. The *Inconel* funnel was leached in 4M HNO_3 - 0.5M HF to remove deposited radioactivity, mainly ^{106}Ru. Twelve tests were run by this procedure. Three tests were made with each of the three plant sludges, two with Tank 13 sludge plus cesium-loaded zeolite, and one with Tank 13 sludge plus cesium eluate from the *Duolite* (Registered trademark of Diamond Shamrock Co.) process.[3] (This solution is ∿2M Na_2CO_3 and contains ^{137}Cs.)

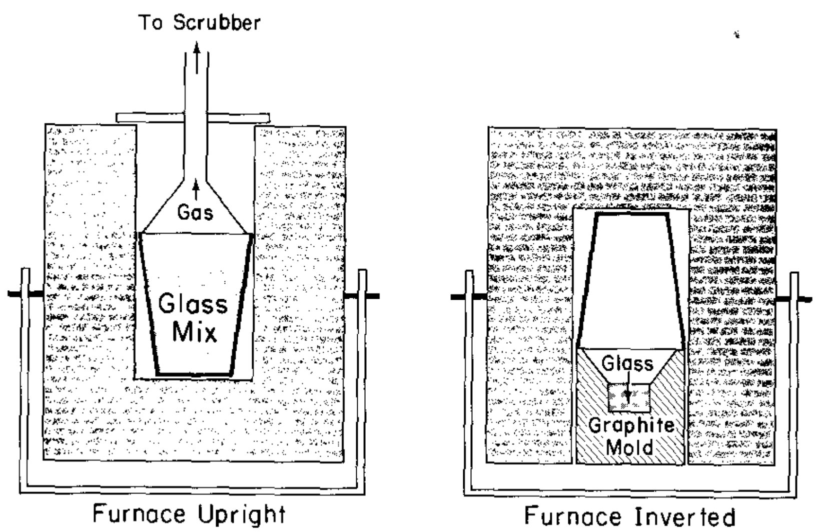

FIGURE 1. Furnace for Melting Glass

Scrubber and funnel leach solutions were analyzed by gamma spectroscopy, alpha counting, and ^{90}Sr-^{90}Y determinations. Table 4 summarizes results for ^{137}Cs. Cesium volatility from plant sludges was low as expected from previous studies.[1] Titanium in the glass mix efficiently suppresses cesium volatility. Cesium volatility with cesium-loaded zeolite and sludge was also low. The low cesium volatility in the test with Tank 13 sludge plus cesium eluate from the *Duolite* process[3] indicates that sorption of cesium onto zeolite may not be required if glass is used as the matrix for long-term solidification of SRP wastes. This would simplify the process and result in some cost savings. If this were done, sodium would be supplied by the cesium eluate and not from the glass mix.

TABLE 4

Cesium Volatilization During Glass Melting[a]

Glass	*Tests*	*% Volatilized*
18-40-5[b]	3	0.33
18-40-13	3	0.22
18-25-15	3	0.45
18-40-13/Cs[c]	1	0.10
18-30-13/Z[d]	2	0.05
Average		0.27

a. Samples heated 3 hr at 1150°C in tilt furnace.

b. 18 is mix number, 40 is wt % sludge, and 5 is tank number.

c. Cs refers to cesium eluate from *Duolite* process.[3]

d. Z refers to cesium-loaded zeolite (*Linde* AW-500, product of Union Carbide Corporation), 10 wt % in glass.

Ruthenium volatility during glass melting was lower than expected (Table 5). In previous tests with simulated sludges, 10 to 50% of the ruthenium volatilized. This was attributed to nitrate and MnO_2 oxidation of ruthenium to volatile RuO_4. Nitrate and MnO_2 concentrations in plant sludges used in this work were low. Most of the ruthenium deposited on the *Inconel* funnel over the crucible. Volatility of other radioactivity was low (Table 6). Significant quantities of ^{90}Sr, ^{144}Ce, and alpha activity were not expected to volatilize. The small quantities detected may have been caused by entrainment.

TABLE 5

Ruthenium Volatilization During Glass Melting[a]

Glass	*Tests*	*% Volatilized*
18-40-5	3	2.50
18-40-13	3	6.95
18-25-15	3	1.48
18-40-13/Cs	1	0.62
18-30-13/Z	2	0.95
Average		2.94

a. Samples heated 3 hr at 1150°C in tilt furnace.

TABLE 6

Volatilization of Other Nuclides During Glass Melting[a]

Nuclide	*% Volatilized*
^{144}Ce	0.006
^{90}Sr	0.01
Alpha Activity	0.01

a. Samples heated 3 hr at 1150°C in tilt furnace.

LEACHING OF WASTE GLASSES

Some of these glasses were leached in distilled water at 25°C to determine the quantity of radioactivity released as a function of time. The glasses to be leached were removed from the process cells in which they were made because of the possibility of contamination of leach water.

Two methods were used to leach the glasses. In one procedure, leaching was done in 150 ml of stagnant, distilled water at 25°C. Leach water was changed once per day for the first week, once per week for the next four weeks, and monthly thereafter. In the other method, the apparatus shown schematically in Figure 2 was used to leach Glass 18-40-13/Cs. Distilled water at 25°C was circulated through the leach cell containing the glass waste form and then through cation and anion exchange resin beds. Ions leached from the glass were sorbed on the resins, and the waste form was always exposed to deionized water of relatively constant pH. The cation exchange resin was eluted with 25 ml of 4M HNO_3 at the same intervals as described above. The anion exchange resin was eluted with 4M NaOH after 100 days. ^{137}Cs, ^{90}Sr, and alpha activity were sorbed on the cation exchange resin and ^{125}Sb was sorbed on the anion exchange resin. This method provided a 6-fold concentration of leached ions and gave more reliable analytical results because of the low leachability of the glass.

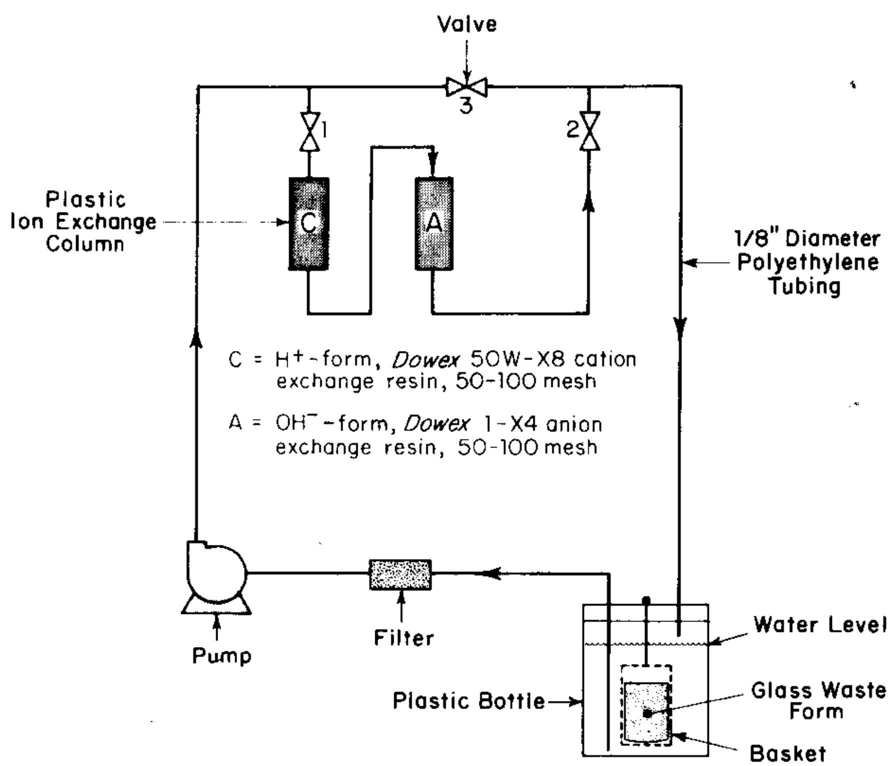

FIGURE 2. Leach Apparatus for Glass Waste Forms

^{137}Cs and ^{125}Sb in leach water were analyzed by low-level gamma spectroscopy; ^{90}Sr by extraction of the ^{90}Y daughter with di(2-ethylhexyl)-phosphoric acid, allowing ^{90}Y to grow back in, and then beta counting of in-grown ^{90}Y; alpha, by gross alpha counting. Results are shown in Tables 7 through 10.

Leachability of radionuclides from waste glasses is in the following order: $^{125}Sb > {}^{90}Sr > {}^{137}Cs >$ alpha activity. No gamma emitting nuclides other than ^{137}Cs and ^{125}Sb were leached from the glass.

Initial leachabilities for all nuclides are 10^{-6} to 10^{-5} g/(cm^2-day). Most leachabilities decrease to 10^{-8} to 10^{-7} g/(cm^2-day) in 2 weeks. In all cases, the fraction of the total nuclide content of the glass leached in 100 days was very small. In Glass 18-40-5, the fraction of the ^{125}Sb that had leached out in 100 days was only 3.7×10^{-4}. Only $\sim 10^{-5}$ of the ^{90}Sr and $\sim 10^{-6}$ of the ^{137}Cs and alpha activity leached out in 100 days. Leachabilities averaged over the entire leach period are very low [10^{-8} to 10^{-6} g/(cm^2-day)]. Based on these leachability data, very good glasses were made with Mix 18 and SRP waste sludges.

TABLE 7

^{137}Cs Leachabilities of Waste Glasses

Leach Time, days	*Leachability, g/(cm²-day)* 18-40-5	18-40-13	18-30-13/Z	18-40-13/Cs	18-25-15
1	3.2×10^{-6}	1.7×10^{-6}	3.0×10^{-6}	1.1×10^{-6}	1.2×10^{-5}
2	7.9×10^{-7}	4.5×10^{-7}	6.6×10^{-7}	1.0×10^{-7}	8.2×10^{-8}
3	2.5×10^{-7}	2.0×10^{-7}	2.2×10^{-7}	9.3×10^{-8}	8.2×10^{-8}
4	1.9×10^{-7}	1.6×10^{-7}	1.4×10^{-7}	5.9×10^{-8}	8.2×10^{-8}
7	1.2×10^{-7}	2.7×10^{-8}	1.4×10^{-7}	4.1×10^{-8}	3.8×10^{-7}
14	4.5×10^{-8}	2.3×10^{-8}	4.2×10^{-8}	3.0×10^{-8}	2.9×10^{-7}
21	2.3×10^{-8}	1.2×10^{-8}	4.1×10^{-8}	2.4×10^{-8}	2.5×10^{-7}
35	1.7×10^{-8}	4.1×10^{-8}	2.9×10^{-8}	1.0×10^{-8}	1.6×10^{-7}
45	2.3×10^{-8}	1.2×10^{-8}	2.0×10^{-8}	6.4×10^{-9}	1.6×10^{-7}
75	4.3×10^{-9}	5.4×10^{-9}	6.3×10^{-9}	9.4×10^{-8}	8.1×10^{-8}
100	3.9×10^{-9}	3.0×10^{-9}	5.3×10^{-9}	8.7×10^{-8}	4.1×10^{-8}
Fraction of ^{137}Cs Leached in 100 days	4.3×10^{-6}	2.8×10^{-6}	4.9×10^{-6}	3.6×10^{-6}	2.0×10^{-5}
Leachability based on total leach time	5.9×10^{-8}	3.5×10^{-8}	5.6×10^{-8}	4.9×10^{-8}	2.3×10^{-7}

TABLE 8

^{90}Sr Leachabilities of Waste Glasses

Leach Time, days	*Leachability, g/(cm²-day)*				
	18-40-5	*18-40-13*	*18-30-13/Z*	*18-40-13/Cs*	*18-25-15*
1	1.9×10^{-5}	4.2×10^{-5}	1.1×10^{-5}	2.8×10^{-5}	2.0×10^{-5}
2	1.3×10^{-6}	9.5×10^{-7}	4.8×10^{-7}	1.2×10^{-6}	1.5×10^{-6}
3	2.8×10^{-7}	1.8×10^{-7}	1.2×10^{-7}	4.9×10^{-7}	-
4	1.6×10^{-7}	7.9×10^{-8}	9.5×10^{-8}	2.7×10^{-7}	-
7	1.7×10^{-7}	3.4×10^{-8}	-	2.0×10^{-7}	7.4×10^{-8}
14	4.7×10^{-8}	1.1×10^{-8}	1.4×10^{-8}	1.2×10^{-7}	4.4×10^{-8}
21	2.0×10^{-8}	1.5×10^{-8}	1.4×10^{-8}	1.0×10^{-7}	3.3×10^{-8}
35	5.0×10^{-9}	3.0×10^{-8}	1.4×10^{-8}	8.5×10^{-8}	1.1×10^{-8}
45	5.0×10^{-9}	2.3×10^{-8}	2.7×10^{-8}	-	2.2×10^{-8}
75	1.2×10^{-9}	6.0×10^{-9}	7.0×10^{-9}	1.1×10^{-7}	5.0×10^{-9}
100	1.2×10^{-9}	6.0×10^{-9}	7.0×10^{-9}	2.2×10^{-7}	5.0×10^{-9}
Fraction of ^{90}Sr leached in 100 days	1.6×10^{-5}	3.5×10^{-5}	1.1×10^{-5}	3.2×10^{-5}	2.0×10^{-5}
Leachability based on total leach time	2.2×10^{-7}	4.4×10^{-7}	1.2×10^{-7}	4.4×10^{-7}	2.3×10^{-7}

TABLE 9

^{125}Sb Leachabilities of Waste Glasses

Leach Time, days	*Leachability, g/(cm²-day)* 18-40-5	18-40-13	18-30-13/Z	18-25-15
1	9.5×10^{-5}	1.9×10^{-5}	3.1×10^{-5}	4.8×10^{-5}
2	2.2×10^{-5}	3.6×10^{-6}	3.7×10^{-6}	6.0×10^{-6}
3	1.5×10^{-5}	2.3×10^{-6}	1.2×10^{-6}	2.5×10^{-6}
4	1.1×10^{-5}	1.1×10^{-6}	4.4×10^{-7}	2.5×10^{-6}
7	7.4×10^{-6}	4.6×10^{-7}	3.1×10^{-7}	1.8×10^{-6}
14	4.8×10^{-6}	3.1×10^{-7}	2.6×10^{-7}	1.2×10^{-6}
21	5.5×10^{-6}	3.4×10^{-7}	2.4×10^{-7}	6.7×10^{-7}
35	4.2×10^{-6}	1.4×10^{-7}	1.1×10^{-7}	2.8×10^{-7}
45	2.0×10^{-6}	1.0×10^{-7}	1.6×10^{-8}	7.7×10^{-8}
75	2.2×10^{-6}	7.0×10^{-8}	1.2×10^{-8}	1.3×10^{-7}
100	2.2×10^{-6}	4.0×10^{-8}	4.8×10^{-9}	6.1×10^{-8}
Fraction of ^{125}Sb leached in 100 days	3.7×10^{-4}	4.1×10^{-5}	4.3×10^{-5}	7.5×10^{-5}
Leachability based on total leach time	4.6×10^{-6}	5.1×10^{-7}	4.9×10^{-7}	8.8×10^{-7}

TABLE 10

Gross Alpha Leachability of Glass 18-40-13/Cs

Leach Time, days	*Leachability, g/(cm²-day)*
1	1.6×10^{-6}
2	4.9×10^{-7}
3	9.9×10^{-7}
4	8.2×10^{-7}
7	2.7×10^{-7}
35	6.1×10^{-8}
45	3.8×10^{-8}
75	7.2×10^{-8}
100	1.4×10^{-7}
Fraction of alpha activity leached in 100 days	9.4×10^{-6}
Leachability of alpha activity based on total leach time	1.3×10^{-7}

EFFECT OF HEATING GLASSES AT 500°C OR 600°C ON LEACHABILITY

Samples of waste glasses were heated at either 500°C or 600°C for 1 month to determine the effect of devitrification on leachability. Previous work[1] with Mix 18 glasses containing simulated sludges showed that the maximum devitrification rate occurred around 620°C. Devitrification increased the leachability by a factor of three.[1]

After heating, the glasses containing actual waste sludge were leached in 150 ml of stagnant distilled water. The sampling schedule was approximately as before. Leach samples were analyzed by the same methods as previously discussed. Results are shown in Table 11 through Table 14.

TABLE 11

^{137}Cs Leachabilities of Waste Glasses Heated for 1 Month at 500°C or 600°C

Leach Time, days	*Leachability, g/(cm²-day)* 18-40-5[a]	18-40-5[b]	18-40-13[a]	18-40-13[b]	18-30-13/Z[a]
1	1.7×10^{-8}	1.9×10^{-8}	3.3×10^{-6}	3.9×10^{-6}	8.1×10^{-7}
2	1.3×10^{-7}	8.6×10^{-8}	8.1×10^{-8}	1.0×10^{-6}	2.2×10^{-7}
3	1.7×10^{-8}	8.6×10^{-8}	4.1×10^{-7}	4.8×10^{-7}	1.2×10^{-7}
4	1.6×10^{-7}	1.3×10^{-7}	4.9×10^{-7}	6.7×10^{-7}	6.6×10^{-8}
7	1.0×10^{-7}	1.3×10^{-7}	5.6×10^{-7}	4.1×10^{-7}	3.1×10^{-8}
14	5.8×10^{-8}	1.5×10^{-7}	1.6×10^{-7}	5.6×10^{-7}	1.7×10^{-8}
21	6.6×10^{-8}	3.3×10^{-7}	2.3×10^{-7}	1.2×10^{-6}	1.0×10^{-8}
28	5.8×10^{-8}	1.3×10^{-7}	4.6×10^{-7}	1.8×10^{-6}	1.3×10^{-8}
56	2.4×10^{-8}	5.3×10^{-8}	3.0×10^{-7}	4.7×10^{-6}	1.3×10^{-8}
84	2.9×10^{-8}	7.5×10^{-8}	2.1×10^{-7}	8.8×10^{-6}	9.7×10^{-9}
Fraction of ^{137}Cs leached in 84 days	1.3×10^{-6}	5.9×10^{-6}	2.1×10^{-5}	3.2×10^{-4}	1.8×10^{-6}
Leachability based on total leach time	1.7×10^{-8}	1.0×10^{-7}	3.1×10^{-7}	4.8×10^{-6}	2.7×10^{-8}

a. Heated at 500°C.

b. Heated at 600°C.

TABLE 12

^{90}Sr Leachabilities of Waste Glasses
Heated for 1 Month at 500°C or 600°C

Leach Time, days	*Leachability, g/(cm²-day)* 18-40-5[a]	18-40-5[b]	18-40-13[a]	18-40-13[b]	18-30-13/Z[a]
1	$3.0x10^{-4}$	$2.2x10^{-5}$	$3.7x10^{-4}$	$6.8x10^{-5}$	$9.1x10^{-5}$
2	$2.8x10^{-5}$	$8.1x10^{-6}$	$4.9x10^{-6}$	$5.5x10^{-6}$	$5.7x10^{-6}$
3	$1.4x10^{-5}$	$6.4x10^{-6}$	$2.6x10^{-5}$	$3.6x10^{-6}$	$2.7x10^{-6}$
4	$1.0x10^{-5}$	$7.7x10^{-6}$	$1.4x10^{-5}$	$4.0x10^{-6}$	$1.4x10^{-6}$
7	$4.5x10^{-6}$	$6.7x10^{-6}$	$6.9x10^{-6}$	$3.6x10^{-6}$	$1.4x10^{-6}$
14	$2.8x10^{-6}$	$9.6x10^{-6}$	$2.3x10^{-6}$	$3.8x10^{-6}$	$6.9x10^{-7}$
21	$2.3x10^{-5}$	$1.1x10^{-5}$	$2.2x10^{-6}$	$3.8x10^{-6}$	$4.7x10^{-7}$
28	$1.7x10^{-6}$	$8.4x10^{-6}$	$3.1x10^{-6}$	$3.8x10^{-6}$	$1.5x10^{-7}$
56	$6.6x10^{-7}$	$3.0x10^{-6}$	$1.3x10^{-6}$	$4.2x10^{-6}$	$5.0x10^{-7}$
84	$5.9x10^{-7}$	$2.2x10^{-6}$	$7.2x10^{-7}$	$4.5x10^{-6}$	$1.8x10^{-7}$
Fraction of ^{90}Sr leached in 84 days	$5.4x10^{-4}$	$2.9x10^{-4}$	$4.3x10^{-4}$	$2.9x10^{-4}$	$1.4x10^{-4}$
Leachability based on total leach time	$7.0x10^{-6}$	$5.0x10^{-6}$	$6.4x10^{-6}$	$4.3x10^{-6}$	$2.1x10^{-6}$

a. Heated at 500°C.

b. Heated at 600°C.

TABLE 13

^{125}Sb Leachabilities of Waste Glasses Heated for 1 Month at 500°C or 600°C

Leach Time, days	*Leachability, g/(cm^2-day)* 18-40-5[a]	18-40-5[b]	18-40-13[a]	18-40-13[b]	18-30-13/Z[a]
1	$3.5x10^{-7}$	$7.8x10^{-6}$	$2.9x10^{-5}$	$2.9x10^{-6}$	$3.6x10^{-5}$
2	$1.4x10^{-5}$	$1.5x10^{-5}$	$1.7x10^{-5}$	$9.7x10^{-7}$	$1.3x10^{-5}$
3	$1.3x10^{-5}$	$1.6x10^{-5}$	$9.6x10^{-6}$	$9.7x10^{-7}$	$2.9x10^{-6}$
4	$7.8x10^{-6}$	$1.9x10^{-5}$	$8.3x10^{-6}$	$9.7x10^{-7}$	$2.8x10^{-6}$
7	$3.7x10^{-6}$	$2.0x10^{-6}$	$3.6x10^{-6}$	$6.2x10^{-7}$	$1.8x10^{-6}$
14	$9.4x10^{-7}$	$2.2x10^{-5}$	$1.3x10^{-6}$	$8.1x10^{-7}$	$8.2x10^{-7}$
21	$1.9x10^{-6}$	$2.8x10^{-5}$	$1.2x10^{-6}$	$2.2x10^{-6}$	$7.0x10^{-7}$
28	$2.4x10^{-6}$	$1.6x10^{-5}$	$8.8x10^{-7}$	$1.6x10^{-6}$	$4.6x10^{-7}$
56	$9.5x10^{-7}$	$5.2x10^{-6}$	$5.6x10^{-7}$	$2.9x10^{-6}$	$5.8x10^{-7}$
84	$8.0x10^{-7}$	$4.8x10^{-6}$	$3.3x10^{-7}$	$4.1x10^{-6}$	$3.0x10^{-7}$
Fraction of ^{125}Sb leached in 84 days	$1.2x10^{-4}$	$5.6x10^{-4}$	$9.8x10^{-5}$	$1.9x10^{-4}$	$7.8x10^{-5}$
Leachability based on total leach time	$1.6x10^{-6}$	$9.7x10^{-6}$	$1.5x10^{-6}$	$2.9x10^{-6}$	$1.2x10^{-6}$

a. Heated at 500°C.

b. Heated at 600°C.

TABLE 14

Gross Alpha Leachabilities of Waste Glasses Heated for 1 Month at 500°C or 600°C

Leach Time, days	*Leachability, g/(cm²-day)*		
	18-30-13/Z[a]	*18-40-13*[a]	*18-40-13*[b]
1	2.8×10^{-7}	1.8×10^{-8}	4.1×10^{-7}
2	4.9×10^{-7}	3.1×10^{-7}	1.0×10^{-7}
3	3.4×10^{-7}	3.3×10^{-7}	6.3×10^{-7}
4	1.8×10^{-7}	3.9×10^{-7}	4.9×10^{-7}
7	1.6×10^{-7}	1.8×10^{-7}	3.9×10^{-7}
14	6.0×10^{-8}	3.4×10^{-8}	2.8×10^{-7}
21	4.7×10^{-8}	3.8×10^{-8}	3.0×10^{-7}
28	4.7×10^{-8}	6.0×10^{-8}	4.2×10^{-7}
56	5.6×10^{-8}	4.4×10^{-8}	2.8×10^{-7}
84	5.6×10^{-8}	4.4×10^{-8}	1.6×10^{-7}
Fraction of alpha activity leached in 84 days	4.1×10^{-6}	4.0×10^{-6}	1.8×10^{-5}
Leachability based on total leach time	6.1×10^{-8}	6.0×10^{-8}	2.7×10^{-7}

a. Heated at 500°C.

b. Heated at 600°C.

The initial ^{90}Sr leachabilities of 10^{-4} g/(cm^2-day) may have resulted from contamination of the samples in the process cell during heating. Leachabilities based on the entire 84-day leach period are shown in Table 15. Heating the glasses at 500°C or 600°C increased the ^{90}Sr leachability by a factor of approximately 10. However, the final product still has a leachability of $\sim 10^{-5}$ g/(cm^2-day), which is considered low for waste forms.

Heating Glasses 18-40-5 and 18-30-13/Z at 500°C did not significantly affect the ^{137}Cs leachability. However, heating Glass 18-40-13 at 600°C increased the ^{137}Cs leachability from 10^{-8} to 10^{-6} g/(cm^2-day). Glass 18-40-5 heated similarly increased in ^{137}Cs leachability from 10^{-8} to 10^{-7} g/(cm^2-day). Heating at 500°C or 600°C did not affect leachability of alpha activity.

Microscopic examination (1000X) and x-ray analyses of the glasses indicated that Glass 18-40-13 was devitrified by heating 1 month at 600°C, and Glass 18-40-5 heated at 600°C and Glass 18-30-13/Z heated at 500°C did not devitrify. As with simulated sludges,[1] nepheline was found in the devitrified phase of Glass 18-40-13.

TABLE 15

Comparison of Leachabilities [g/(cm^2-day)] of Heated and Unheated Waste Glasses

	Unheated	*500°C*[a]	*600°C*[a]
	Strontium-90		
18-40-5	2.2×10^{-7}	7.0×10^{-6}	5.0×10^{-6}
18-40-13	4.4×10^{-7}	6.4×10^{-6}	4.3×10^{-6}
18-30-13/Z	1.2×10^{-7}	2.1×10^{-6}	-
	Cesium-137		
18-40-5	5.9×10^{-8}	1.7×10^{-8}	1.0×10^{-7}
18-40-13	3.5×10^{-8}	3.1×10^{-7}	4.8×10^{-6}
18-30-13/Z	5.6×10^{-8}	2.7×10^{-8}	-
	Gross Alpha		
18-40-13	1.3×10^{-7}	6.0×10^{-8}	2.7×10^{-7}
18-30-13/Z	-	6.1×10^{-8}	-

a. Heated 1 month.

These results show that glass containing SRP waste sludge could devitrify if heated to 600°C, but low-leachable, crystalline products would form. However, normal storage temperature for waste glass would be much less than 600°C, and devitrification is not expected.

CONCLUSIONS AND FUTURE WORK

The results of this study indicate that SRP waste sludges, sludge-zeolite mixtures, and sludge-cesium eluate can be vitrified into a high-quality borosilicate glass at 1150°C. No problems were encountered with sulfate, mercury, or other sludge components. Volatilization of radioactivity during melting was 0.3% for ^{137}Cs, <3% for ^{106}Ru, and $\leq$0.01% for other radionuclides. Product glasses had initial leachabilities of 10^{-6} to 10^{-5} g/(cm^2-day) decreasing to 10^{-8} to 10^{-7} g/(cm^2-day) after $\sim$2 weeks. Heating product glasses at 500°C or 600°C increased long-term leachability from 10^{-8} to 10^{-7} g/(cm^2-day) to the still low value 10^{-6} g/(cm^2-day).

In future work, glasses containing actual sludges and zeolite will be made by the in-pot melting technique using 304L stainless steel containers. Volatilization of radionuclides, corrosion of container, and product quality will be determined. Aged samples will be evaluated for long-term stability.

REFERENCES

1. J. A. Kelley. *Evaluation of Glass as a Matrix for Solidification of Savannah River Plant Waste. Nonradioatcive and Tracer Studies.* USERDA Report DP-1382, E. I. du Pont de Nemours & Company, Savannah River Laboratory, Aiken, SC (1975).

2. J. A. Kelley, J. A. Stone, and T. S. McMillan. *Sampling and Analyses of Savannah River Plant High-Level Waste Sludges.* USERDA Report DP-1399, E. I. du Pont de Nemours & Company, Savannah River Laboratory, Aiken, SC (1975).

3. J. R. Wiley. *Removal of Cesium from Savannah River Plant Waste Supernate.* USERDA Report DP-1388, E. I. du Pont de Nemours & Company, Savannah River Laboratory, Aiken, SC (1975).