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

NONRADIOACTIVE AND TRACER STUDIES

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ABSTRACT

One option for long-term management of Savannah River Plant high-activity waste is solidification and storage in a retrievable surface storage facility to be located on the plantsite. This study demonstrated that SRP waste can be incorporated into a borosilicate glass at 1150°C.

Tests with simulated waste indicate that alkaline sludge stored in SRP waste tanks can be solidified in borosilicate glass containing up to 45 wt % sludge. For melting at 1150°C, the optimum glass mixture is 52.5 wt % SiO_2, 10.0% B_2O_3, 22.5% Na_2O, 5.0% CaO, and 10.0% TiO_2.

Aluminum increases glass melt viscosity and can limit the amount of sludge solidified. Sulfate has limited solubility; above 0.8 to 1.0 wt % sulfate, a separate, water-soluble, cesium-rich phase is formed.

During melting, $\sim$0.5% of the cesium, 10 to 50% of the ruthenium, and all of the mercury present in the glass mixture are volatilized.

At 25°C, initial leachabilities for both ^{137}Cs and ^{85}Sr are $\sim 10^{-6}$ g/(cm^2-day) and both decrease to $\sim 10^{-8}$ g/(cm^2-day) after 40 days.

Gamma irradiation to 10^{10} rads and alpha decay in the glass matrix do not significantly affect the glass waste forms.

Devitrification of waste glasses occurs near 600°C, but leachability is increased by only a factor of $\sim$3.

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

NONRADIOACTIVE AND TRACER STUDIES

INTRODUCTION

Studies are in progress at the Savannah River Laboratory (SRL) to determine methods for possible solidification and storage of Savannah River Plant (SRP) high-level liquid radioactive waste. In one of several options under consideration, solidified waste would be stored in an on-site, retrievable surface storage facility until the waste could be shipped to a federal repository.

An earlier report[1] described in detail the origins and characteristics of SRP waste, the criteria for acceptable solid forms, and potential solid forms for SRP waste. That study was used to formulate the conceptual process shown in Figure 1.

SRP waste, stored in underground tanks, consists of an alkaline salt solution, solid salt cake, and an insoluble sludge layer containing large amounts of iron, aluminum, manganese, and many other elements. In the conceptual process, waste would be removed from a tank by dissolving the salt cake with water and sluicing the slurry of sludge and solution from the tank. Sludge and solution would be separated by centrifugation and filtration. ^{137}Cs, the principal biological hazard in the solution, would be removed by an ion exchange process and sorbed onto zeolite. Sludge would be washed to remove salts, dried, and blended with the cesium-zeolite for solidification into either concrete or glass. The mass of sludge would be much greater than that of cesium-zeolite, so that sludge is the controlling factor in solidification process chemistry. In this report, the feasibility of incorporating simulated, nonradioactive SRP waste into borosilicate glass is demonstrated. Studies of the vitrification of actual SRP waste will be described in a subsequent report. Studies of waste removal from tanks, separation of sludge and salt solution, removal of radionuclides from salt solution, and solidification of waste in concrete will also be described in other reports.

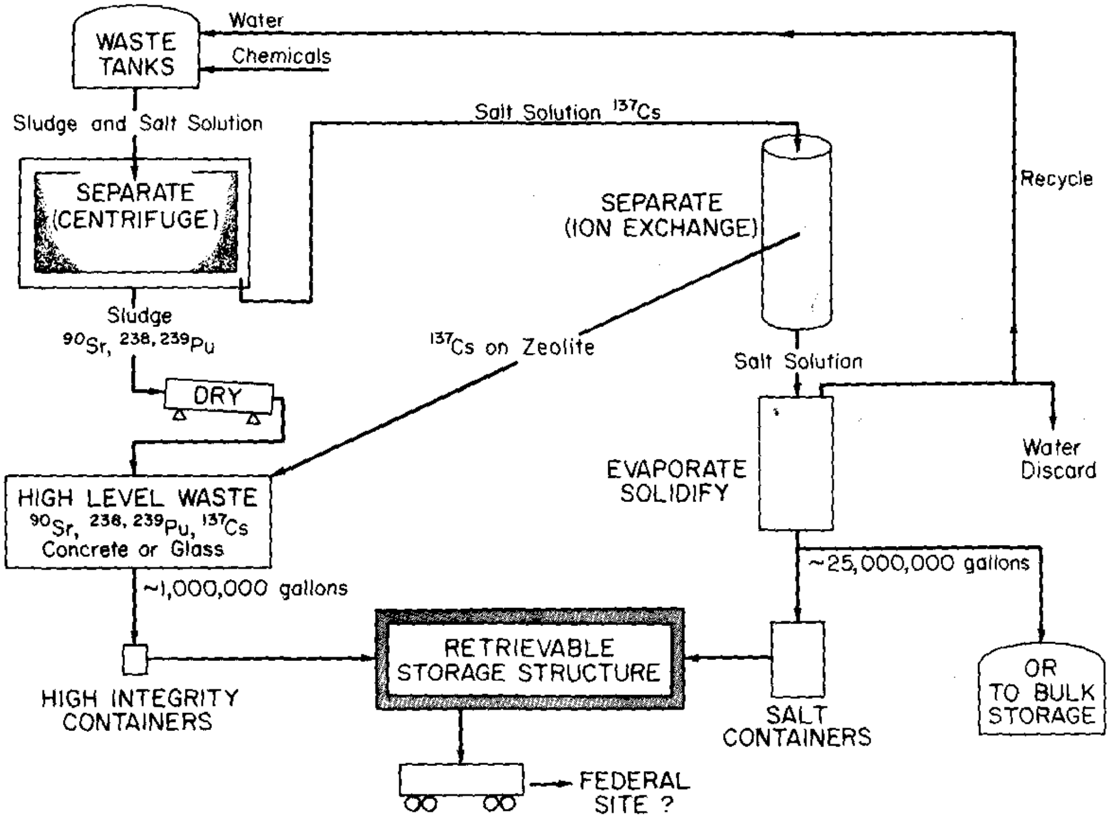


FIGURE 1. Conceptual Waste Solidification Process

SELECTION OF BOROSILICATE GLASS

Most glasses have sufficient mechanical strength and radiation stability for solidification of SRP high-level waste. High thermal conductivity is inherent to most glasses but is not crucial for SRP waste because of its low power density. Under accident conditions, a low leach rate is probably the most important attribute of a glass waste form.

Processes for the solidification of radioactive waste into phosphate and borosilicate glasses have been developed.[2-4] However, phosphate glasses devitrify with a 1000-fold increase in leach rate.[2] On the other hand, devitrified borosilicate glasses are only slightly more leachable than amorphous glasses (Figure 2). Because of this, phosphate glasses were not considered acceptable as solid matrices for long-term storage of SRP wastes.

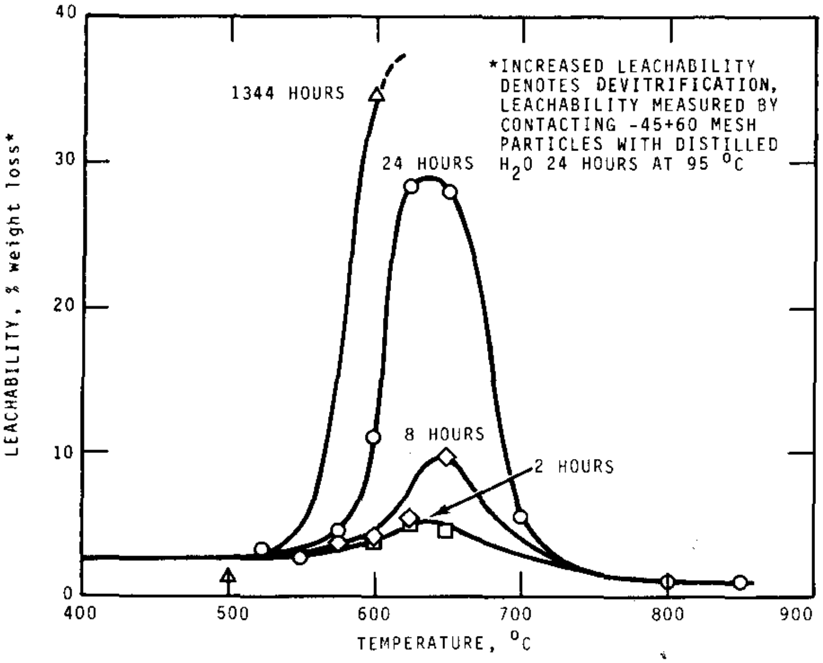
A number of borosilicate glass processes have been developed for solidification of radioactive wastes.[3-4] In most of these processes, SiO_2, B_2O_3, CaO, Na_2O, and other selected additives are blended with radioactive wastes, causing fission products, corrosion products, and other chemicals from fuel reprocessing to be added. The mixture is melted at 1050 to 1250°C. Leachabilities of most vitreous products are 10^{-5} to 10^{-7} g/(cm^2-day). The composition of the glass mix blended with waste to form the final product depends on the composition of waste. For example, wastes with high sodium content require a low-sodium glass mix to ensure that the product does not contain excess sodium. The glass mix composition may also be affected by other elements in waste.

FEASIBILITY STUDIES

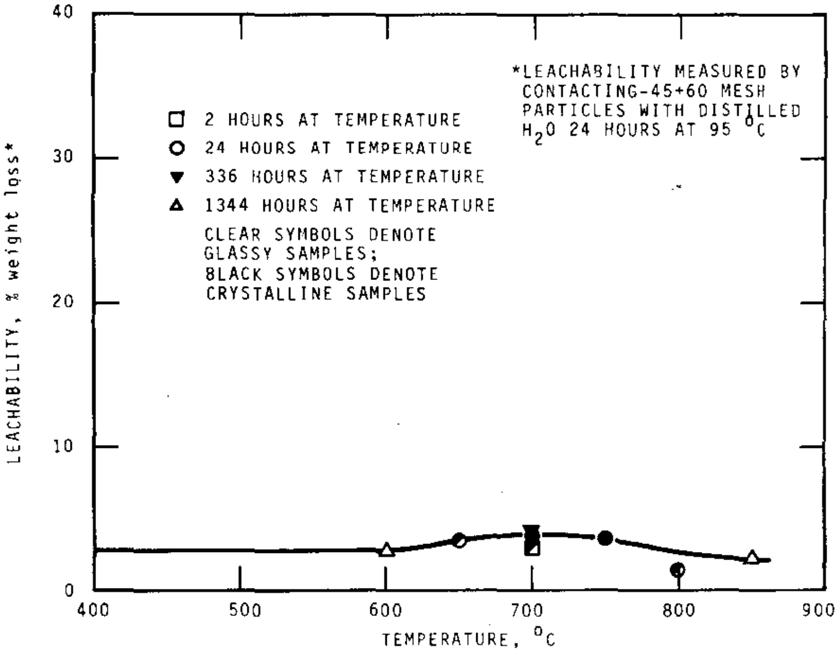
Theoretical models[3,4] were used to estimate appropriate compositions of borosilicate glass for SRP waste. Preliminary studies with simulated sludge indicated that borosilicate glasses of high sludge content could be made.

Models for Glass Formulation

Glasses are composed of network formers and network modifiers. Silicon, boron, and aluminum are network formers because they bond to oxygen and form an extended network. Aluminum and boron lower the melting temperature, increase chemical stability (as measured by leach tests), and slow the rate of devitrification of glass. Too much aluminum and boron in glass make the viscosity



Phosphate Glass



Borosilicate Glass

FIGURE 2. Devitrification of Phosphate and Borosilicate Glasses (from Reference 2, p. 5.9)

of the melt too high. Other elements used in glass formation, such as sodium, potassium, calcium, and sludge components, fit into interstices of the glass network and are called network modifiers. Na_2O and K_2O lower the melting temperature of glass, but too much of either reduces chemical stability.

Two semi-empirical studies[3,4] resulted in guidelines for formulation of acceptable glasses. The important atom ratios of glass components are:

Designation	Ratio
A	$\frac{\text{Si}}{\text{Al+B}}$
B	$\frac{\text{oxygen}}{\text{network formers}}$
C	$\frac{\text{network formers}}{\text{network modifiers}}$
D	$\frac{\text{network modifiers}}{\text{oxygen-[2 (network formers)]}}$

When Ratio A is >1.5, leachability is low. Melting point of glass increases as A increases. With Ratio B between 2.2 and 2.4, glass formation is best and leachability is low. Excess oxygen is needed to balance the electronic charge of network modifiers. Density increases as A decreases and B increases. Ratio C should be ∿2 for good glass formation. As C decreases, the glass network is disrupted and the tendency for glass formation decreases. Ratio D represents the ratio of network modifiers to excess oxygen not required for network formers to be four-coordinate. D should be as near as possible to 2.

A model developed at the Hahn-Meitner Institute[5] uses the formula in Table 1 for determining optimum glass composition. The suggested glass composition is 4 mol SiO_2/2 mol B_2O_3/1 mol Al_2O_3/2 mol CaO/1 or 3 mol Na_2O plus 20 wt % waste.

Preparation of Simulated SRP Waste Sludges

Since waste sludge composition can vary markedly from tank to tank, three types of simulated sludges were prepared on the basis of plant processes and some preliminary sludge analyses. These three compositions (Table 2) are expected to cover the range of compositions to be encountered with actual waste. Nonradioactive strontium was added for subsequent leach testing because strontium and plutonium are the principal biological hazards in sludge.

In early work, preparing small lab-scale batches of simulated sludge was found to be tedious and time-consuming, and sludge properties varied from batch to batch. Because of this, 50-lb batches of simulated sludges were prepared in large-scale equipment. This ensured that variations in results would not be caused by variations in sludge starting material.

TABLE 1

Hahn-Meitner Institute Model

$(10-2X-2Y)SiO_2/XB_2O_3/YAl_2O_3/2CaO/1$ or $3\ Na_2O$

$Y = 0.5$ to 1.0; m.p. = 1100 - 1200°C

$X = \sim 2$ with $Y > 0.5$

Suggested glass composition:

$4SiO_2/2B_2O_3/1Al_2O_3/2CaO/1$ or $3\ Na_2O$

plus

20 wt % waste

TABLE 2

Simulated SRP Waste Sludges

Sludge I:	50% $Fe(OH)_3$, 50% $AL(OH)_3$
Sludge II:	40% $Fe(OH)_3$, 40% $Al(OH)_3$, 20% HgO
Sludge III:	50% $Fe(OH)_3$, 50% MnO_2

All contain 400 ppm Sr

Preliminary Experiments

Twelve glass formulations were prepared with Type III simulated sludge. Table 3 shows the glass compositions and calculated atom ratios. Formulation 5 contained all atom ratios in the range specified by the model.[3,4] The glass components were mixed as dry solids. Boric acid supplied B_2O_3, and Na_2CO_3 supplied Na_2O. Titanium in Formulation 8 reduces volatility of cesium.[6] The formulations were heated at 850 to 900°C in either porcelain or graphite crucibles for ∿1 hr to remove H_2O and CO_2, heated in a furnace at 1200 to 1275°C for 1 hr, transferred to a furnace at ∿400°C for 1 hr, and cooled to ambient temperature. Test results are shown in Table 4. Formulations 5-10 formed homogeneous, dark brown glasses, with densities of 2.47 to 2.84 g/cm³.

These preliminary tests showed that simulated waste sludge could be incorporated into glass and that models used to determine relative amounts of glass components are valid. Although the models are not exact, they provide useful guidelines. On the basis of these preliminary tests, a more thorough study was begun of the solidification of SRP waste sludge in borosilicate glass.

TABLE 3

Compositions and Atom Ratios of Borosilicate Glasses Containing Simulated Sludge

Mix	*Mix Composition, wt %*							*Atom Ratios*			
Formula	SiO_2	B_2O_3	Al_2O_3	Na_2O	*CaO*	TiO_2	*Sludge III*	*A*	*B*	*C*	*D*
1	75[a]	-	-	-	-	-	25	-	2.35	3.83	0.75
2	65[a]	10	-	-	-	-	25	3.76	2.21	4.20	1.12
3[b]	61	9.5	1.5	3	-	-	25	3.35	3.25	3.11	1.28
4[c]	59	11.5	1.5	3	-	-	25	2.72	2.23	3.32	1.33
5[d]	50	15	-	10	-	-	25	1.93	2.30	1.94	1.72
6[e]	28.8	12.8	12	8	17.6	-	20	0.79	2.45	1.30	1.70
7[f]	38	22	-	8	12	-	20	1.00	2.30	1.72	1.95
8[g]	42	8	2	16	4	8	20	2.57	2.77	1.02	1.28
9	40	15	10	10	-	-	25	1.06	2.22	1.99	2.31
10	30	15	10	10	10	-	25	0.79	2.41	1.36	1.80
11[h]							25	-	-	-	-
12[i]		10					25	-	-	-	-

---

a. Sea sand
b. Corning 7740 glass + sludge
c. Corning 7740 glass + 2% B_2O_3 + sludge
d. "Ideal" composition based on model
e. Hahn-Meitner Institute formulation[5]
f. Jülich formulation[7]
g. Karlsruhe formulation[7]
h. Plant soil near Laboratory, 75 wt %
i. Same as *h*, 65 wt %.

TABLE 4

Properties of Glasses for Sludge Incorporation

Formulation	*Glass Quality*	*Glass Density, g/cm³*	*Formation, °C*
1	Poor; still granular	-	1275
2	Poor; "honeycomb" appearance	-	1275
3	Fair; inhomogeneous	-	1275
4	Fair; inhomogeneous	-	1275
5	Good; dark brown	2.63	1200
6	Good; dark brown	2.57	1200
7	Good; dark brown	2.84	1200
8	Good; dark brown	2.71	1200
9	Good; dark brown	2.47	1200
10	Good; dark brown	2.63	1275
11	Poor; still granular	-	1275
12	Poor	-	1275

EVALUATION OF GLASSES

Tests were conducted with Sludges I and III to define the optimum glass mix for future studies with actual waste. Sludge II was used only in mercury volatilization tests. Selection of the optimum mix was based on sludge content, leach rates, melt viscosity, and product homogeneity. Further tests were conducted with the optimum mix to determine strontium and cesium leach rates, the effects of gamma radiation and alpha decay on the glass products, possible effects of devitrification, volatility of cesium, ruthenium, and mercury during melting, sulfate solubility, the effect of Li_2O on melt viscosity, and compressive strength of the glasses.

Selection of Optimum Mix

Tables 3 and 5 show compositions of glass mixes used to incorporate simulated sludges. (Mixes 1 through 4 and 11 through 13 did not form good glasses.) For reference, the compositions of Corning 7740 *Pyrex* (Registered trademark of Corning Glass Works) and National Bureau of Standards 710 glasses are also given.

All glasses were melted at 1150°C for 3 hr, annealed at ~500°C for 1 hr, and then allowed to cool to ambient temperature in the annealing furnace. With >50 wt % Sludge III, the products were granular and unacceptable. With >35 wt % Sludge I, the glass melt was too viscous (because of aluminum) for easy pouring.

TABLE 5

Compositions of Borosilicate Glass Mixes, wt %

Mix	SiO_2	B_2O_3	Al_2O_3	Na_2O	CaO	TiO_2
5	66.7	20.0	-	13.3	-	-
6	36.0	16.0	15.0	10.0	23.0	-
7	47.5	27.5	-	10.0	15.0	-
8	52.5	10.0	2.5	20.0	5.0	10.0
9	53.3	20.0	13.4	13.3	-	-
10	40.0	20.0	13.4	13.3	13.3	-
14	52.5	10.0	-	10.0	17.5	10.0
15	36.0	16.0	5.0	10.0	23.0	10.0
16	52.5	10.0	-	17.5	10.0	10.0
17	36.0	16.0	5.0	17.0	16.0	10.0
18	52.5	10.0	-	22.5	5.0	10.0
19	36.0	16.0	5.0	25.0	8.0	10.0
Corning 7740 *Pyrex*	81.0	12.8	2.0	4.2	-	-
NBS 710[a]	70.5	-	-	8.7	11.6	-

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[a] This glass also contains: 7.7% K_2O; 1.1% Sb_2O_3; 0.2% SO_3; 0.2% R_2O_3.

Glasses prepared in this manner from Sludges I and III were characterized in leach tests (Table 6). 8 to 12 g of the test glass was crushed, sieved to 0.25-0.08 in. (10 mesh), washed with acetone to remove fines, dried, weighed, and leached for 24 hr at ∿99°C in a Soxhlet extractor (Figure 3). The leached glass was reweighed, and leach solutions were analyzed for sodium by atomic absorption and for strontium by emission spectroscopy. Bulk leach rates were calculated by dividing the fractional weight loss, or fraction of sodium or strontium leached by the product of the specific surface area of the crushed glass and the time leached. Surface area of crushed glass, 0.25 to 0.08 in., as measured by the B.E.T. method using krypton, was 41 cm^2/g.

Sodium leachability generally increased as sludge content increased, which was expected because sludge contains network modifiers (iron and manganese) that disrupt the glass framework. Sodium leachabilities for glasses with Sludge I were less than those for Sludge III for similar loadings because Sludge I contains 50 mol % $Al(OH)_3$ (a network former).

Strontium leachability was generally less than that of sodium. Wider apparent variations in strontium leaching are attributed to analytical limitations at low concentrations (∿0.01 ppm).

TABLE 6

Soxhlet Leach Tests, 24 hr at ∿99°C

	Bulk Leach Rate, g/(cm²-day)		
Glass	*Total*	*Na*	*Sr*
5-25-3[a]	1.3×10^{-4}	1.1×10^{-4}	$<8.6 \times 10^{-5}$
5-35-3	1.2×10^{-4}	1.7×10^{-4}	$<7.7 \times 10^{-5}$
5-45-3	1.2×10^{-4}	2.0×10^{-4}	$<5.4 \times 10^{-5}$
5-25-1	2.2×10^{-5}	5.3×10^{-5}	$<9.2 \times 10^{-5}$
6-25-3	1.7×10^{-4}	2.2×10^{-4}	7.2×10^{-5}
6-35-3	1.7×10^{-4}	3.2×10^{-4}	1.3×10^{-4}
6-45-3	1.6×10^{-4}	3.8×10^{-4}	1.1×10^{-4}
6-25-1	2.8×10^{-4}	2.8×10^{-4}	1.5×10^{-4}
6-35-1	3.8×10^{-4}	4.2×10^{-4}	4.3×10^{-4}
7-25-3	2.0×10^{-4}	2.4×10^{-4}	2.4×10^{-4}
7-45-3	3.2×10^{-4}	9.0×10^{-4}	2.6×10^{-4}
7-25-1	3.1×10^{-4}	3.2×10^{-4}	6.0×10^{-5}
7-35-1	1.4×10^{-4}	1.7×10^{-4}	9.0×10^{-5}
8-25-3	7.6×10^{-5}	4.8×10^{-5}	1.1×10^{-4}
8-35-3	4.9×10^{-5}	5.8×10^{-5}	5.1×10^{-4}
8-45-3	6.3×10^{-5}	7.8×10^{-5}	1.1×10^{-4}
8-25-1	5.1×10^{-5}	3.4×10^{-5}	$<8.5 \times 10^{-5}$
9-25-3	1.4×10^{-4}	1.3×10^{-4}	$<8.9 \times 10^{-5}$
9-35-3	1.1×10^{-4}	2.3×10^{-4}	7.3×10^{-5}
9-45-3	1.1×10^{-4}	2.4×10^{-4}	$<5.4 \times 10^{-5}$
9-25-1	8.8×10^{-5}	1.3×10^{-4}	$<8.6 \times 10^{-5}$
10-25-3	6.1×10^{-5}	2.7×10^{-4}	$<6.9 \times 10^{-5}$
10-35-3	8.5×10^{-5}	1.8×10^{-4}	6.7×10^{-5}
10-45-3	6.8×10^{-5}	1.6×10^{-4}	5.7×10^{-5}
10-25-1	3.0×10^{-5}	2.6×10^{-4}	1.0×10^{-5}
14-35-3	7.3×10^{-5}	1.5×10^{-4}	5.9×10^{-5}
14-45-3	5.6×10^{-5}	1.0×10^{-4}	1.6×10^{-5}
14-55-3	6.6×10^{-5}	2.4×10^{-4}	7.2×10^{-5}
14-25-1	9.5×10^{-5}	6.9×10^{-5}	7.1×10^{-5}
15-45-3	9.0×10^{-5}	1.2×10^{-4}	9.2×10^{-5}
15-55-3	1.4×10^{-4}	1.4×10^{-4}	2.0×10^{-4}
15-35-1	2.5×10^{-4}	2.0×10^{-4}	1.1×10^{-4}
16-25-1	9.3×10^{-5}	2.0×10^{-4}	$<9.4 \times 10^{-5}$
17-25-1	1.6×10^{-4}	4.8×10^{-4}	8.5×10^{-5}
18-45-3	7.1×10^{-5}	3.3×10^{-4}	$<4.6 \times 10^{-5}$
18-35-1	8.5×10^{-5}	1.7×10^{-4}	$<6.2 \times 10^{-5}$
19-45-3	2.0×10^{-4}	1.3×10^{-3}	1.2×10^{-4}
19-35-1	3.4×10^{-4}	8.5×10^{-4}	6.0×10^{-5}
Corning 7740	3.8×10^{-6}	-	-
NBS 710	1.7×10^{-4}	1.3×10^{-4}	-

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[a] 5 is mix number; 25 is wt % sludge; 3 is Sludge III.

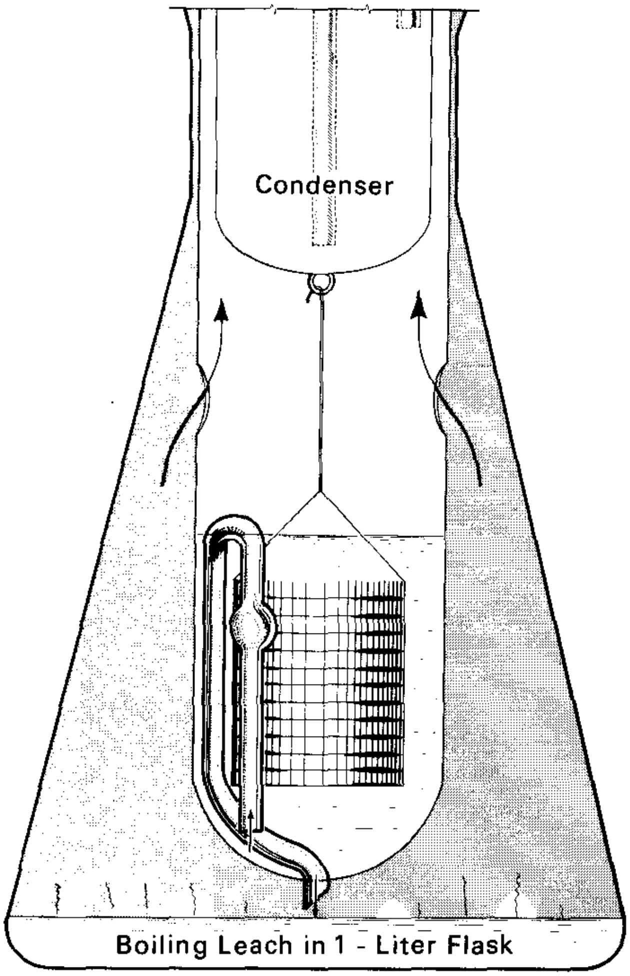

FIGURE 3. Leaching Extractor for Glass

For comparison, Corning 7740 *Pyrex* glass and National Bureau of Standards Glass 710 were leached by the method described above. The leachabilities of the sludge-containing glasses are similar to, and in some cases lower than, the National Bureau of Standards soda-lime-silica glass.

Mix 18 had the best combination of desirable properties and was selected for further testing.

A test was also made to demonstrate that cesium-zeolite can be incorporated into borosilicate glass. A glass containing 50 wt % zeolite (Na-form chabazite) was melted at 1150°C and annealed at ∿500°C. The product contained 24.0 wt % SiO_2, 9.8% Al_2O_3, 24.2% B_2O_3, 17.8% (Na_2O, 12.1% CaO, and 12.1% TiO_2. Under the same leaching conditions as for the sludge glasses, the leach rate based on weight loss was 3.3 x 10^{-4} g/(cm^2-day) at 99°C.

Strontium and Cesium Leach Rates

Because extrapolating high-temperature leach data to ambient temperature is difficult, glasses were prepared with tracer amounts of ^{137}Cs and ^{85}Sr and leached at ambient temperature to obtain more-accurate leach rates.

Glasses containing 35 wt % Sludge I and 45 wt % Sludge III, each containing ^{137}Cs and ^{85}Sr were prepared with Mix 18, which has a low leach rate, contains titanium for cesium retention, and has a low melting temperature.

These glasses (designated as 18-35-1 and 18-45-3 for Mix 18, wt % sludge, and sludge type) were crushed and sieved to 0.25-0.08 in. and leached in stirred distilled water at ambient temperature ($\sim$25°C). Leach solutions were analyzed for ^{137}Cs and ^{85}Sr by low-level gamma counting. Leachabilities (Table 7) were calculated as before. These data confirm the preliminary tests showing that simulated SRP waste sludges can be incorporated into a low-leachable glass.

Effect of Gamma Irradiation on Glasses

Glasses containing actual SRP waste sludge would be exposed to $\sim 10^{10}$ rads of gamma radiation in 100 yr of storage. The effect of such exposure was evaluated by irradiating crushed and monolithic samples of glasses 18-35-1 and 18-45-3 with ^{60}Co to 10^{10} rads at $\sim$65°C. No changes in leachabilities or appearance were observed. These results were not unexpected because borosilicate glasses have been irradiated to 10^{11} rads without significant effects.[8]

Effect of Alpha Decay on Glass

Little is known of the effect of helium accumulation from alpha decay of actinides in glass waste forms. Normal borosilicate glasses have a high permeability or diffusivity and can be saturated with gas at several thousand psi without damaging the glass when the pressure is released.[9] However, incorporation of network modifiers may decrease permeability or diffusivity, so that decay helium may not be able to escape before generating sufficient stress to damage the glass. The magnitude of these stresses required to damage glass have not been measured,[10] but a critical stress of 1000 psi has been estimated from measured tensile strengths of borosilicate glass (∿930 psi).[11]

Two glasses, one containing 0.5 wt % ^{244}Cm and the other 1 wt % ^{238}Pu, were prepared with Mix 18 containing 45% sludge III (Glass 18-45-3). Properties of the glasses are summarized in Table 8.

TABLE 7

Leach Rates for Glasses 18-35-1 and 18-45-3 at 25°C

	Leachability, g/(cm^2-day			
	^{137}*Cs*		^{85}*Sr*	
Leach Time, days	*18-35-1*	*18-45-3*	*18-35-1*	*18-45-3*
1	1.9×10^{-6}	2.8×10^{-6}	2.66×10^{-6}	1.02×10^{-6}
4	1.07×10^{-6}	5.49×10^{-7}	1.23×10^{-6}	2.04×10^{-7}
7	1.88×10^{-7}	4.12×10^{-7}	2.74×10^{-7}	1.52×10^{-7}
11	6.11×10^{-7}	7.85×10^{-7}	5.69×10^{-7}	2.72×10^{-7}
16	8.06×10^{-7}	6.90×10^{-7}	8.32×10^{-7}	2.21×10^{-7}
21	8.23×10^{-7}	1.27×10^{-6}	4.94×10^{-7}	4.83×10^{-7}
42	1.58×10^{-8}	7.42×10^{-8}	4.91×10^{-8}	1.43×10^{-8}
49	1.04×10^{-8}	2.09×10^{-7}	1.45×10^{-8}	3.42×10^{-8}
64	2.77×10^{-8}	7.34×10^{-8}	1.90×10^{-8}	1.25×10^{-8}
72	2.87×10^{-8}	7.14×10^{-8}	9.07×10^{-9}	1.03×10^{-8}
78	1.71×10^{-8}	7.80×10^{-8}	1.21×10^{-8}	1.69×10^{-8}
93	6.29×10^{-8}	8.10×10^{-8}	3.32×10^{-8}	1.29×10^{-8}
99	3.65×10^{-8}	6.82×10^{-8}	1.94×10^{-8}	8.76×10^{-6}

TABLE 8

Properties of Waste Glass Forms Containing ^{244}Cm or ^{238}Pu

	^{244}*Cm*	^{238}*Pu*
Glass, grams	16.4	14.5
^{244}Cm or ^{238}Pu, mg[a]	81	140
Density, g/(cm^3)[b]	3.047	3.116
Alpha dose rate, 10^{12} particles/(cm^3)(min)	2.7	1.0

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[a] Determined calorimetrically.

[b] Measured two days after preparation.

The alpha dose rate in the ^{244}Cm glass is $\sim$2400 times, and in the ^{238}Pu glass $\sim$1060 times, the initial rate calculated for glass containing composite SRP waste. These two factors increase rapidly with time because the calculated dose rate in SRP waste glass would decrease rapidly because of complete decay of some of the radionuclides.

Measured density of the glasses and a silicon standard are shown in Table 9. Variations with respect to the standard established that the change in glass densities may be significant statistically, but too slight ($\sim$0.05%) to affect waste form properties adversely.

TABLE 9

Measured Density of Glass Waste Forms at 21°C

Age of Test Glass, days	*Equivalent Age of Glass Containing SRP Waste, yr*		*Density, g/cm^3*		
	^{244}Cm	*^{238}Pu*	*^{244}Cm*	*^{238}Pu*	*Si Std*
2	14	6	3.0474	3.1164	2.3290
40	9100	1100	3.0456	3.1153	2.3293
42	10,000	1400	3.0453	3.1155	2.3292
150	$>10^6$	-	3.0399	-	2.3291

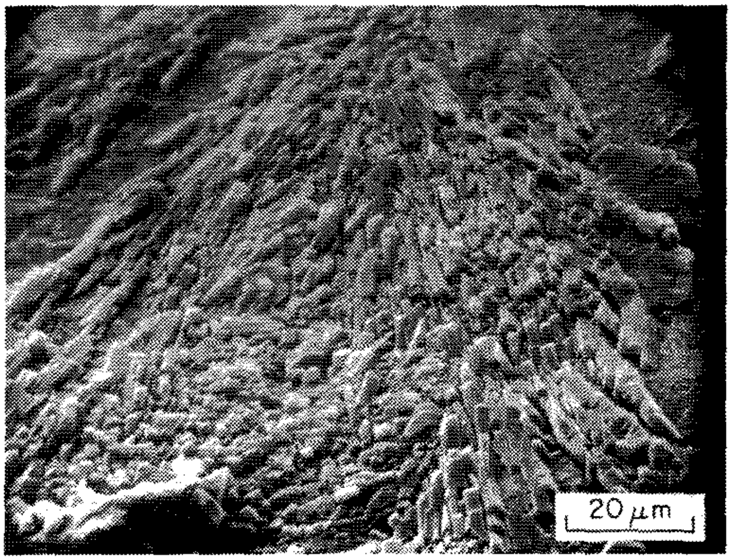
The porosity of a nonradioactive glass of the same composition was estimated to be <0.003% by scanning electron microscopy. No pores were detected at maximum magnification (20,000 X), which would have shown pores as small as $\sim 7 \times 10^4$ Å^2 in a field of $\sim 3 \times 10^9$ Å^2. Calculations based on porosity and the amount of decay helium in the glass indicate that the tensile stress generated by SRP waste in a glass with this porosity will exceed 10 psi only after 100 yr. In the test glass with ^{244}Cm, which has not cracked after simulation of $>10^6$ yr, calculated tensile stress is >2500 psi.[12]

These results indicate that structural damage to glass waste forms containing alpha-bearing SRP waste should be minimal during several hundred years of storage.

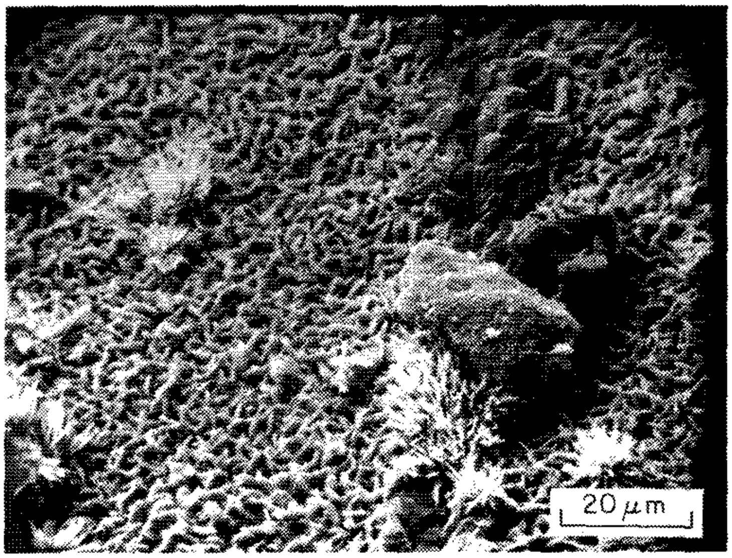
Devitrification of Glasses

Glasses 18-35-1 and 18-45-3 were heated in air at 600°C for one month to determine the effects of prolonged heating. Powder X-ray diffraction showed that Glass 18-35-1 devitrified significantly and Glass 18-45-3 devitrified only slightly.

Powder X-ray diffraction showed the crystalline phase in Glass 18-35-1 to be nepheline ($NaAlSiO_4$), but did not identify conclusively the crystalline phase in Glass 18-45-3; possibilities include $MnFe_2O_4$, Fe_2TiO_4, Mn_2TiO_4, and Mn_3O_4. Nepheline has been reported previously in devitrified borosilicate glasses with high Na_2O content.[5] Glasses with high Na_2O content were found to devitrify at ~600°C in a few hours. Electron photomicrographs of devitrified glasses are shown in Figure 4.



Glass 18-35-1



Glass 18-45-3

FIGURE 4. Electron Photomicrographs of Devitrified Glasses

Leachability of the devitrified glasses was determined at ∿99°C for 24 hr. Devitrification increased the sodium leach rates from 1.7×10^{-4} to 5.0×10^{-4} g/(cm^2-day) for Glass 18-35-1, and from 3.3×10^{-4} to 1.0×10^{-3} g/(cm^2-day) for Glass 18-45-3. These results are consistent with published data,[2] which indicate that devitrification does not increase significantly the leachability of borosilicate glass. The crystalline phase, nepheline, is very insoluble; the increase in leachability has been attributed to leaching of the residual amorphous glass,[5] probably because of decrease of network formers. Leachability of phosphate glass increases a thousandfold with devitrification.[2]

Devitrification of Glasses 18-35-1 and 18-45-3 was also studied by differential thermal analysis. As indicated in Figure 5, devitrification begins for both glasses at ∿560°C and reaches a maximum rate at 615°C. For Glass 18-35-1, a second exothermic peak occurs at 745°C. Crystalline products formed by extended heating at 745°C could not be identified by powder X-ray diffraction.

These tests indicate that devitrification of glasses containing SRP sludge would be very slow. Even if devitrification occurred, leach rates would still be ∿10^{-6} g/(cm^2-day).

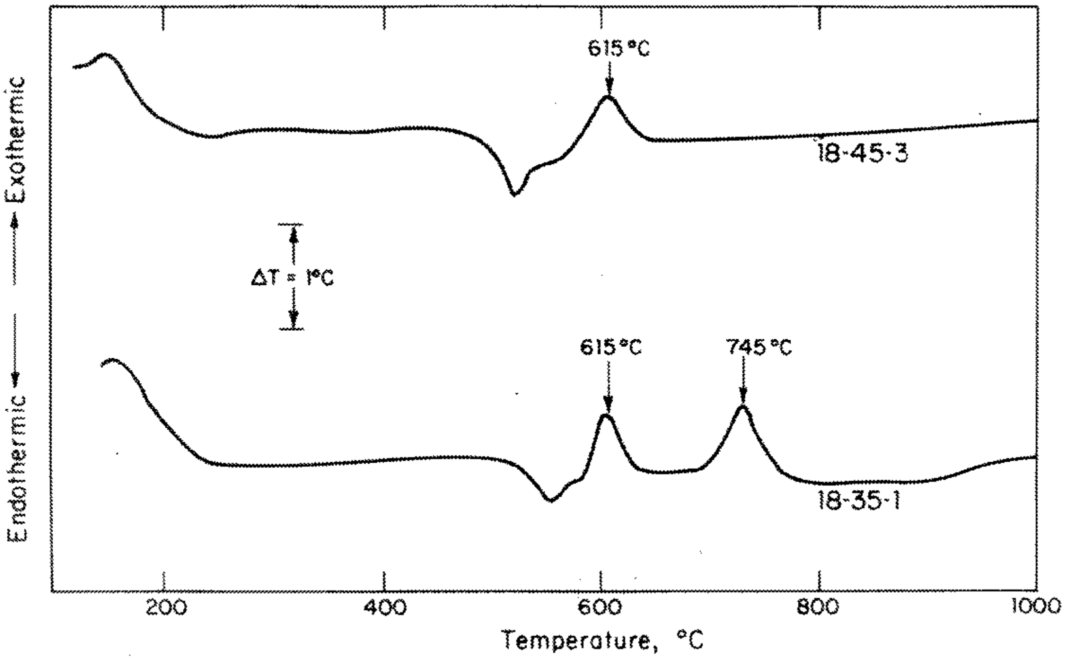


FIGURE 5. Differential Thermal Analysis of Glasses 18-45-3 and 18-35-1

Cesium Volatility During Glass Melting

Tests were conducted to evaluate cesium volatility during glass melting. Other workers[6] have shown that B_2O_3, MoO_3, and TiO_2 in a glass melt reduce cesium volatility (Figure 6). TiO_2 is reported to be more desirable than MoO_3 because TiO_2 is more soluble in borosilicate glasses.

Tests were made with cesium-loaded zeolite (using ^{137}Cs tracer) and with a mixture of Sludge III and cesium-loaded zeolite (Table 10). The apparatus shown in Figure 7 was used to determine cesium volatility. Most of the cesium that volatilized from the glass was deposited in the inverted funnel over the crucible. Only ∿10% of the cesium volatilized from the glass was deposited in the condenser and traps.

Tests 1 and 2 show that cesium volatility from cesium-loaded zeolite with no glass-forming additives is very low (0.01 to 0.03%). Tests 3 through 6 show that cesium volatility is not affected by the source of B_2O_3 and that TiO_2 reduces cesium volatility. Tests 7 and 8 show that cesium volatility increases in the absence of TiO_2. Tests 9 and 10 show that cesium volatility is low from Sludge III and from a Sludge III cesium-zeolite mixture.

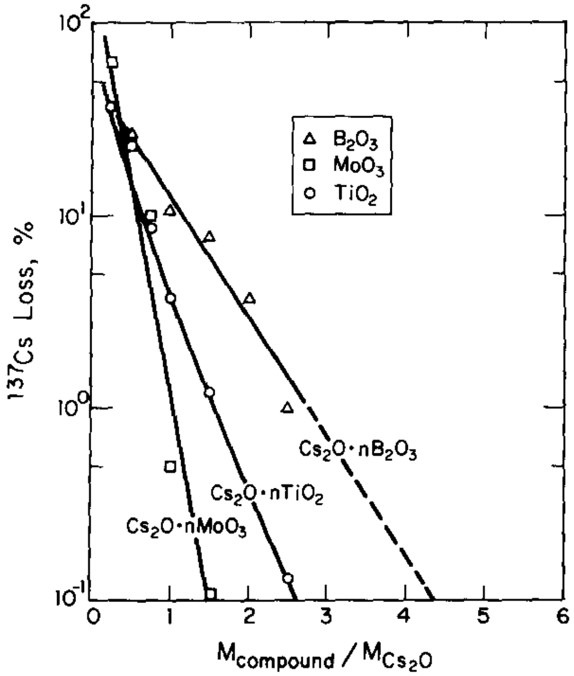


FIGURE 6. Loss of ^{137}Cs During Melting (1 hr at 1000°C) in the Presence of B_2O_3, MoO_3, and TiO_2 (from Reference 6)

TABLE 10

Volatilization of Cesium During Glass Melting
(3 hr at 1150-1175°C)

		Glass-Forming Components, wt %						*Cesium*
Test	*Zeolite*	*Sludge III*	B_2O_3	*CaO*	Na_2O	TiO_2	SiO_2	*Volatilized, %*
1	100	-	-	-	-	-	-	0.01
2	100	-	-	-	-	-	-	0.03
3[a]	50	-	20	10	10	10	-	0.17
4[a]	50	-	20	10	10	10	-	0.43
5[b]	50	-	20	10	10	10	-	0.26
6[b]	50	-	20	10	10	10	-	0.47
7	55.1	-	22.5	11.2	11.2	-	-	1.35
8	55.1	-	22.5	11.2	11.2	-	-	1.03
9	-	45	5.5	2.8	12.4	5.5	28.8	0.21
10	10	35	5.5	2.8	12.4	5.5	28.8	0.55

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a. B_2O_3 supplied by H_3BO_3
b. B_2O_3 and Na_2O supplied by $Na_2B_4O_7$

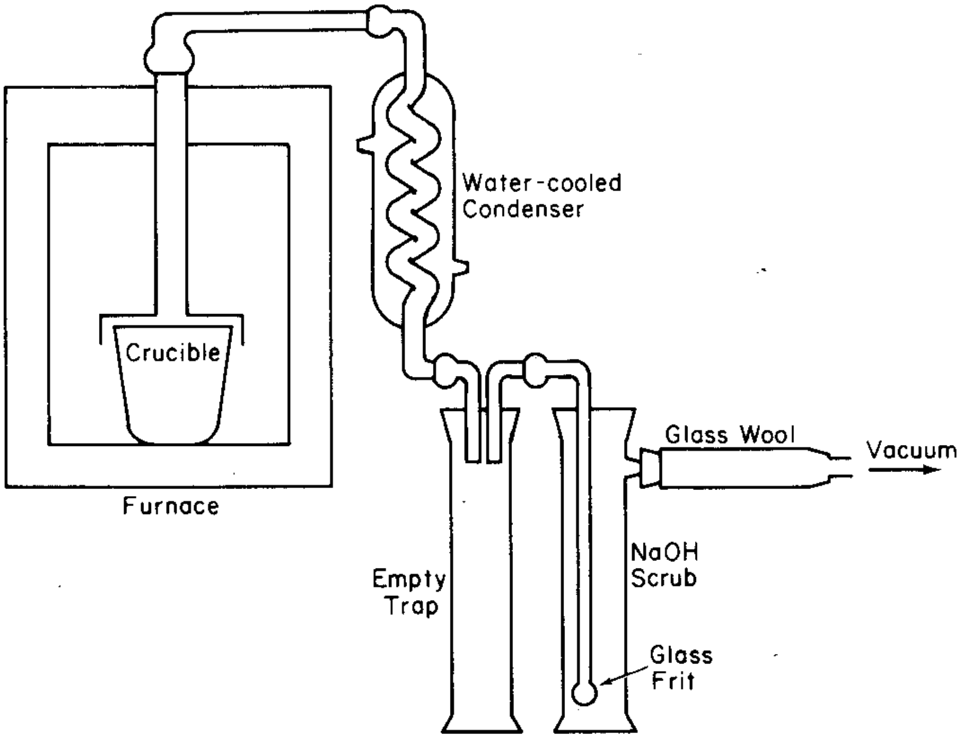

FIGURE 7. Volatility Apparatus

Ruthenium Volatility During Glass Melting

Ruthenium volatility during glass melting was measured. Other workers[6] have shown that ruthenium volatility is mainly a function of nitrate concentration in the glass mix (Figure 8). Nitrate oxidizes ruthenium to volatile RuO_4 during melting.

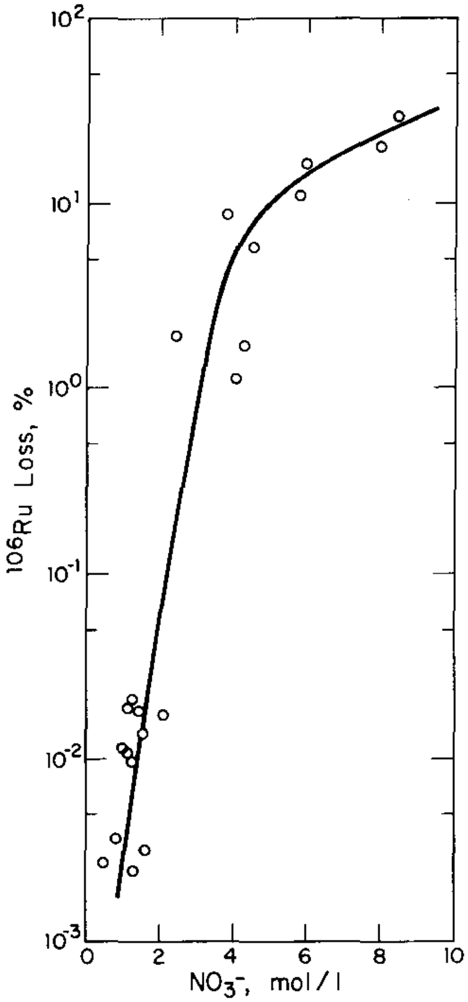

FIGURE 8. Loss of ^{106}Ru as a Function of the Nitrate Concentration in Glass Melt (from Reference 6)

Tests were made with the same apparatus (Figure 7) used for evaluation of cesium volatility (Table 11). ^{106}Ru tracer was added to the glass mix as a dilute caustic nitrite solution.

Tests were made with both Sludge I and Sludge III at various nitrate concentrations. The glass mix was heated for 3 hr at 1150 to 1175°C. As in the cesium tests, most of the ruthenium that volatilized from the glass mix was deposited in the inverted funnel over the crucible.

TABLE 11

Volatility of Ruthenium during Glass Melting
(3 hr at 1150 to 1175°C)

Test Number	*Sludge Type*	*Wt % Nitrate*	*% Ru Volatilized*
1	I (Fe-Al)	1	10.1
2	I (Fe-Al)	5	27.1
3	I (Fe-Al)	10	29.6
4	III (Fe-Mn)	0	50.3
5	III (Fe-Mn)	10	54.7

These results indicate that nitrate in the glass mix containing Sludge I affects ruthenium volatility, but not as much as does MnO_2 in Sludge III. Apparently MnO_2 oxidizes ruthenium to RuO_4 more effectively than does nitrate.

Mercury Volatility During Glass Melting

The temperature and nature of mercury volatilization during glass melting were studied using the apparatus shown in Figure 7. In these tests, 40% Sludge II, which contains 20 wt % HgO, was melted with Mix 18. During melting, metallic mercury was observed in the horizontal tube of the volatility apparatus at ∿580°C and continued to volatilize at higher temperatures.

Volatilization of metallic mercury from Sludge II was also studied by thermogravimetric analysis. Mercury began to volatilize at ∿350°C and continued to ∿600°C. No plugging problems were encountered.

Sulfate Solubility in Glass

The solubility of sulfate in glasses containing simulated SRP sludges was determined. SRP sludge contains sulfate, and published data[4,13] indicate that sulfates are not compatible with borosilicate glasses - a second phase segregates during melting. The segregated sulfate phase is highly leachable and rich in cesium.

Various sulfates (Ba, Na, and Nd) were mixed in Glasses 18-35-1 and 18-45-3, melted for 3 hr at 1150°C, and then cooled in a graphite mold. In some cases, a sulfate phase formed on the surface of the glass and could be dissolved easily with water. The types and amounts of sulfate incorporated into the glass is given in Table 12. Amounts of sulfate actually dissolved in the glass were not determined; the amount of sulfate added to the glass mixes was increased until a separate sulfate phase formed on the glass surface, indicating that the solubility had been exceeded.

TABLE 12

Solubility of Sulfates in Glass
(1150°C for 3 hr)

Glass	*Sulfate Cation*	*Solubility of Sulfate, wt %*
18-35-1	Ba	1.12
18-45-3	Ba	0.90
18-45-3	Na	0.90
18-45-3	Nd	0.79

Solubility limits for $BaSO_4$ and Na_2SO_4 are the same, but $Nd_2(SO_4)_3$ is slightly less soluble. This small difference may not be significant because $Nd_2(SO_4)_3$ is less thermally stable than Na_2SO_4 and would be expected to decompose during prolonged heating at 1150°C.[14] At 1150°C, most sulfates expected in SRP waste sludge would convert to Na_2SO_4 in the glass melt. Na_2SO_4 is thermally stable and evaporates congruently from a glass melt at ∿1400°C. Potassium, rubidium, and cesium sulfates are more thermally stable than Na_2SO_4 or other common sulfates. The high thermal stability of Cs_2SO_4 could explain the cesium-rich sulfate phase segregated from borosilicate glasses.

Compressive Strengths of Glasses

In order to compare the strength of glass to other waste forms being studied at SRL, the compressive strengths of glass products containing simulated SRP sludges were measured. Cylinders, 0.5-in. diameter by 1-in. long, were made with Glasses 18-35-1 and 18-45-3. The cylinder ends were cut parallel and polished, and breaking strengths were determined with a hydraulic press.

Compressive strengths for both glasses were 85,000 ±20,000 psi. Both shattered into small fragments upon breaking. These results show that glass waste forms would be much stronger than some other types, such as concrete.

Effect of Li_2O on Glass Viscosity

Since aluminum in Sludge I limits the amount that can be incorporated into Mix 18, tests were made to determine the effects of substituting Li_2O for Na_2O. Other workers[15] have shown that a Li_2O-Na_2O mixture results in a lower viscosity melt than either pure oxide.

About 0.2 to 4.0% Li_2O was substituted for the same amount of Na_2O in the Glass 18-35-1, and the glasses were melted at 1150°C. Qualitative comparisons of melt viscosities were made by observing ease of pouring. The glasses were also leached by the Soxhlet method to determine effects of Li_2O on leachability.

Melt viscosity decreased as more Li_2O was substituted. Viscosity of Glass 18-45-1 with 4% Li_2O substituted for Na_2O was approximately the same as the viscosity of Glass 18-35-1 with no Li_2O. In previous tests, Glass 18-45-1 had to be heated to 1400°C to be easily poured.

Li_2O had a slight detrimental effect on leachability. With 4% Li_2O substituted for Na_2O in Glass 18-35-1, the leach rate increased $\sim$30%.

These results show that small amounts of Li_2O can be substituted for Na_2O in a glass mix to reduce melt viscosity.

CONCLUSIONS AND FUTURE WORK

This work demonstrated that SRP waste can be solidified as a low-leachable, strong, borosilicate glass by melting with appropriate glass formers at 1150°C. Sludge content would be $\leq$45 wt %, depending on the amount of aluminum and sulfate in the sludge. An off-gas system would be required for removing volatilized cesium, ruthenium, and mercury. The effects of gamma radiation, alpha decay, and devitrification during prolonged storage would be insignificant.

In future work, actual SRP waste will be incorporated into glass. Sludge contents will be as high as aluminum and sulfate permit. The extent of cesium and ruthenium volatilization during melting will be determined. Li_2O will be added to the glass mix if high-viscosity melts are encountered. Products will be characterized by leachability at ambient temperature. The effects of extended storage at elevated temperature will also be evaluated.

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