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EVALUATION OF GLASS AS A MATRIX FOR SOLIDIFYING SAVANNAH RIVER PLANT WASTE: PROPERTIES OF GLASSES CONTAINING Li_2O

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E. I. DU PONT DE NEMOURS AND COMPANY
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ABSTRACT

Properties of waste forms made of borosilicate glass containing Li_2O combined with both simulated and actual Savannah River Plant (SRP) waste sludges were studied. The glass former, Frit 21, is presently the leading candidate for vitrifying SRP waste in a proposed process for long-term waste management. Devitrification of waste forms was inhibited by sludge components uranium and nickel, but was promoted by aluminum. Devitrification increased the leach rate of waste forms containing simulated sludges up to a factor of 20 in high-temperature leach tests and could be qualitatively correlated with the leach rate of waste forms containing actual sludges in room temperature tests. Room-temperature leach rates were diffusion controlled throughout a 100-day test. Although sulfate solubility in Frit 21-sludge melts could be raised from 1 wt % to 2.5 wt % by slight modifications of the frit, this should not be necessary since Na_2SO_4 washes from actual sludges to levels below 0.5 wt %. It was demonstrated that waste forms can be dissolved in boiling 5M HNO_3 if waste recovery becomes necessary.

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INTRODUCTION

Radioactive waste produced from reprocessing nuclear fuel for defense programs at Savannah River Plant (SRP) is stored in large underground tanks on the plant site. This alkaline waste comprises an insoluble sludge, primarily oxides or hydrated oxides of Fe, Al, and Mn, crystalline salt cake, and a nearly saturated supernatant solution.[1] Most waste actinides and fission products, except ^{137}Cs, have low solubility in alkaline solution and are primarily in the sludge phase.

Methods to solidify SRP waste for long-term storage are being developed at Savannah River Laboratory (SRL). The solidification process currently being tested begins with removing the waste, as a slurry, from the tanks and separating the insoluble sludge by centrifugation.[2] The salt solution is decontaminated by ion exchange.[3] Radioactive sludge and radionuclides separated by ion exchange will be mixed together and solidified in borosilicate glass (Figure 1).

Initial development of methods to vitrify SRP waste provided a large amount of experimental data for waste forms containing both actual and simulated waste and Frit 18, which is a borosilicate glass with no lithium.[4,5,6] Substituting 4 wt % Li_2O for 4 wt % Na_2O in a newer frit composition, indentified as Frit 21 (Table 1), reduces the melt viscosity.[7] Frit 21-sludge glasses are more homogeneous due to convective stirring in the melt and easier to pour out of the melter than Frit 18 glasses. Thus, Frit 21 is presently the favored glass frit for vitrifying SRP waste.

Properties of glasses made with Frit 21 and a variety of actual and simulated sludges are described. The properties discussed are devitrification, leach rate, compatability with sulfates, and dissolution by HNO_3. Devitrification, which is conversion of the waste form from an amorphous glass to a crystalline solid, affects the mechanical strength of the waste form and its ability to resist leaching by water. Leach resistance is a principal criterion for judging the quality of a waste form because accidental contact by water can provide a direct path for radionuclides to enter the biosphere. The only major component in SRP

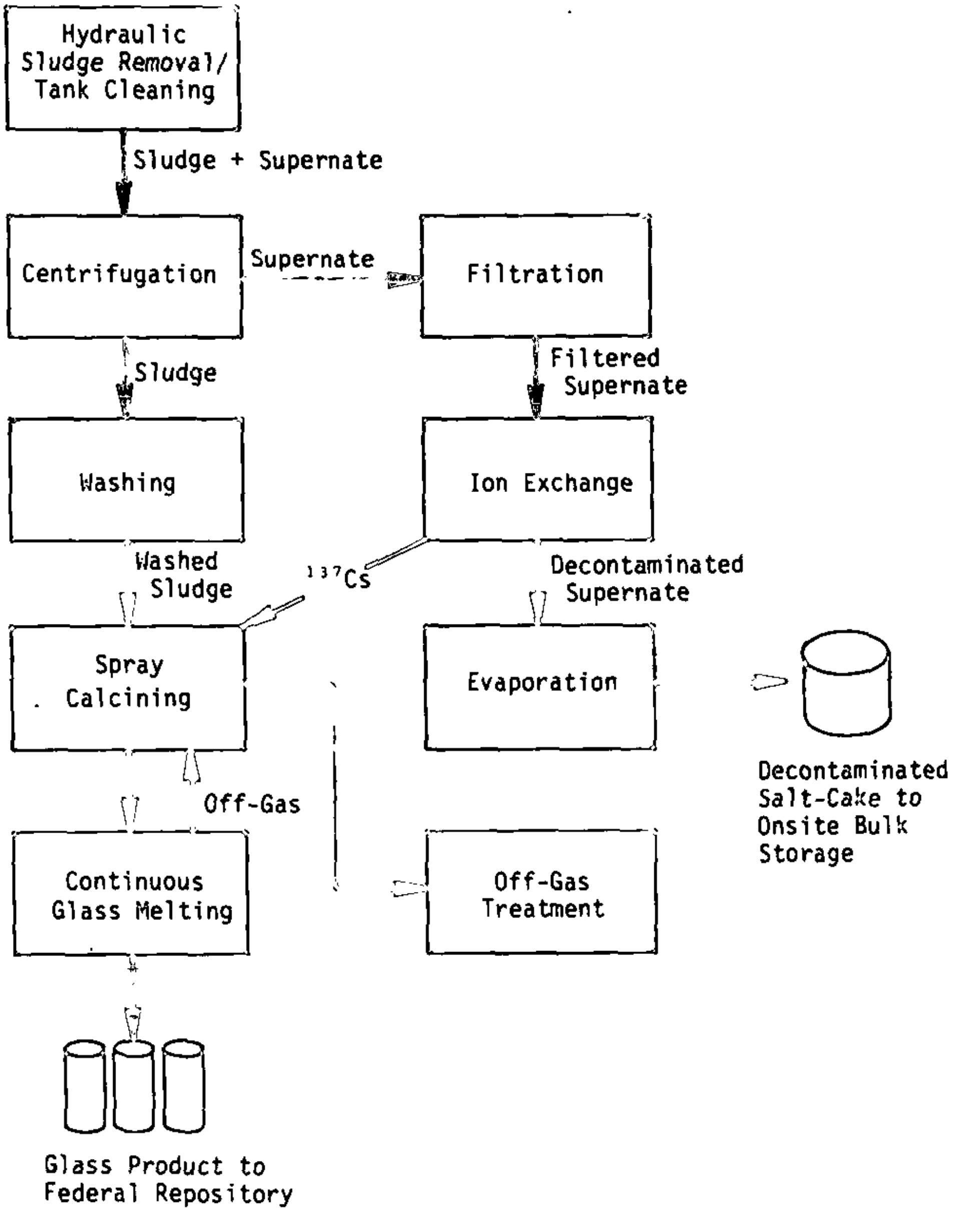

FIGURE 1. Reference Process for Waste Solidification

TABLE 1

Composition of Glass Frits, wt %

	Frit 18	*Frit 21*
SiO_2	52.5	52.5
Na_2O	22.5	18.5
TiO_2	10.0	10.0
B_2O_3	10.0	10.0
CaO	5.0	5.0
Li_2O	-	4.0

waste with low solubility in borosilicate glass is sodium sulfate. The sodium sulfate must be washed from SRP sludge before vitrification; otherwise, a highly leachable sulfate layer will form on the glass surface. Dissolving waste forms in HNO_3 could provide a means to recycle substandard waste forms or to retrieve actinide elements from the waste.

DEVITRIFICATION

The effects of simulated sludges and sludge components on devitrification of waste glasses were determined. Uranium and nickel oxides strongly inhibit devitrification, while aluminum oxide promotes it; but oxides of the other major sludge components do not have a significant effect. Soxhlet leach rates of waste glass samples were increased up to a factor of 20 by devitrification. Differential thermal analysis (DTA) accurately reflected the behavior of the metal-oxide doped glasses during extended heating. Thus, DTA results can be used to predict the relative devitrification of waste glasses containing simulated sludges.

Previous studies of incorporation of SRP waste in glass showed that sludge composition (Table 2) had a great effect on thermal behavior of the waste glass.[5] For example, waste glass containing sludge from Tank 13 devitrified when heated one month at 600°C, and devitrification increased the ^{137}Cs leach rate of the glass 100-fold. However, glass containing Tank 5 sludge did not devitrify.

The objective of this work was to determine which sludge components affected devitrification and to explain the thermal behavior of waste glasses containing simulated sludges.

TABLE 2

Major Components of Three SRP Sludges, wt %

	Tank 5	*Tank 13*	*Tank 15*
Fe_2O_3	46.4	52.7	6.0
Al_2O_3	3.3	17.7	86.3
MnO_2	20.2	18.4	4.9
U_3O_8	21.5	6.2	1.5
CaO	0.9	4.2	0.4
NiO	7.7	0.8	0.9

Differential Thermal Analysis

Glass samples were prepared from Frit 21 as previously reported.[8] The samples were heated, and thermograms were recorded on a Du Pont thermoanalyzer. Data reported were reproducible to within 10°C. Devitrification was confirmed by microscopic examination and x-ray.

The composition of the glass samples and their thermal transitions are listed in Table 3. With all compositions, an endothermic transition was observed between 480 and 535°C (Figure 2) at the softening point (T_s). At this transition temperature, the viscosity of glass is 10^{11} to 10^{12} poise.[9] In nearly all cases, an exothermal reaction due to devitrification of the glass was also observed. At this second transition temperature (T_d), the maximum rate of transformation of amorphous glass to crystalline material occurs. DTA gives no information about the mechanism of the transformation. It may occur by nucleation of new crystals or by growth on ~~the few seed~~ crystals.

CaO, MnO_2, and Fe_2O_3 all had little effect on devitrification. As in the study of the effects of sludge components on leach rates, low concentrations of Fe_2O_3 seem to have a larger effect than higher concentrations. At low concentrations, U_3O_8 and NiO both increased T_d and decreased the size of the exothermal reaction. This means that the rate or extent of devitrification (peak size) was also reduced. The glass with a higher U_3O_8 concentration (5.5 wt %) had no devitrification peak; devitrification might have occurred, but the rate was too small to be seen by DTA. Al_2O_3 decreased T_d drastically and increased the rate or extent of devitrification.

TABLE 3

Composition of Glass Samples and Their Thermal Transitions

Material Added to Glass Frit 21		*Temperature, °C*[a]	
Additive	*Amount, wt %*[b]	T_s	T_d
None	-	518	623
CaO	1.2	514	632
NiO	2.4	521	645
U_3O_8	2.1	511	633
U_3O_8	5.5	514	-
MnO_2	1.2	507	623
MnO_2	6.6	493	608
Al_2O_3	21.1	525	576
Fe_2O_3	1.4	517	637
Fe_2O_3	14.5	513	627
Fe_2O_3	19.3	508	620
Tank 13[c]	35.0	504	606
Tank 5[c]	35.0	535	660
Tank 15[c]	35.0	479	597
Frit 21 without TiO_2	-	484	597

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[a] Reproducible to ±10°C.

[b] Wt % of glass sample.

[c] Did not contain uranium, but had higher nickel content.

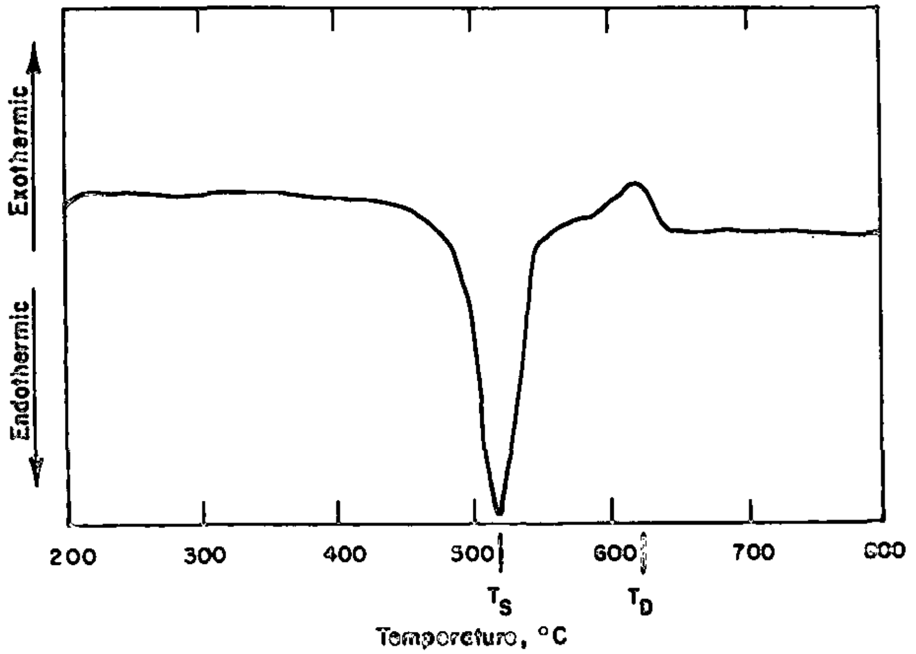

FIGURE 2. Thermogram of Frit 21
T_s = 518°C
T_d = 623°C

The DTA data explained results of previous studies[5] in which glasses containing Tank 13 sludge devitrified at 600°C, but glasses containing Tank 5 sludge did not. Tank 5 sludge has much more U_3O_8 and NiO, which hinder devitrification. Tank 13 sludge has more Al_2O_3, which promotes devitrification. Use of the DTA data should allow prediction of the thermal stability of glasses not tested previously. Thus, glass containing Tank 15 sludge, which has a very high Al_2O_3 content and little U_3O_8 and NiO, was expected to devitrify readily. DTA data for this glass showed a strong exothermal reaction at 597°C, confirming this expectation.

The decrease in T_d observed upon omitting TiO_2 from Frit 21 was unexpected. TiO_2 is a well-known nucleating agent for glass devitrification. In conjunction with the leach data previously reported, this result shows that TiO_2 probably is more of an integral part of the glass structure than had been supposed. TiO_2 is often referred to as an intermediate because of its glass-forming tendency, although it is not a true "glass former."[10] However, Rao found that TiO_2 played an intimate role in the structure of K_2O-PbO_2-SiO_2-TiO_2 over wide composition ranges, and showed that the TiO_2 was incorporated in the network.[11]

Most of the sludge components added to Frit 21 had little effect on the T_s of the resulting glass. MnO_2 and Fe_2O_3 appeared to decrease T_s more than other components. Again, TiO_2 seemed to be an integral part of the glass, since leaving it out decreased T_s. (Rao[11] observed that increasing the concentration of TiO_2 increased T_s to a maximum and then decreased it. This certainly does not contradict the behavior observed here.) Why T_s for the glass containing Tank 15 sludge was so low (479°C) is presently unknown.

Long-Term Heating

Glasses were heated for various periods as long as a month to correlate their devitrification behavior with DTA results and to determine whether some transitions were not observed by DTA because of low devitrification rates.

Glass samples containing 21.1% Al_2O_3 and 78.9% Frit 21 were heated for 24, 48, and 72 hours at 600°C. In all cases, the glass became opaque, white, and chalky. Analysis of powdered samples showed that nepheline ($NaAlSiO_4$) had formed. A similar sample containing Al_2O_3 was heated for only 6 hours at 550°C. A fine-grain crystalline material formed. The heat-treated sample was leached in a Soxhlet extractor, as described in Reference 8. The leach rate calculated from sample weight loss was 15 times higher than that of the nondevitrified (amorphous) glass. However, a large amount of powdered material was observed on the bottom of the leaching apparatus. Thus, the amount of material actually dissolved was less than the sample weight loss.

For high-aluminum sludges, the cooling rate of the waste glass after pouring could be critical. Slow cooling is likely to cause devitrification. Fast cooling may cause cracking by thermal shock. The optimum procedure should be to cool very slowly from the pouring temperature to some temperature above T_d. To avoid devitrification, the molten glass should then be cooled rapidly to a temperature near T_s. Next, the glass should be cooled slowly to ambient temperature. Tests with large glass forms would be required to demonstrate the feasibility of this three-step cooling procedure.

Samples of glasses containing U_3O_8 were heated for 30 days at 600°C; no significant crystallization occurred. Examination of the samples indicated that U_3O_8 hinders devitrification by preventing nucleation. On the surface of the glass, small chips of material (probably bits of insulation from the furnaces) had nucleated crystals, which had grown to 100 μm in length. However, there was no crystallization in the bulk of the material. Thus, the presence of U_3O_8 did not affect the growth of crystals once nucleated.

Samples of glasses containing NiO, CaO, and MnO_2 were all heated 30 days at 600°C with little crystallization detectable by x-ray diffraction. After 90 hours heating, glasses containing MnO_2 did show microscopic crystallization at the surface or near cracks in the glass. Much more of this type of localized crystallization was observed after 190 hours.

A sample containing 19.3 wt % Fe_2O_3 was heated 30 days at 600°C. Powder diffraction patterns showed a crystalline material had formed. Although not identical to Fe_2O_3, it was very similar in structure. This sample was approximately 15 times more leachable than an unheated sample.

Samples of glasses were made containing simulated sludges prepared at the semiworks. These sludges were similar to those listed in Table 2, except that they did not contain uranium and were somewhat higher in nickel. Powder diffraction of glasses containing simulated Tank 13 and Tank 15 sludges showed large amounts of several crystalline products, but glass containing simulated Tank 5 sludge showed only traces. These results indicate that DTA data from glass doped with sludge-component metal oxide can be used to predict the relative devitrification of hydroxide-based sludges.

LEACH RATE

Accelerated Tests Using Simulated Waste: Effect of Sludge Composition

Soxhlet leach tests showed that glass samples containing U_3O_8, NiO, MnO_2, or CaO all had higher leach rates (measured by sample weight loss) than glass without additives. However, the leach rates never exceeded five times the leach rate of the glass without additives. At low concentrations, Fe_2O_3 and Al_2O_3 both increased the leach rate (Al_2O_3 only slightly) and at higher amounts, the leach rate decreased. Eliminating TiO_2 from the glass increased the leach rate by a factor of three.

The effect of adding any sludge component was similar for the two glass compositions. Thus, the substitution of 4 wt % Li_2O for Na_2O had little effect on the leach rate of the glass. Both glass compositions are compatible with all major constituents of SRP sludge.

Previous studies of the incorporation of SRP waste in glass[4,5] showed that the leach rate, thermal properties, and the amount of sludge incorporated into the glass depend on sludge composition. Leach rates of the glass waste forms varied by a factor of 10. Glasses containing sludge from Tank 5F did not devitrify when heated one month at 600°C, but glass containing Tank 13H sludge (similar in composition to Tank 5F sludge) did. Also, only about 25 wt % of Tank 15H sludge could be incorporated in the glass, compared to 40 wt % of other sludges. More Tank 15H sludge could be incorporated in the glass if 4 wt % Li_2O were substituted for 4 wt % Na_2O in the glass.[12] This section describes the effect of the sludge components on the leach rate of Frit 21. Also comparison to similar effects with Frit 18 is presented.

Preparation of Glass Samples

The principal components of SRP sludge are Fe_2O_2, Al_2O_3, MnO_2, and U_3O_8 (Table 4), which are expected to be the major determinants of the properties of the glass. However, sludge composition among individual tanks varies widely. Therefore, samples were prepared to test the effects of each component at two or three different concentrations in each of two glass frits (Table 1). Additional samples were prepared with NiO and with CaO to determine their effect on each glass frit.

Glass samples were prepared by mixing the oxide of a metal sludge component with one of the glass frit compositions. This mixture was heated three hours at 1150°C, poured into a graphite mold, annealed at 500°C for one hour, and then allowed to cool slowly to room temperature (<3°C/min).

Effects of Components on Leach Rates

Crushed glass samples, 3 to 7 g with particles 0.300 to 3.175 mm in diameter, were leached 24 hours in a Soxhlet extractor (Figure 3) at 99°C.

NiO, CaO, and U_3O_8, when added to either glass composition, made glasses with leach rates two to four times higher than those of the glass frit alone. The effect of CaO was unexpectedly large, indicating that the CaO content of glasses used for waste forms should be restricted. The increased leach rates caused by addition of NiO and CaO to the glass is most likely due to disruption of the glass network by the +2 metal ion.

The leach rates of glass containing Fe_2O_3, MnO_2, or Al_2O_3 were qualitatively similar to those containing NiO or U_3O_8; leach rate decreased as the amount of metal oxide added increased. When the highest amounts were added, the leach rate of the glass was roughly that of the glass with no metal oxide added (Figures 4 and 5). Since iron and manganese both tend toward the +2 state at higher alkali content, the high leach rates at low amounts added reflected the same behavior as noted above for CaO and NiO. TiO_2 decreased the leach rate of the glass. This is an unexpected benefit because TiO_2 was included in the glass frit to reduce the volatility of cesium from the melt.

TABLE 4

Major Components of SRP Sludge Expressed as Oxides

	Composition,[a] *wt % in Sludge*	
Oxide	*Average*	*Range*
Fe_2O_3	31.5	4.5 - 46.9
Al_2O_3	18.7	2.8 - 63.3
MnO_2	8.5	2.7 - 17.1
U_3O_8	7.9	0 - 18.5
Na_2O	4.4	1.3 - 8.2
NiO	3.6	0.4 - 8.0
CaO	2.2	0.3 - 4.1
SiO_2	1.7	0.4 - 6.8
HgO	1.3	0.1 - 3.0
Nd_2O_3	1.0	0.3 - 1.2
	80.8	

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a. Based on 19 batches of SRP sludge from 8 waste tanks.

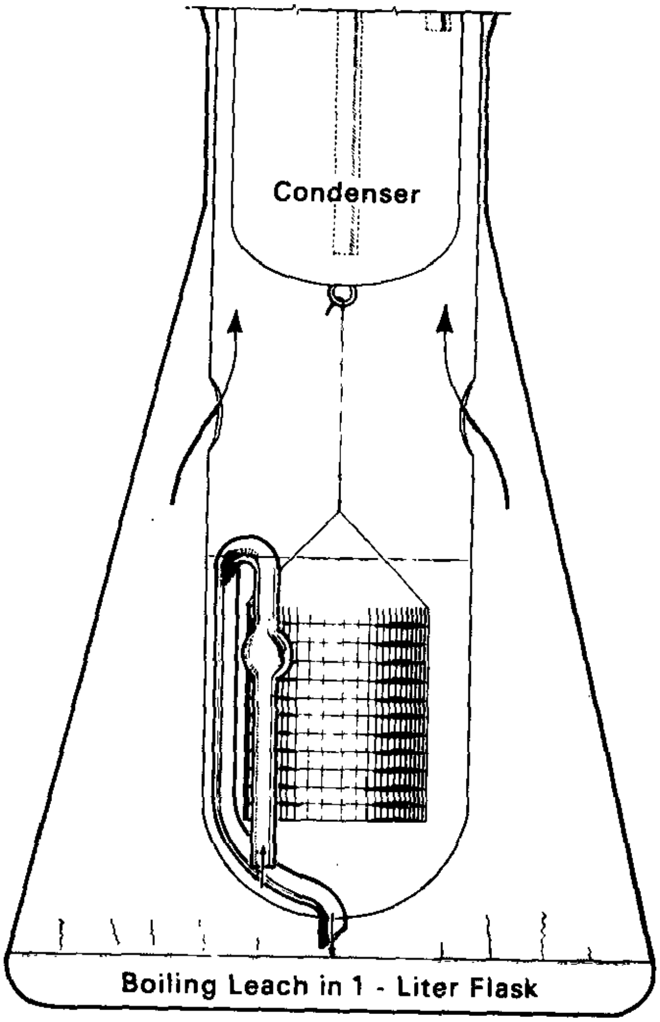

FIGURE 3. Soxhlet Extractor

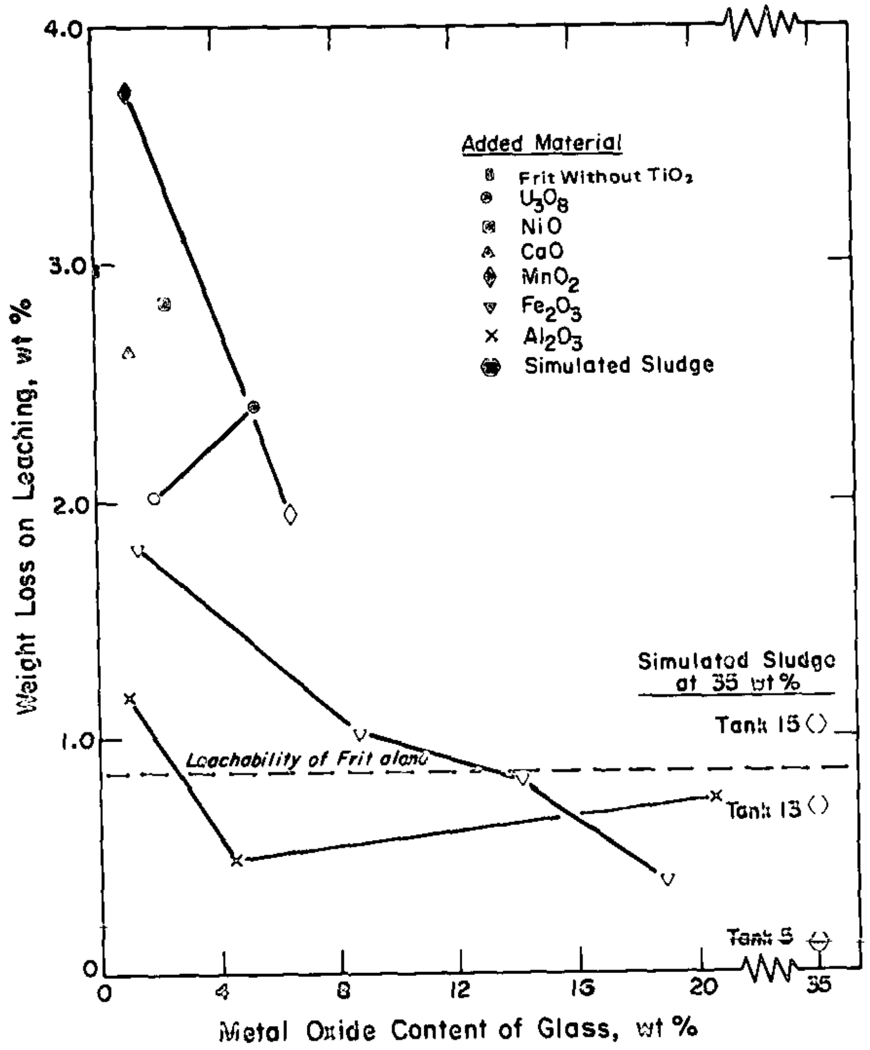

FIGURE 4. Leach Rate of Sludge Components in Frit 18

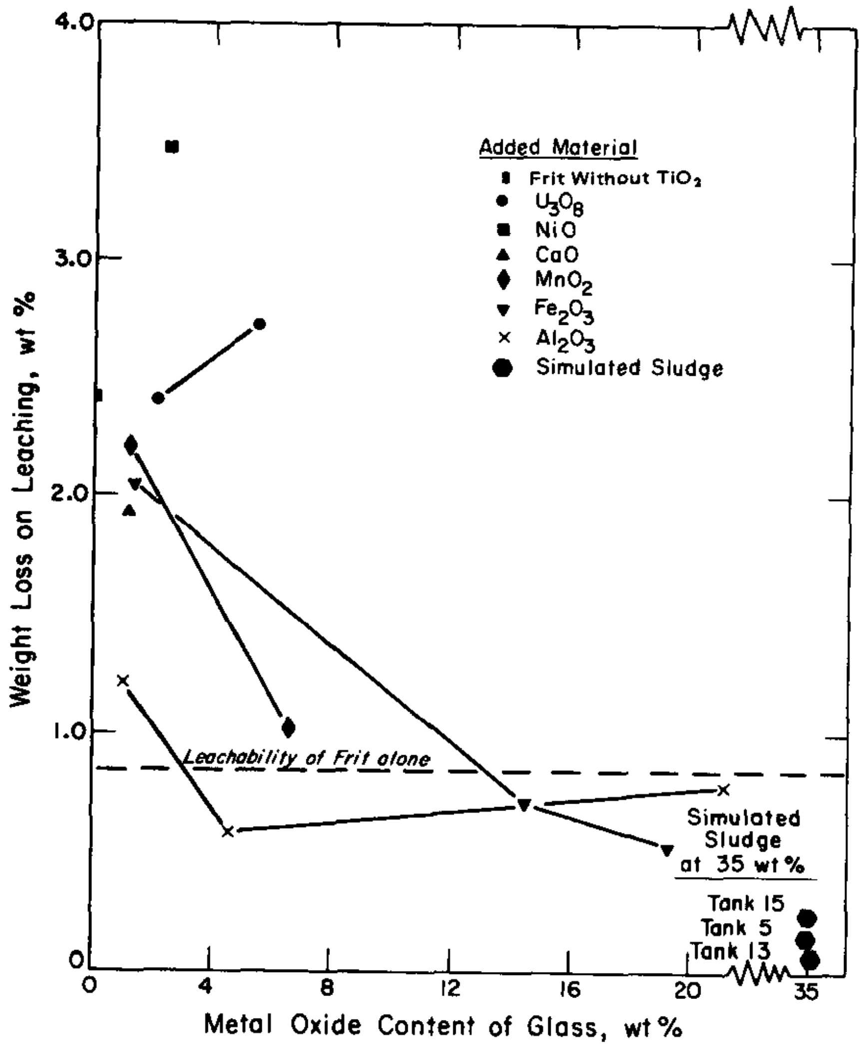

FIGURE 5. Leach Rate of Sludge Components in Frit 21

The leach rate of glasses containing simulated sludges was less than would have been predicted from the leaching of glasses containing sludge components individually. The most likely explanation is that the +2 cations are chemically bound by other components of the sludge. Glasses containing both Tank 5 and Tank 13 simulated sludge contained large numbers of octahedral crystals. X-ray diffraction and spark-source mass spectrometry showed large amounts of Ca, Ni, Mn as well as iron in these crystals. Thus, the concentration of these sludge components actually present in the glassy phase was much lower than expected.

Long-term Tests Using Actual Wastes

Leaching of radionuclides from glasses made with actual SRP sludges into static, distilled water was measured during a 100-day period. Test results showed that:

- Leach rates of Frit 21 glasses are as low as those for Frit 18 glasses.
- ^{137}Cs, ^{90}Sr, and Pu all leach from the glasses at nearly equal rates.
- Leaching is diffusion-controlled for at least the first 100 days. Appreciable glass dissolution does not occur over this time period.

Procedure

Glass buttons were made by mixing 65 wt % Frit 21 and 35 wt % dried, powdered SRP sludge. Six sludges were available (Table 5). The mixtures were melted at 1150°C for three hours, poured into graphite crucibles, and annealed one hour at 500°C. Buttons each weighed about 10 g and had surface areas of about 12 cm^2. Because the buttons had been inspected for evidence of insoluble sulfate (p. 30), their surfaces were contaminated during handling in the high level caves. Prior to the leach tests, the buttons were decontaminated by being dipped into a dilute detergent solution and rinsed with water. Effectiveness of this method was shown by handling a nonradioactive button in the high level caves, decontaminating its surface, and using it as a blank in the leach tests. Almost no activity was found in water samples for that button. Frit 18 buttons made in an earlier campaign[5] had clean surfaces so they were not decontaminated.

TABLE 5

Principal Components of Washed, Dried Sludges[d]

	Tanks 4F,6F	*Tank 5F*	*Tank 12H*	*Tank 13H*	*Tank 15H*	*Tank 16H*
A. Principal Metal Ions, wt %						
Fe	32.77	28.90	4.49	25.57	5.29	13.91
Al	2.28	1.57	30.16	8.70	18.75	16.61
Mn	1.99	5.83	1.69	7.85	2.45	2.59
U	9.22	10.81	[a]	4.18	3.77	4.49
Na	2.95	5.66	1.03	2.58	2.45	2.19
Sr	1.70[c]	1.29[c]	[b]	3.50[c]	1.80[c]	[b]
Ca	2.28	0.90	2.13	1.76	0.52	2.87
Hg	0.65	0.12	1.12	2.32	2.51	2.80
Ni	6.29	6.34	0.46	0.45	0.73	0.30
B. Principal Anions, wt %						
NO_3^-	0.12	1.16	0.42	0.31	0.19	0.32
NO_2^-	0.02	0.12	0.17	0.01	0.16	0.15
SO_4^{2-}	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
PO_4^{3-}	0.69[c]	0.32[c]	[b]	2.15[c]	2.87[c]	[b]
C. Principal Radionuclides, mCi/g						
^{90}Sr	123.0	177.5	41.4	30.1	55.0	53.6
^{144}Ce	30.5	1.5	17.4	0.3	5.4	0.6
^{106}Ru	11.4	1.3	1.7	0.08	1.0	0.2
^{137}Cs	0.7	0.9	0.05	0.3	0.1	0.2
^{154}Eu	0.7	0.6	0.5	0.08	0.4	0.1
^{125}Sb	1.4	0.9	0.3	0.06	0.3	0.04
^{60}Co	1.1	1.1	<0.01	0.01	0.06	0.02
Gross α	0.4	0.1	0.7	0.2	0.1	0.15

---

a. None detected.

b. Not determined.

c. $Sr_3(PO_4)_2$ carrier added.

d. Data from Reference 2. Differences between these samples and those in Table 2 reflect heterogeneity of SRP wastes. Compositions are reported as wt % of the metal ion in the total sludge mass, i.e., Fe rather than Fe_2O_3.

Each button was leached in 300 mL of static, distilled water. Water was changed on the same schedule used previously[5] to facilitate comparing the results. Eight Frit 21 buttons, four Frit 18 buttons, and two nonradioactive buttons (one with no contamination history) were leached. Pu and ^{137}Cs in leach water were measured by alpha- and gamma-pulse height analysis using low-level counters. ^{90}Sr was determined by extracting ^{90}Y into di-2-ethylhexyl phosphoric acid and counting the ^{90}Y by liquid scintillation.

Results

Leach rates are usually expressed in terms of weight loss per unit area exposed to water. For highly leach resistant matrices such as glass, leach rates are most easily obtained by measuring the fractional amount of an isotope released to the water.

$$\text{Leach Rate (g/cm}^2\text{-day)} = \left(\frac{\text{Isotopic activity in water}}{\text{Isotopic activity in glass}}\right)\left(\frac{\text{Sample weight}}{\text{Surface area} \times \text{time}}\right)$$

Leach rates based on ^{137}Cs, ^{90}Sr, and Pu were similar (Tables 6-8). Leach rates were 10^{-5} to 10^{-6} g/cm^2-day initially, decreased rapidly during the first week, and were 10^{-7} to 10^{-8} g/cm^2-day after 100 days. These leach rates are similar to those reported for Frit 18 glasses.[5]

Data in Tables 6-8 show the scatter which is typical of leach tests.[13] Plotting cumulative leach rates, obtained by integrating leach rate over time, helps smooth the data and facilitates interpreting the results. These plots (Figures 6-8) show the similarity between leach rates of Frit 18 and Frit 21 glasses. In general, the order of leach rates for the buttons is not the same for each isotope. This is not surprising, because migration of monovalent cesium, divalent strontium, and polyvalent plutonium should depend on the details of each glass structure.

In all three plots, glass made with combined sludges from Tanks 4 and 6 had the lowest leach rates. On the average, Tank 13 sludge-glasses had the highest leach rates. The combined Tank 4 and 6 sludge had the highest iron concentration among all the sludges; however, Tank 13 also contained a preponderance of iron (Table 5). Leach rates of glass made with Tank 15 sludge (which contained the largest amount of aluminum) was nearly equal for the three nuclides. Leach rates for this glass was near the overall average.

TABLE 6

Glass Leach Rates Based on ^{137}Cs

Glass Type[a]	*Leach Rate (g/cm^2-day)*									
(Days)	*1*	*2*	*4*	*7*	*14*	*21*	*35*	*50*	*74*	*100*
21-35-4,6	3.7D-07[c]	8.8D-07	7.5D-08	7.6D-08	3.1D-08	9.5D-08	7.7D-08	1.5D-08	1.0D-07	9.4D-09
21-35-5A	2.2D-07	2.0D-07	3.0D-07	2.0D-07	1.3D-07	1.0D-07	5.2D-08	1.4D-08	2.2D-08	3.6D-08
21-35-5B	3.8D-07	3.8D-07	1.1D-06	6.1D-07	2.9D-06	-	1.8D-07	4.1D-08	1.8D-08	6.5D-09
21-35-13A	3.3D-07	2.4D-07	6.3D-07	2.7D-07	1.5D-07	3.0D-06	1.1D-07	-	1.5D-08	3.5D-08
21-35-13B	2.9D-07	1.4D-07	2.7D-07	4.5D-07	2.8D-05	3.6D-06	5.7D-07	2.7D-07	1.1D-07	9.4D-08
21-35-13C	1.6D-07	1.3D-08	1.2D-07	2.2D-07	1.2D-07	2.4D-04	2.7D-06	7.2D-08	3.1D-08	3.2D-08
21-35-15	3.8D-07	2.6D-07	3.5D-07	3.9D-07	9.6D-07	1.6D-06	1.6D-07	3.9D-08	1.2D-07	6.6D-08
21-35-16	5.2D-06	8.0D-07	1.6D-06	4.0D-07	6.2D-07	9.5D-06	4.80-07	1.7D-07	4.2D-07	2.1D-07
18-40-5	4.0D-06	4.5D-07	2.1D-07	-	8.8D-07	1.6D-06	7.1D-08	2.8D-08	2.5D-08	3.0D-08
18-40-13	1.6D-06	8.3D-07	4.5D-07	4.1D-07	3.6D-06	3.9D-06	3.1D-08	2.0D-08	6.2D-08	1.3D-07
18-40-13Cs[b]	9.0D-06	9.1D-07	3.0D-07	2.7D-07	2.1D-07	1.6D-07	8.1D-08	6.4D-08	4.6D-08	9.0D-07
18-45-5	1.5D-05	1.2D-06	8.5D-07	1.0D-06	7.2D-07	5.6D-07	1.8D-07	1.5D-07	8.1D-08	3.7D-07

---

a. Glass is designated by: Frit number - wt % sludge - sludge source (Tank).

b. Contained additional ^{137}Cs from SRP waste supernate.

c. Leach rates are given in exponential form, i.e., 3.7D-07 = 3.7 × 10^{-7}.

TABLE 7

Glass Leach Rates Based on ^{90}Sr

Glass Type[a]	Leach Rate (g/cm^2-day)									
(Days)	1	2	4	7	14	21	35	50	74	100
21-35-4,6	7.6D-07[c]	2.8D-07	1.2D-07	4.6D-08	1.7D-08	8.6D-09	5.5D-09	5.4D-09	3.5D-09	1.0D-08
21-35-5A	9.7D-07	1.3D-06	1.5D-06	1.1D-06	7.4D-07	3.4D-07	1.1D-07	6.9D-08	8.3D-08	1.1D-07
21-35-5B	8.2D-07	1.7D-06	1.4D-06	1.8D-06	1.3D-06	-	1.9D-07	7.2D-08	4.3D-08	1.6D-07
21-35-13A	2.1D-06	2.2D-06	2.9D-06	1.9D-06	1.3D-06	8.6D-07	4.5D-07	-	1.6D-07	1.4D-07
21-35-13B	3.7D-07	4.0D-07	1.7D-06	1.6D-06	9.1D-07	6.7D-07	3.3D-07	3.3D-07	2.1D-07	2.2D-07
21-35-13C	1.7D-07	2.2D-07	3.5D-07	2.4D-07	1.6D-07	2.8D-07	8.9D-08	6.5D-08	4.2D-08	5.6D-08
21-35-15	7.7D-07	4.4D-07	5.8D-07	6.9D-07	4.0D-07	2.3D-07	8.1D-08	5.3D-08	3.8D-08	1.1D-07
21-35-16	3.1D-07	1.9D-07	1.5D-07	1.4D-07	1.0D-07	8.8D-08	5.3D-08	5.1D-08	4.1D-08	4.4D-08
18-40-5	1.3D-06	2.5D-07	1.4D-07	-	1.0D-07	7.4D-08	3.0D-08	2.0D-08	1.3D-08	3.0D-08
18-40-13	1.7D-05	5.9D-06	3.4D-06	2.8D-06	2.3D-06	1.5D-06	-	6.8D-07	2.4D-07	5.5D-07
18-40-13Cs[b]	2.1D-06	2.6D-07	1.4D-07	1.7D-07	1.0D-07	8.3D-08	6.6D-08	3.1D-08	2.1D-08	2.5D-07
18-45-5	-	5.6D-06	3.2D-06	3.8D-06	2.6D-06	1.7D-06	6.8D-07	2.4D-07	1.7D-07	3.0D-07

---

a. Glass is designated by: Frit number - wt % sludge - sludge source (Tank).

b. Contained additional ^{137}Cs from SRP waste supernate.

c. Leach rates are given in exponential form, i.e., 7.6D-07 = 7.6 × 10^{-7}.

TABLE 8

Glass Leach Rates Based on Plutonium

Glass Type[a]	*Leach Rates (g/cm^2-day)*									
(Days)	*1*	*2*	*4*	*7*	*14*	*21*	*35*	*50*	*74*	*100*
21-35-4,6	2.2D-08[c]	2.9D-07	5.2D-07	1.5D-08	4.4D-09	1.4D-08	4.8D-09	4.8D-09	2.1D-09	1.9D-09
21-35-5A	3.7D-06	3.4D-07	1.8D-06	4.2D-07	9.7D-08	8.2D-08	3.6D-08	2.4D-08	4.2D-08	1.6D-08
21-35-5A	7.8D-07	2.8D-07	4.0D-07	7.7D-07	9.6D-08	-	1.9D-07	4.0D-08	1.9D-08	1.5D-08
21-35-13A	6.4D-07	1.4D-06	7.3D-06	1.2D-06	5.5D-07	-	5.4D-07	-	2.7D-07	4.8D-08
21-35-13B	2.5D-06	2.2D-06	1.8D-06	2.8D-06	1.3D-06	8.9D-07	5.1D-07	6.1D-07	8.6D-08	9.2D-08
21-35-13C	3.5D-07	-	3.1D-07	1.9D-07	2.0D-07	8.5D-07	1.5D-07	1.1D-07	3.2D-09	9.2D-09
21-35-15	3.6D-06	1.4D-06	6.4D-07	7.3D-07	7.8D-07	6.9D-07	5.9D-07	3.7D-07	2.6D-07	4.6D-08
21-35-16	1.2D-06	3.5D-07	5.0D-07	1.9D-07	1.4D-07	2.5D-07	9.0D-08	9.2D-08	7.4D-08	1.2D-08
18-40-5	1.1D-06	1.3D-07	2.3D-08	-	1.7D-08	1.0D-06	6.5D-09	6.6D-09	3.4D-09	3.6D-09
18-40-13	7.3D-07	1.6D-07	7.1D-08	1.4D-07	1.5D-07	1.4D-07	1.3D-07	2.0D-07	1.4D-07	5.4D-08
18-40-13Cs[b]	1.2D-06	1.4D-07	8.1D-08	3.1D-07	4.0D-08	5.9D-08	4.0D-08	2.6D-08	2.0D-08	3.7D-08
18-45-5	1.7D-05	1.4D-06	4.8D-07	1.1D-07	1.2D-07	1.0D-07	3.1D-8	3.0D-08	3.9D-08	2.3D-08

---

a. Glass is designated by: Frit number - wt % sludge - sludge source (Tank).

b. Contained additional ^{137}Cs from SRP waste supernate.

c. Leach rates are given in exponential form, i.e., 2.2D-08 = 2.2×10^{-8}.

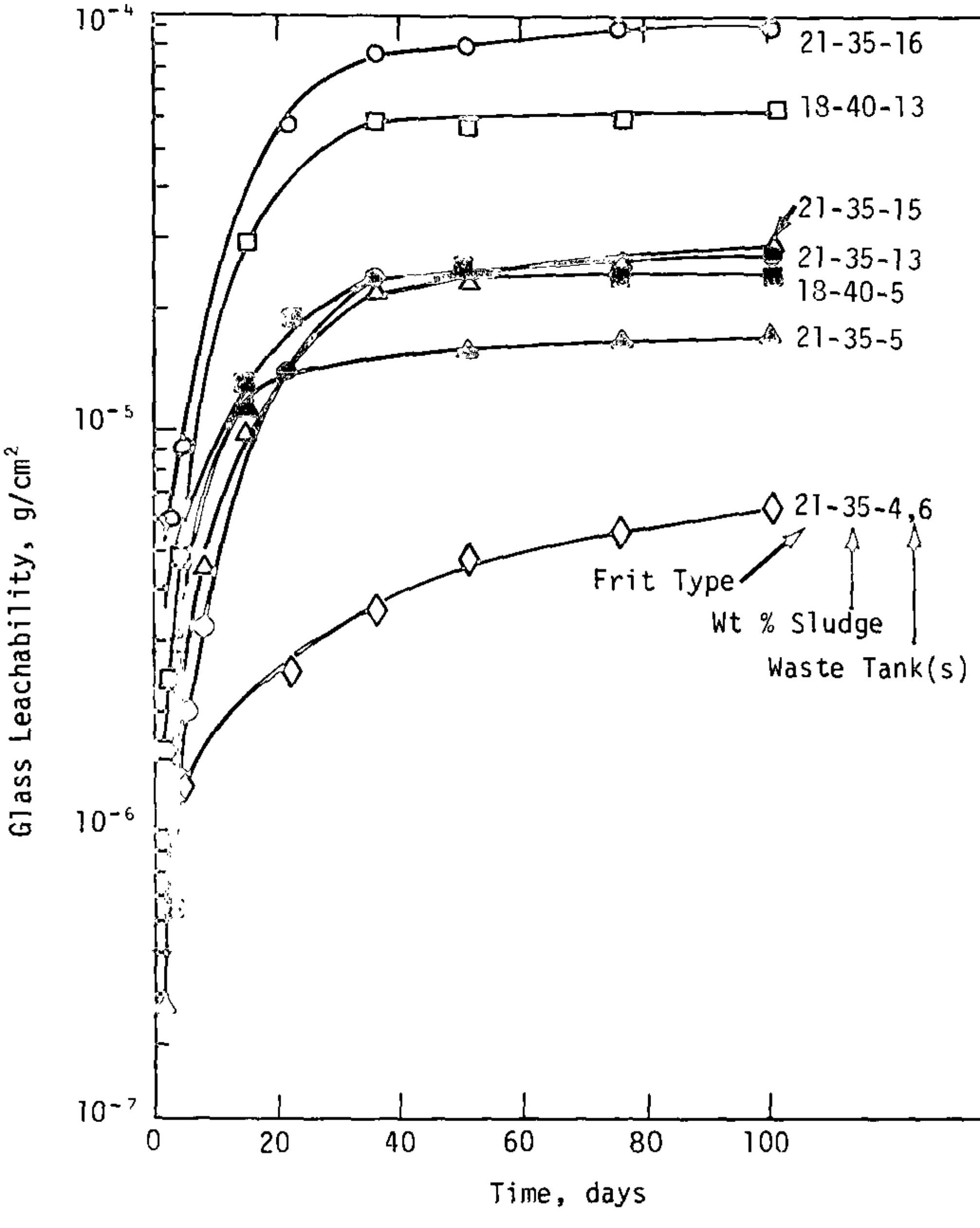

FIGURE 6. Glass Leach Rate Based on ^{137}Cs

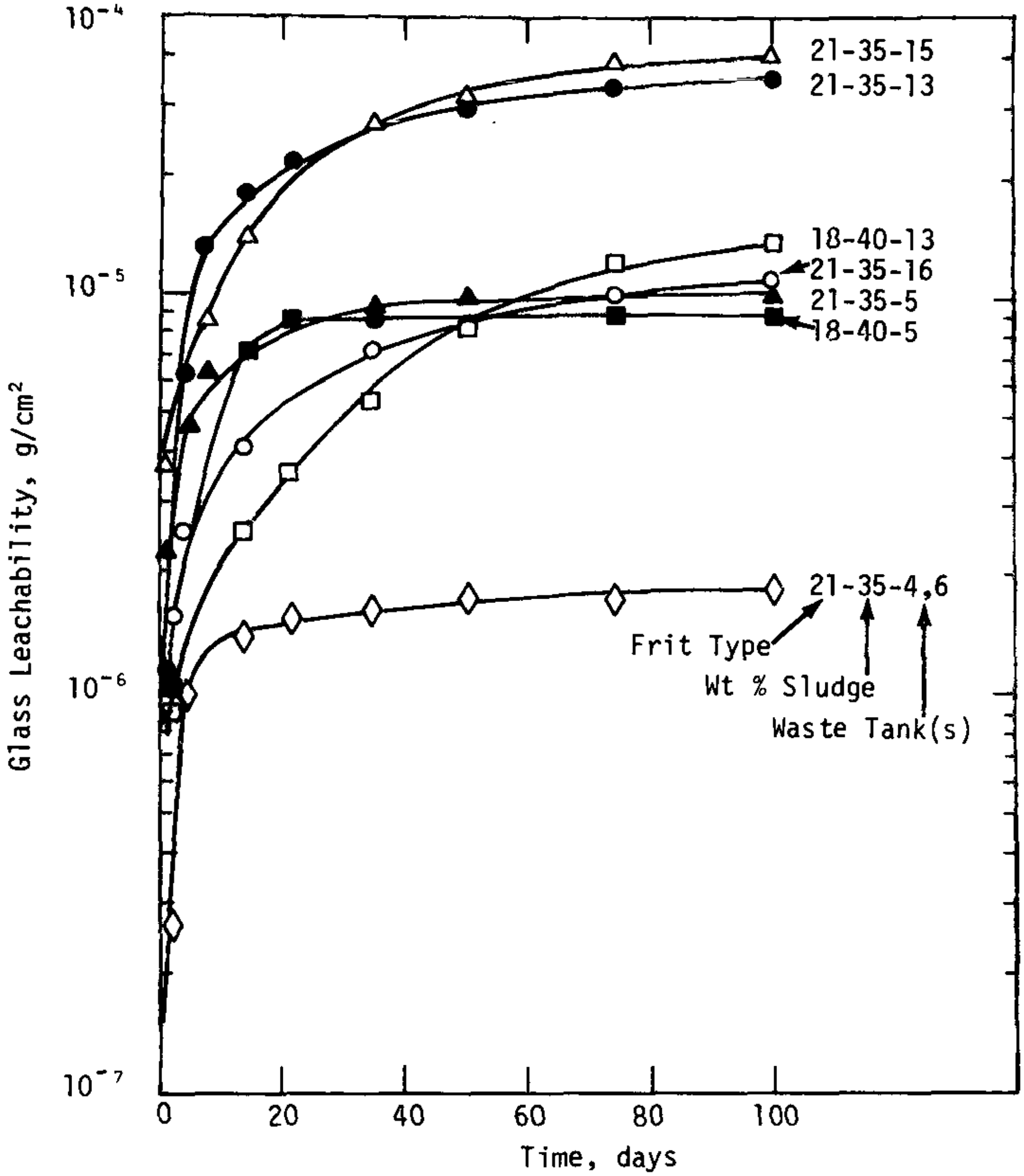

FIGURE 7. Glass Leach Rate Based on Plutonium

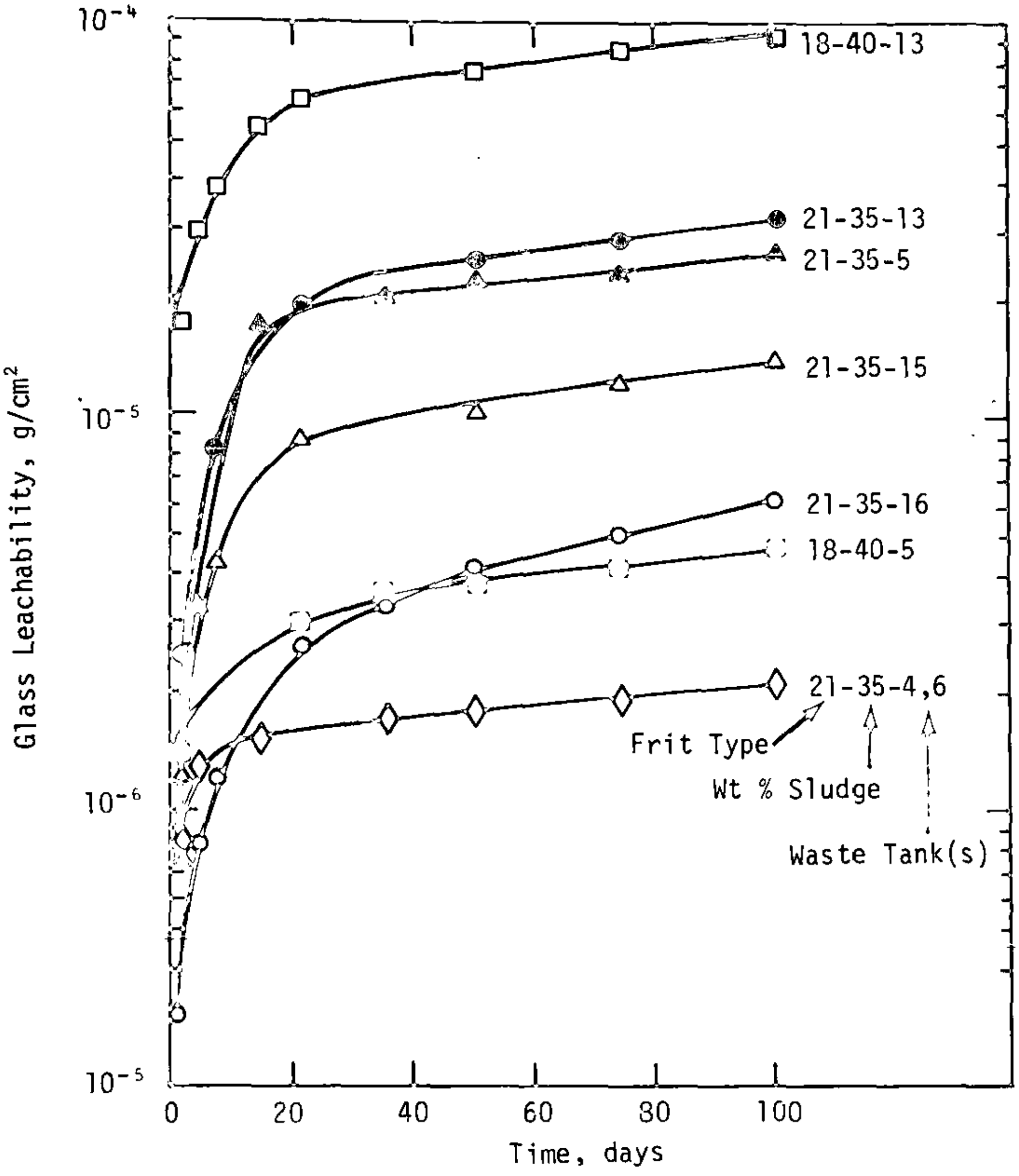

FIGURE 8. Glass Leach Rate Based on ^{90}Sr

Leach Model

Several models predict the cumulative fraction of nuclides leached by diffusion from the glass surface and by glass dissolution. Typical models which include both leaching mechanisms are those by Godbee and Joy:[14]

$$\frac{VF}{A} = (Dk)^{1/2} \left[(t + \frac{1}{2k}) \text{ erf } \sqrt{kt} + (\frac{t}{\pi k})^{1/2} e^{-kt} \right] \qquad (1)$$

and Wallace and Stone (SRL):

$$\frac{VF}{A} = \frac{v}{2a} \left[at + (at + 1/2) \text{ erf } \sqrt{at} + (\frac{at}{\pi})^{1/2} e^{-at} \right] \qquad (2)$$

In both equations, V is the volume of the waste form, A is its surface area, and F is the fraction of radioactivity leached. D is the diffusion coefficient; k and a are rate constants. In Wallace and Stone's model, $D = v^2/4a$. For any time, t, both models give nearly equal results.

Both models predict that leaching is diffusion-controlled for small values of the time constant (at or kt <<1) and dissolution-controlled after very long times. For the model of Wallace and Stone

$$\frac{VF}{A} \approx (\frac{4D}{\pi})^{1/2} t^{1/2} \quad (at \ll 1) \qquad (3)$$

$$\frac{VF}{A} \approx vt \qquad (at \gg 1) \qquad (4)$$

Fitting data in Figures 6-8 to Equation 2 showed that very small values of a ($a < 10^{-3}$) are required for the calculated curve to have the same shape as the experimental curve. For instance, if $a = 10^{-3}$, the calculated curve when normalized to the experimental point at t = 50 days is not sharp enough to match the leach data (Figure 9). For $a < 10^{-3}$, the value for at is much less than 1, even when t = 100 days. Thus, leaching of the glass waste forms was still diffusion-controlled after 100 days.

Figure 9 shows that Equation 3, the diffusion-controlled form of Equation 2, can be fit to typical leach data for t >7 days. (Note that the experimental data from Figure 9 were divided by the glass density, 2.79 g/cm^3, to adjust its units to those of Equation 3). The resulting diffusion coefficient (D) is equal to 9.6×10^{-14} cm^2/day.

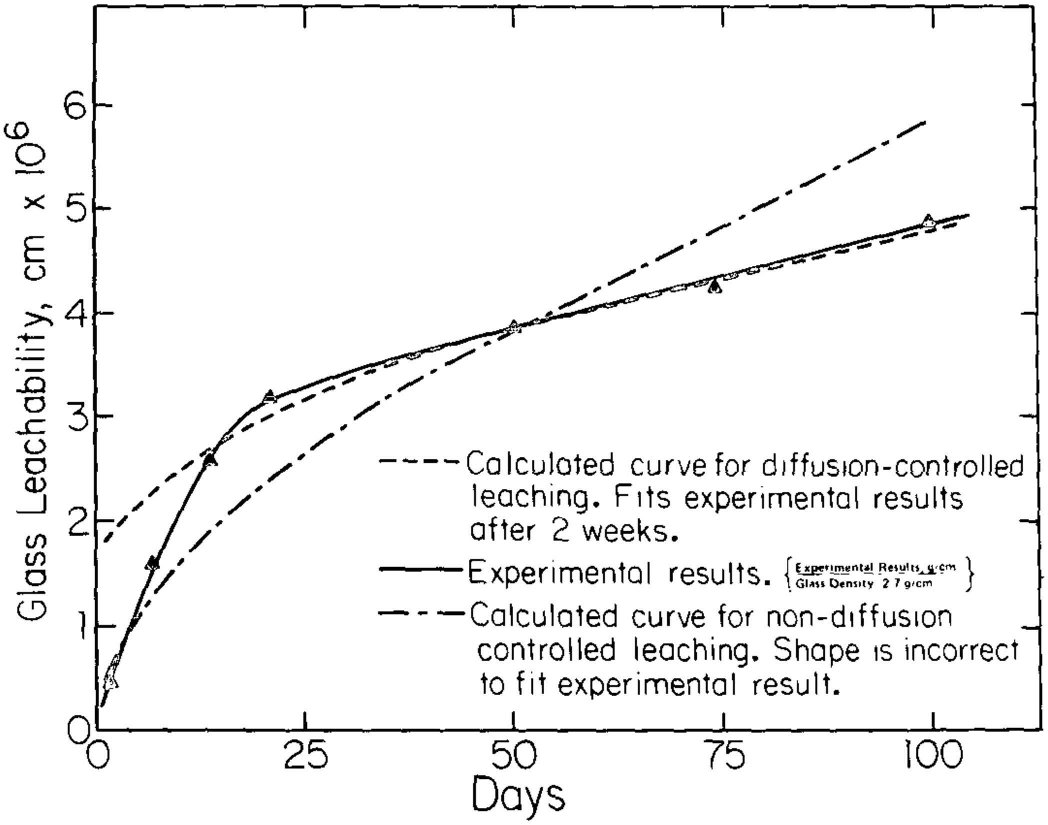

FIGURE 9. Experimental and Calculated Leach Rate of Glass 21-35-15

Experimental results for t = 1 to 7 days fell below the calculated curve. This could be due to the initial washing the Frit 21 buttons received. However, the Frit 18 curves have the same shapes for short times. In static water, time is required for leached nuclides to migrate away from the glass surface. The concentration gradient between glass and solution is thus lowered. This would slow diffusion of nuclides from the glass. ~~When leach water is~~ changed frequently, as it is during the first week of leaching, leachability results would be lower than can be accounted for by Equations 1 or 2.

SULFATE SOLUBILITY

If excess sulfate ions are present in the waste, alkali metal sulfates segregate into a separate phase during a glass melting. This is undesirable for containment of radioactive waste because the segregated sulfate phase is water soluble and rich in cesium. Figure 10 compares a homogeneous glass waste form with one containing excess sulfate ions.

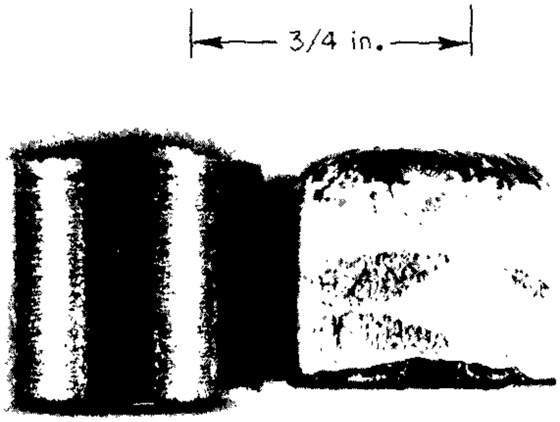

FIGURE 10. Effect of Sulfate on Glass Waste Forms

Sulfate solubility in Frit 21 glasses can be increased from about 1 wt % to about 2.5 wt % by slight modifications of the glass-forming mixture, but such modifications will probably be unnecessary because the sulfate concentrations in all washed SRP sludges analyzed thus far are less than 0.5 wt %. Sulfate solubility is also about 1 wt % in Frit 18 glasses.

Table 9 lists four tests with composition changes intended to improve sulfate solubility. In each test, a mixture of 35 wt % simulated Tank 13 sludge, 60 wt % modified glass Frit 21, and 5 wt % sulfate (as Na_2SO_4) were melted for 3 hours at 1150°C in a porcelain crucible. The hot porcelain crucible was placed in a nickel crucible where it shattered upon cooling. The glass fragments were leached overnight with water at room temperature. Sulfate in the leach water was measured by a sulfate-specific electrode.[15]

Adding phosphoric acid to Frit 21 or increasing the amount of B_2O_3 gave the greatest improvements in sulfate solubility (Table 9); however, excess amounts of either additive can compromise other desirable properties of the glass. While increasing sulfate solubility, phosphate lowers resistance of the glass to water leaching. As the amount of boron, a network former, is increased, the melt may become more viscous and more difficult to pour. Sulfate solubilities (Table 9) are therefore probably close to the maximum attainable by minor modifications of Frit 21 without producing undesirable side effects.

TABLE 9

Improving Sulfate Solubility in Glass Waste Forms

Test	*Modification of Frit 21*	*Reason*	*Sulfate Ion Solubility, wt %*
1	None		1.25
2	5 wt % metallic Si for 5 wt % SiO_2	To reduce sulfate ion to SO_2	1.21
3	Add 5 wt % ZnO	$ZnSO_4$ reported soluble in borosilicate glass	1.41
4	Add 10 wt % H_3PO_4	SO_4^{2-} is soluble in phosphate glass	1.75
5	Increase B_2O_3 to 20 wt %	$Na_2B_2O_7$ is more stable than Na_2SO_4 at melt temperature	2.48

Incorporating actual SRP waste into borosilicate glass showed that sulfate levels in washed sludges were low enough for homogeneous waste forms to be made. Thirteen batches of washed and dried SRP waste sludge were available from tests of sludge-supernate separation by centrifugation.[2] These batches comprised sludges from seven SRP waste tanks (Table 5). Borosilicate glass buttons containing 35 wt % sludge and 65 wt % Frit 21 were made from each of the thirteen batches.

Portions of each sludge and Frit 21 were mixed and then heated at 1150°C for 3 hours in a muffle furnace. The melts were removed from the furnace and poured into graphite molds. Melts containing high-aluminum sludges (Tanks 12, 15, and 16) were viscous but pourable. The graphite molds were placed in a 500°C oven for 1 hour to anneal the glasses.

The resulting 5- to 10-g buttons were inspected visually. All buttons prepared from the thirteen sludge batches were smooth and homogeneous. There was no evidence of segregation of a sulfate phase. These results are added confirmation of the compatibility of SRP sludges and borosilicate glass.

DISSOLUTION IN HNO_3

Laboratory tests showed that radionuclides can be recovered from glass waste forms by dissolving the glass in HNO_3. Recovery of radionuclides from glass may be necessary to permit recycling of substandard batches in a solidification process.

Borosilicate glasses containing 35 wt % simulated SRP sludges dissolved in 5M HNO_3 more rapidly at 100°C than at 60°C. Glass made with simulated Tank 13 sludge dissolved faster than glass made with simulated Tank 5 sludge. Dissolution rates were not affected by increasing HNO_3 concentration from 5M to 8M, by making the HNO_3 dissolvent 0.15M in HF, or by substituting 4 wt % Li_2O for 4 wt % Na_2O in the glass mix. Of the numerous sludge components, MnO_2 had the greatest effect on dissolution rate. Nitric acid dissolvent contained >99% of the plutonium added to a waste form; less than 1% remained with the insoluble silica.

Experimental Technique

Preparation of Laboratory-Scale Glass Waste Forms. Glass forms (8 to 10 grams) were made from the glass frits (65 wt %) and simulated sludges (35 wt %) listed in Tables 1 and 2. All components were thoroughly mixed with a high-speed grinder. Resulting powders were transferred to a porcelain crucible and melted at 1150°C for 3 hours. Melts were poured into graphite crucibles and annealed at 500°C for 1 hour.

Dissolution Tests. Individual glass forms were dissolved in 200 ml of HNO_3 in a distilling flask equipped with a thermometer and reflux condenser. The acid-glass mixture was stirred at moderate speed with a magnetic stirring bar.

The rate of dissolution was determined by weighing the glass before and after each test (Figure 11). After each test, undissolved glass in the dissolving flask was washed and sieved through 3/16-inch stainless steel mesh; the residue retained on the mesh was washed with acetone, dried, and weighed. To avoid skewing the results by including fine silica particles which would not dissolve in HNO_3, anything that passed through the mesh was considered dissolved.

Experimental Design. To minimize the number of experiments needed to identify the important factors affecting the dissolution rate, experimental conditions were varied in accordance with a Plackett-Burman[11] experimental design (Table 10). Five factors were tested at two levels each: temperature, HNO_3 concentration, presence of fluoride, lithium content, and sludge type. This approach provided a qualitative estimate of the relative importance of the selected factors.

A second Plackett-Burman experiment was designed to determine which of the principal metal oxides in sludge significantly altered the glass dissolution rate. The metal oxides and their concentrations included in the test are listed in Table 11. The maximum

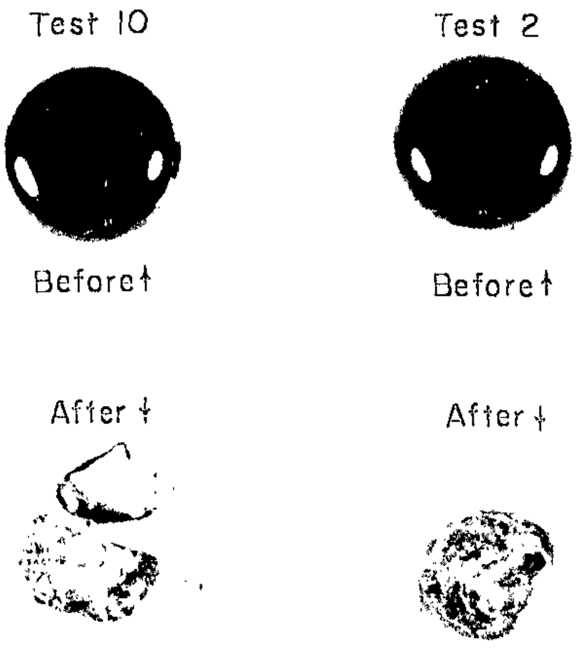

FIGURE 11. Dissolving Test of Glass Waste Forms

concentrations correspond approximately to those found in SRP sludges. The amount of Fe_2O_3 in the test glasses was varied because the concentrations of the other sludge components and the total amount of sludge were fixed by the design of the experiment.

Results

Analysis of initial test results according to this experimental design showed that, at the 90% confidence level,

- Glass waste forms dissolve faster at 100°C than at 60°C.
- Glass forms made with simulated Tank 13 sludge dissolve faster than those made with simulated Tank 5 sludge.
- 5M HNO_3 dissolves glass forms as rapidly as 8M HNO_3.
- Adding fluoride to make the HNO_3 dissolvent 0.15M in aluminum-complexed HF (Al/F = 4/1) did not accelerate dissolution.
- Substitution of 4 wt % Li_2O for Na_2O to decrease the viscosity of the glass melt did not affect dissolution.

TABLE 10

Five-Factor Experiment to Measure Dissolution Rate of Glass Forms

	Dissolvent					
Test	*Temp, °C*	*HNO_3, M*	*F^-, M*	*Glass Frit*[a]	*Sludge-Like Tank*[b]	*Measured Dissolution Rate, grams/hr*
1	100	8	0.0	21	13	6.93
2	100	5	0.15	21	13	4.00
3	60	8	0.15	21	5	0.35
4	100	8	0.15	18	5	0.85
5	100	8	0.0	18	5	1.19
6	100	5	0.0	18	13	4.49
7	60	5	0.0	21	5	0.16
8	60	5	0.15	18	13	0.63
9	60	8	0.0	21	13	0.58
10	100	5	0.15	21	5	1.21
11	60	8	0.15	18	13	0.61
12	60	5	0.0	18	5	0.79

---

[a] Table 1. 21 contains Li_2O, 18 does not.

[b] Table 2.

TABLE 11

Variations in Sludge Components Incorporated into Glass Waste Forms for Dissolution Rate Measurements

Oxide	*Concentration, mol %*
MnO_2	0 and 25
Al_2O_3	0 and 30
CaO	0 and 10
NiO	0 and 10
Fe_2O_3	35 to 100
Total oxides[a]	20 and 35

---

[a] Wt % in glass waste form.

In the second Plackett-Burman test, glasses containing MnO_2 dissolved faster than those containing no MnO_2. The other components (Table 11) had no effect on dissolution rate. If Fe_2O_3 content affected dissolution rate, the total amount of residual metal oxides would have appeared significant. However, the Fe_2O_3 content did not affect dissolution rate.

To verify the results of the second experiment, dissolution rates were measured for a series of glasses containing varying proportions of Fe_2O_3 and MnO_2 (Figure 12). For each level of MnO_2 content, duplicate glass buttons were dissolved and the dissolution rates were measured. The observed rates of the duplicate runs are connected by vertical lines in the figure. The data show a clear trend of increased dissolution rate with increased manganese oxide content, which verified the Plackett-Burman experiment.

In the first test, glasses containing simulated Tank 13 sludge (16 mole % MnO_2) dissolved faster than those containing simulated Tank 5 sludge (23 mole % MnO_2), apparently contradicting the increase of dissolution rate with increased MnO_2 content found in the present tests. Therefore, glasses made from both sludges were examined microscopically. Sludge 13 glasses were homogeneous and amorphous. Sludge 5 glasses were mostly amorphous, but also contained a number of crystal-like platelets (Figure 13). X-ray spectroscopy showed that these platelets contained manganese and all the other sludge components, but no silicon. Precipitation of manganese in these platelets possibly lowered the amount of manganese remaining in the Sludge 5 glass matrix to a level below that in the Sludge 13 glass. The more rapid dissolution of Sludge 13 glass would then be consistent with the trend found in the second test. Other tests showed that the glass matrix dissolves much faster than the crystalline material.[6]

Recovery of Plutonium from Glass Waste Forms

An 8-gram glass button containing 35 wt % simulated Tank 13 sludge was prepared according to the method described on page 32, except that ^{239}Pu in nitric acid solution was added to the mixture before melting. The button was dissolved in 200 ml of 5M HNO_3 at 100°C in ∿2 hours, and the insoluble silica residue was separated by filtration. The residue was washed with an additional 200 ml of 5M HNO_3, and the residue was filtered from the wash solution. The residue was dissolved in 50 ml of concentrated HF. The ^{239}Pu activity found in the acid solutions (Table 12) shows that >99% of the plutonium dissolved in the nitric acid while <1% remained adsorbed on the insoluble residue.

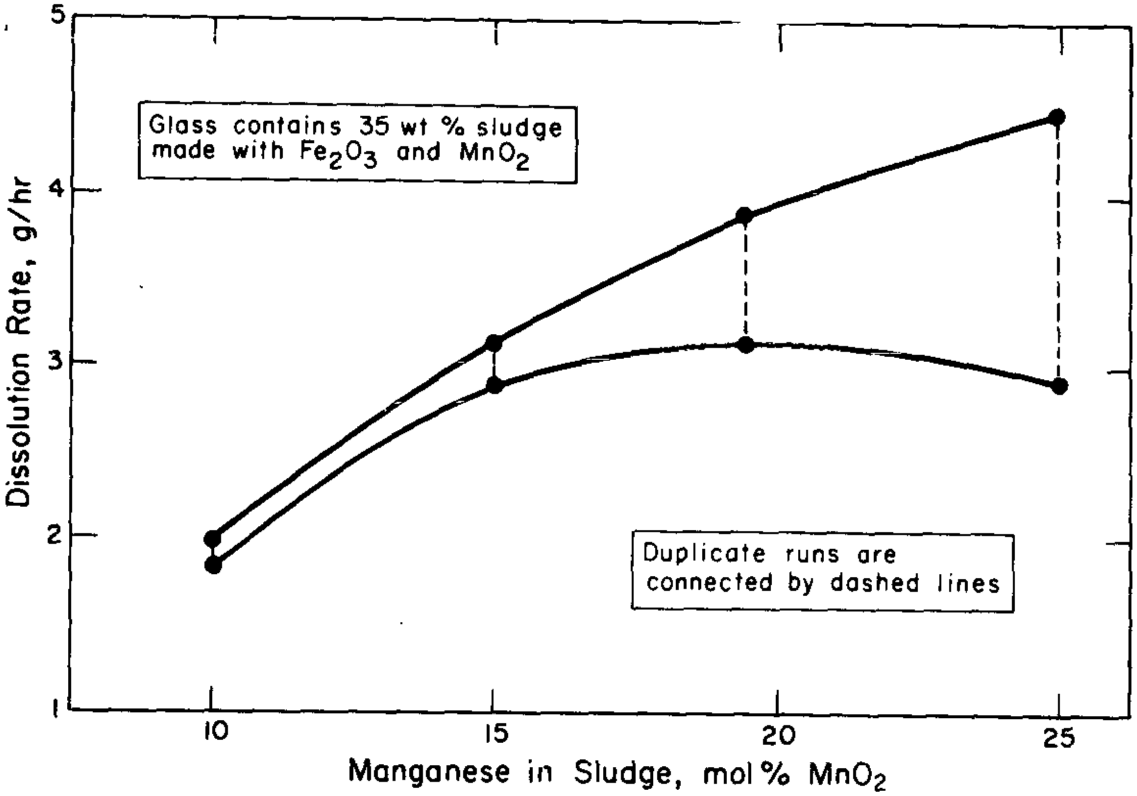

FIGURE 12. Dissolution of Glass Waste Forms Containing 35 wt % Fe-Mn Sludge

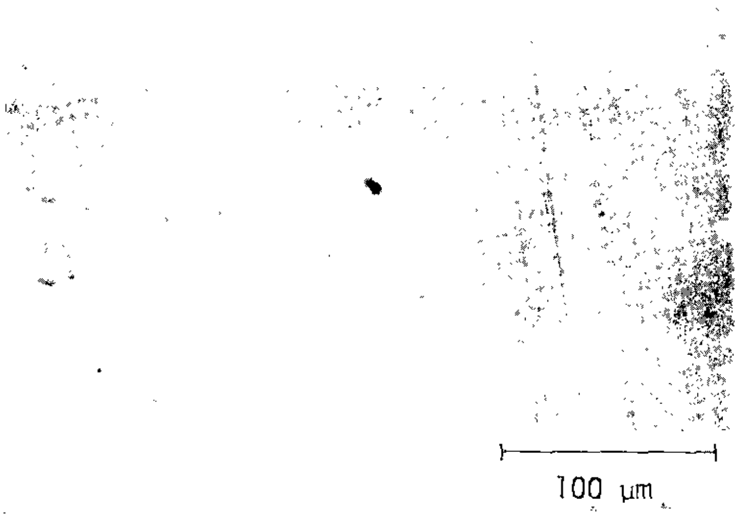

FIGURE 13. Cross Section of Glass Waste Form Containing Simulated Tank 5 Sludge

TABLE 12

Plutonium Recovery by Dissolving Glass Waste Forms in 5M HNO_3

Solution	*Total Activity in Solution, dis/min*	*Plutonium Recovered*
200 ml HNO_3 from dissolving glass waste form	3.6×10^6	>99%
200 ml HNO_3 from washing the residue	5.5×10^4	
50 ml concentrated HF from dissolving the residue	5.3×10^3	<1%

REFERENCES

1. *Integrated Radioactive Waste Management Plan: Savannah River Plant, Aiken, South Carolina.* USERDA Report SRO-TWM-76-1, U. S. Energy Research and Development Administration, Savannah River Operations Office, Aiken, SC (1977).

2. J. A. Stone. *Separation of SRP Waste Sludge and Supernate.* USERDA Report DP-1441, E. I. du Pont de Nemours and Co., Savannah River Laboratory, Aiken, SC (1976).

3. J. R. Wiley. *Decontamination of Savannah River Plant Waste Supernate.* USERDA Report DP-1436, E. I. du Pont de Nemours and Co., Savannah River Laboratory, Aiken, SC (1976).

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

5. J. A. Kelley. *Evaluation of Glass as a Matrix for Solidification of Savannah River Plant Waste. Radioactive Studies.* USERDA Report DP-1397, E. I. du Pont de Nemours and Co., Savannah River Laboratory, Aiken, SC (1975).

6. J. A. Kelley and W. N. Rankin. *Correlation of Radionuclide Leach Rates with Microstructures of Glasses Containing Savannah River Plant Waste.* USERDA Report DP-1411, E. I. du Pont de Nemours and Co., Savannah River Laboratory, Aiken, SC (1976).

7. M. J. Plodinec. *Viscosity of Glass Melts Containing Simulated SRP Waste.* USDOE Report DP-1507, E. I. du Pont de Nemours and Co., Savannah River Laboratory, Aiken, SC (1978).

8. *Savannah River Laboratory Quarterly Report, Waste Management, January-March 1977.* USERDA Report DPST-77-125-1, E. I. du Pont de Nemours and Co., Savannah River Laboratory, Aiken, SC (1977).

9. G. W. Morey. *The Properties of Glass.* 2nd ed., p. 165, Reinhold Publishing Co., New York (1954).

10. F. V. Tooley. *Handbook of Glass Manufacture.* Vol. 1, Books for Industry, New York (1974).

11. B. V. J. Rao. *J. Am. Cer. Soc., 46,* 107 (1963).

12. *Savannah River Laboratory Quarterly Report, Waste Management, July-September 1976.* USERDA Report DPST-76-125-3, E. I. du Pont de Nemours and Co., Savannah River Laboratory, Aiken, SC (1976).

13. J. E. Mendel. *A Review of Leaching Test Methods and the Leach Rates of Various Solid Media Containing Radioactive Wastes.* USAEC Report BNWL-1765, Battelle Memorial Institute, Richland, WA (1973).

14. H. W. Godbee and D. S. Joy. *Assessment of the Loss of Radioactive Isotopes from Waste Solids to the Environment. Part I: Background and Theory.* USAEC Report ORNL-TM-4333, Oak Ridge National Laboratory, Oak Ridge, TN (1974).

15. E. W. Baumann. "A Coated Platinum Sulfate-Selective Electrode." *Analytica Chimica Acta. 99,* 247 (1978).

16. R. L. Plackett and J. P. Burman. "The Design of Optimum Multifactorial Experiments." *Biometrika, 33,* 305 (1946).