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LEACH RATES OF HIGH ACTIVITY WASTE FROM BOROSILICATE GLASS

MASTER

by

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DISCLAIMER

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INTRODUCTION

Borosilicate glass is being evaluated as a matrix for solidification of radioactive waste because it has good mechanical properties, resists leaching by water, and can accommodate a wide variety of wastes. The low leachability of glass-waste forms is especially important for reducing the consequences of an accident during transportation or interim storage. Normally the glass would remain in its container out of contact with water. In the unlikely event the container were breeched, the glass could come into contact with water. The low leach rate of glass would allow time for remedial action before a significant fraction of radioactivity was released.

Leach rates are usually expressed as the rate of glass dissolution in units of $g/(cm^2\text{-day})$. (Slide 1) This expression is chosen because radionuclides are assumed to be uniformly distributed through the glass and to enter solution as the glass dissolves.

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* The information contained in this article was developed during the course of work under Contract No. AT(07-2)-1 with the U. S. Department of Energy.

During the first few days of leaching, these assumptions are not strictly true, because measured leach rates decrease rapidly and sometimes depend on the radionuclide being leached. However, after several weeks, leach rates usually become independent of the time and the radionuclide being leached, so the assumptions are valid for these longer periods.

Borosilicate glass buttons were prepared from actual, fully-radioactive sludges obtained from six high-level waste storage tanks at Savannah River Plant (SRP). SRP waste spans a much wider range of compositions than is expected for light water reactor (LWR) waste. LWR waste, however, will contain a much greater amount of fission products (1). Typical LWR and SRP glass-forming frit compositions are compared on Slide 2. Slide 3 compares LWR and SRP wastes to be added to the frits.

PROCEDURE

Radioactive SRP wastes were mixed with two types of borosilicate glass frit. Both frits had a higher Na/Si ratio ($\sim$0.38) than most commercial borosilicate glasses (0.05-0.07). This higher ratio allowed the radioactive glass to melt at a lower temperature than commercial glass, thus volatility of fission products was minimized. One frit contained 4 wt % Li_2O to reduce viscosity of the melt; the other was Li-free. Frit-sludge mixtures were heated at 1150°C for three hours, poured into graphite molds, and annealed at 500°C for one hour. Buttons contained 25, 30, 35 and 40 wt % SRP waste. Thirty-five wt % was considered the

optimum loading, but lower loadings were necessary to make pourable melts from some of the waste which contained large amounts of aluminum.

The radioactive buttons were placed in stainless steel mesh baskets and immersed in bottles containing 300 mL of static, distilled water. The buttons were transferred to fresh bottles on a predetermined schedule. Leaching in static, distilled water was recommended in a proposed IAEA method (2). However, in Savannah River Laboratory (SRL) experiments the entire button (rather than a single surface) was immersed in the leach water, and the schedule for water changes differed from the IAEA schedule.

Leached ^{137}Cs was measured by γ-ray pulse height analyses. Plutonium activity was determined by planchet counts of the leach water. ^{90}Sr activity was measured by extracting ^{90}Y into di-2-ethylhexyl phosphoric acid and then counting the extractant by liquid scintillation.

RESULTS

Leach rates of ^{137}Cs, ^{90}Sr, and plutonium were approximately equal: 10^{-5} to 10^{-6} g/(cm^2-day) initially; 10^{-7} to 10^{-8} g/(cm^2-day) after two weeks; and 10^{-8} to 10^{-9} g/(cm^2-day) after 100 days. Typical leach rates based on plutonium are shown in Slide 4. Data in Slide 4 show the usual scatter of leach tests (3). Plotting cumulative leachability, obtained by integrating leach rate over time, helps smooth the data and aids interpretation of the

results. (Slide 5) In general, the order of leachability for the buttons is not the same for each isotope. (Slide 6) This is not surprising, because migration of monovalent cesium, divalent strontium, and polyvalent plutonium should depend on the details of each glass structure (Slide 7).

In all three plots, glass made with combined sludges from Tanks 4 and 6 had the lowest leachability. On the average, Tank 13 sludge-glasses had the highest leachabilities. The combined Tank 4 and 6 sludge had the highest iron concentration of all the sludges; however, Tank 13 also contained predominately iron. Leachability of glass made with Tank 15 sludge (which contained the largest amount of aluminum) was nearly equal for the three nuclides. Leachability for this glass was near the overall average. Partial devitrification caused by certain sludge components helps explain the general ordering of leachabilities. Devitrification, which increases leachability, is promoted by aluminum and manganese but retarded by uranium. Although Tank 13 sludge contains less aluminum than sludges from Tanks 15 or 16, it contains more manganese. In previous studies (4), glass containing actual Tank 13 sludge was easily devitrified. The large amount of uranium in combined Tank 4 and 6 sludge and in Tank 5 sludge retards devitrification of glasses made with these sludges. Thus, the general trend of Tank 13 sludge-glasses to be most leachable, those of Tanks 15 and 16 to have intermediate leachability, and glasses made with Tank 5 and

combined Tank 4 and 6 sludge to be least leachable can be explained qualitatively by partial devitrification. Other than effects of partial devitrification, no correlation between sludge composition and glass leachability is apparent.

LEACH MODEL

Several models predict the cumulative fraction of nuclides leached from the glass simultaneously by diffusion and glass dissolution. (Slide 8) One such model has been formulated by R. M. Wallace and J. A. Stone (SRL). Their model is shown on Slide 9. In these equations, V is the volume of the waste form, and A is its geometric surface area. F is the fraction of radionuclides leached after time (t). The diffusion coefficient is $D = v^2/4c$ and c is a rate constant. This model, along with other similar models (5), predicts that leaching is diffusion-controlled for small values of the time constant ($ct \ll 1$) and dissolution-controlled after very long times. Fitting data in Slides 5-7 to this model showed that very small values of c ($c < 10^{-3}$) are required for the calculated curve to have the same shape as the experimental curve. For instance, if $c = 10^{-3}$, the calculated curve when normalized to the experimental point at t = 50 days, does not have the correct shape to match the leach data. (Slide 10) For $c < 10^{-3}$, the value for ct is much less than 1, even when t = 100 days. Thus, leaching of the glass waste-forms was still diffusion-controlled after 100 days.

Slide 10 shows that the diffusion-controlled form of the leach model fits typical leach data for t >7 days. The resulting diffusion coefficient (D) is 9.6×10^{-14} cm^2/day. During the first few days of leaching, diffusion from the glass surface is rapid and the concentration gradient between glass and water is lowered until the nuclides have dispersed throughout the water. The reduced concentration gradient slows the diffusion from the glass and leads to the discrepancy between experimental and calculated leachability.

FUTURE WORK

Future leach tests at SRL will use flowing water during the first week of leaching to eliminate concentration-gradient effects. The effects of salinity and pH on leach rates will also be measured. The tests will be continued long enough to determine dissolution-controlled leach rates.

REFERENCES

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3. J. E. Mendel. *A Review of Leaching Test Methods and the Leachability of Various Solid Media Containing Radioactive Wastes*. USAEC Report BNWL-1765, Battelle, Pacific Northwest Laboratories, Richland, WA (1977).

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5. H. W. Godbee and D. S. Joy. *Assessment of the Loss of Radioactive Isotopes from Waste Solids to the Environment. Part 1: Background and Theory*. USAEC Report ORNL-TM-4333, Oak Ridge National Laboratory, Oak Ridge, TN (1974).

LIST OF SLIDES

SLIDE 1

Measurement of Leach Rate

$$\text{Leach Rate } (g/cm^2\text{-day}) =$$

$$\left(\frac{\text{Isotopic activity in water}}{\text{Isotopic activity in glass}}\right) \times \left(\frac{\text{Sample weight}}{\text{Surface area} \times \text{Time}}\right)$$

SLIDE 2

Composition of Typical Glass Waste Forms

Glass-forming Materials

Component	Composition (wt %) LWR	SRP
SiO_2	34.8	38.1
B_2O_3	12.9	7.3
Na_2O	5.5	13.4
ZnO	5.0	-
K_2O	4.0	-
TiO_2	3.0	7.3
CaO	2.0	4.4
Li_2O	-	2.9

SLIDE 3

Composition of Typical Glass Waste Forms

Waste Materials

Component	Composition (wt %) LWR	SRP
Gd_2O_3	5.5	-
MnO_2	4.2	3.2
Fe_2O_3	1.0	12.0
Al_2O_3	-	7.1
U_3O_8	-	3.0
Fission Product Oxides	19.7	0.03
Actinide Oxides	1.6	0.8

SLIDE 4

Glass Leach Rates Based on Pu Analysis

Glass Type	Leach Rates (g/cm^2-day) 1 (Day)	14 (Days)	100 (Days)
21-35-4,6[a]	2.2×10^{-8}	4.4×10^{-9}	1.9×10^{-9}
21-35-5	3.7×10^{-6}	9.7×10^{-8}	1.6×10^{-8}
21-35-13	6.4×10^{-7}	5.5×10^{-7}	4.8×10^{-8}
21-35-15	3.6×10^{-6}	7.8×10^{-7}	4.6×10^{-8}
21-35-16	1.2×10^{-6}	1.4×10^{-7}	1.2×10^{-8}
18-40-5[b]	1.1×10^{-6}	1.7×10^{-8}	3.6×10^{-9}
18-40-13	7.3×10^{-7}	1.5×10^{-7}	5.4×10^{-8}
18-45-5	1.7×10^{-5}	1.2×10^{-7}	2.3×10^{-8}

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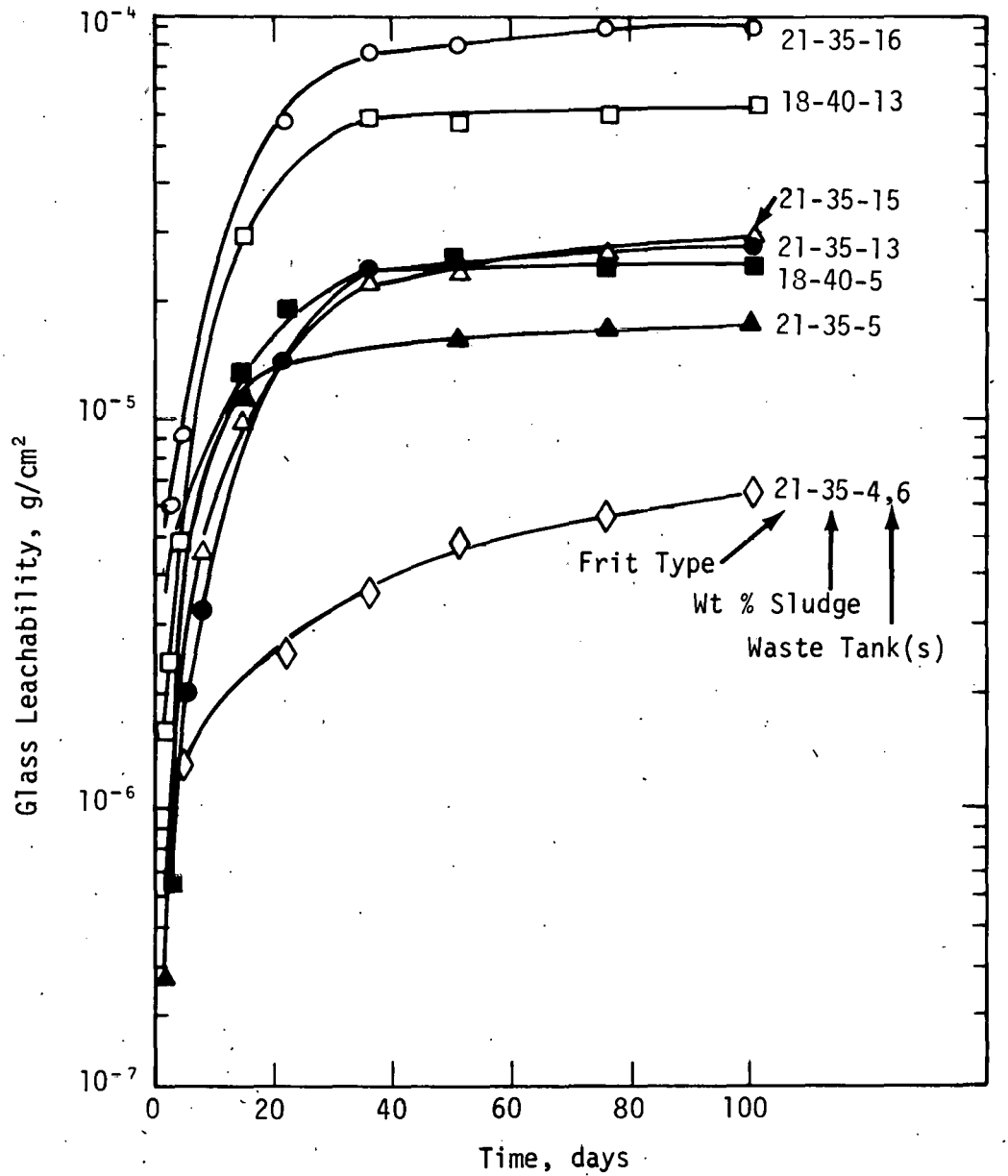
a. 21 is the number of the glass mixture which contains lithium; 35 is wt % sludge; 4 refers to Tank 4 sludge, and 6 refers to Tank 6 sludge.

b. 18 is the number of the glass mixture which contains no lithium; 40 is wt % sludge; 5 refers to Tank 5 sludge.

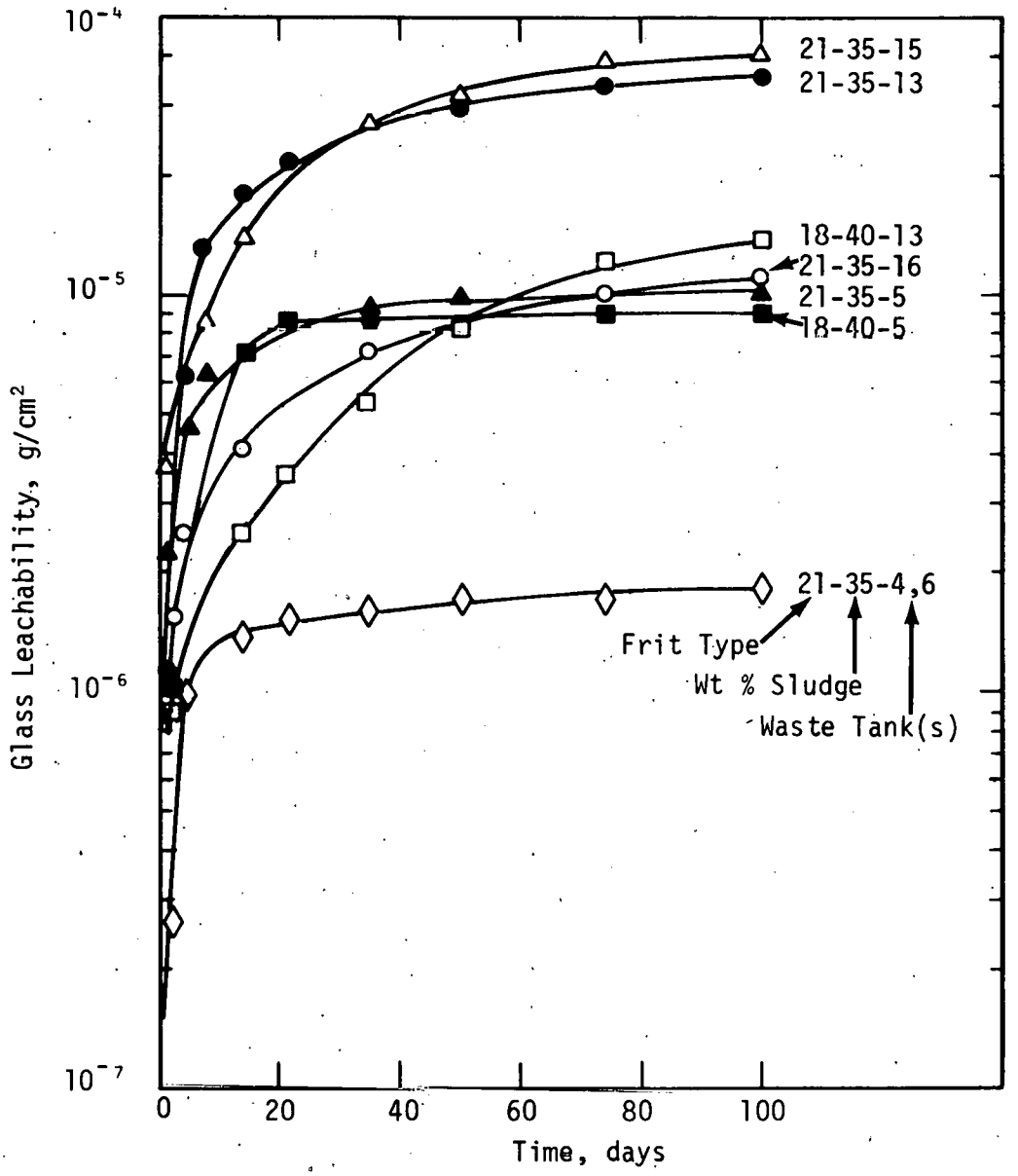
SLIDE 5

Glass Leachability (Based on ^{137}Cs Analysis)



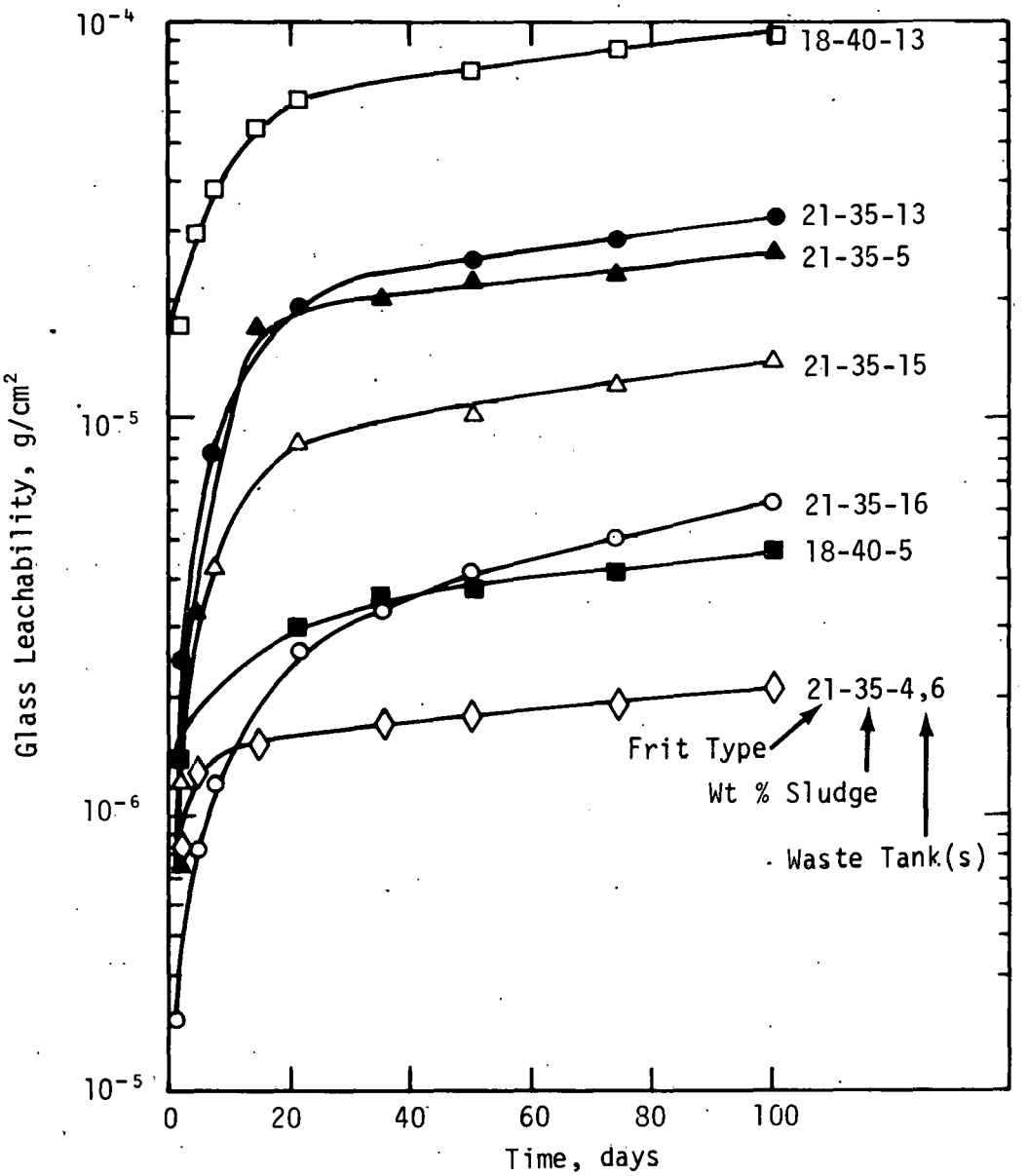
SLIDE 6

Glass Leachability (Based on Plutonium Analysis)



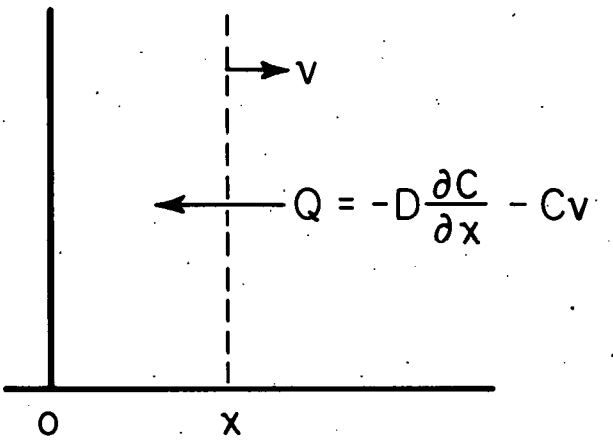
SLIDE 7

Glass Leachability (Based on ^{90}Sr Analysis)



SLIDE 8

Leaching by Simultaneous Diffusion and Dissolution



SLIDE 9

Leachability Model by Wallace and Stone

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

$$\frac{VF}{A} \approx \left(\frac{4D}{\pi}\right)^{\frac{1}{2}} t^{\frac{1}{2}} \quad \text{when } (ct \ll 1) \qquad (2)$$

$$\frac{VF}{A} \approx vt \quad \text{when } (ct \gg 1) \qquad (3)$$

SLIDE 10

Experimental and Calculated Leachability of Glass 21-35-15
(Based on ^{90}Sr Analysis)