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~~AN~~ ASSESSMENT OF SAVANNAH RIVER BOROSILICATE GLASS IN THE REPOSITORY ENVIRONMENT

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ABSTRACT

Since 1973, borosilicate glass has been studied as a matrix for the immobilization of high-level radioactive waste generated at the Savannah River Plant (SRP). In 1977, efforts began to develop and test the large-scale equipment necessary to convert the alkaline waste slurries at SRP into a durable borosilicate glass. A process has now been developed for the proposed Defense Waste Processing Facility (DWPF) which will annually produce approximately 500 canisters of SRP waste glass which will be stored on an interim basis on the Savannah River site.

Current national policy calls for the permanent disposal of high-level waste in deep geologic repositories. In the repository environment, SRP waste glass will eventually be exposed to such stresses as lithostatic or hydrostatic pressures, radiation fields, and self-heating due to radioactive decay. In addition, producing and handling each canister of glass will also expose the glass to thermal and mechanical stresses. An important objective of the extensive glass characterization and testing programs of the Savannah River Laboratory (SRL) has been to determine how these stresses affect the performance of SRP waste glass. The results of these programs indicate that:

- These stresses will not significantly affect the performance of borosilicate glass containing SRP waste.

- SRP waste glass will effectively immobilize hazardous radionuclides in the repository environment.

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AN ASSESSMENT OF SAVANNAH RIVER BOROSILICATE GLASS IN THE REPOSITORY ENVIRONMENT

INTRODUCTION

Radioactive waste from the production of special nuclear materials at the Savannah River Plant (SRP) is currently stored in large underground tanks on the plant site. This alkaline waste is made up of three parts: insoluble sludge, salt cake, and supernate salt solution. The bulk of the waste actinides and fission products are contained in an insoluble sludge of hydroxides and hydrous oxides of iron, aluminum, and manganese.[1-3] The rest of the waste is either in the form of a crystalline salt cake or a nearly saturated supernatant salt solution. This supernatant solution contains nearly all the radiocesium and traces of other radionuclides.[4]

A strategy to immobilize SRP waste for permanent disposal has been developed at the Savannah River Laboratory (SRL). It is currently envisioned that the waste will be immobilized in two stages. This will reduce the initial capital investment and allow the most efficient use of limited resources. The first stage will be designed to immobilize the insoluble sludge, since approximately 95% of the long-lived (>100 yr half-life) radionuclides are contained in the sludge. A second stage for processing high-level waste salt will be built a few years later. This staged approach is depicted in Figure 1.

GLASS PREPARATION, COMPOSITION, AND PHYSICAL PROPERTIES

In the current borosilicate glass process, a slurry containing waste and glass-forming chemicals (in the form of pre-melted glass frit) is fed directly to a continuous glass melter. The slurry dries and fuses at 1150°C to produce a borosilicate glass containing approximately 28 wt % waste oxides. The current glassformer composition has demonstrated its ability to form homogeneous glasses containing the full range of SRP waste compositions.

Waste Vitrification Process

According to present SRP waste management plans, SRP waste sludge will be washed with hot aqueous NaOH in the waste tanks, then water washed to remove soluble salts. This will remove

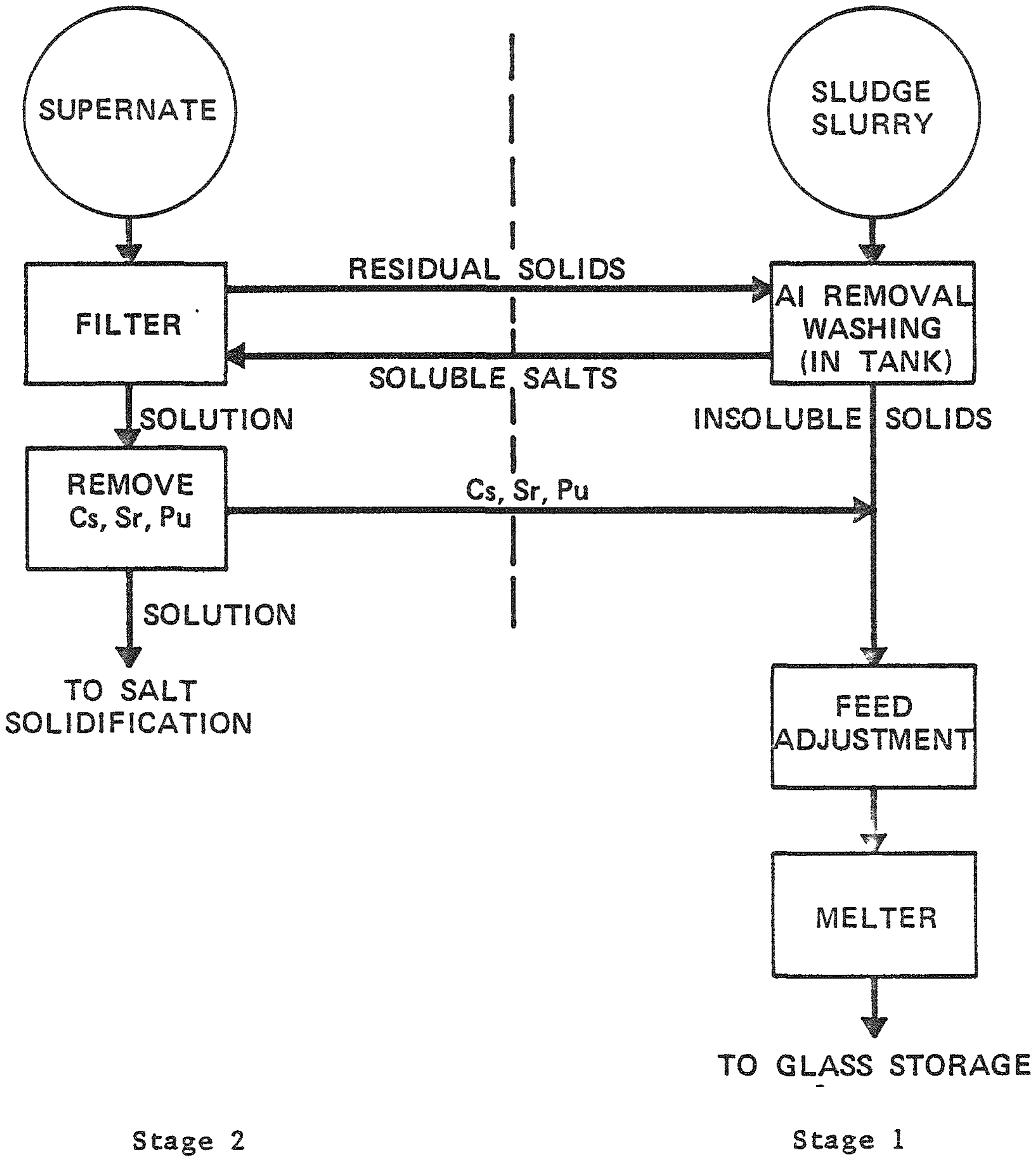


FIGURE 1. Reference Process for Immobilization of SRP Waste

approximately half of the aluminum in the waste, and thus reduce the amount of waste to be vitrified (converted into glass) by about 25%. This sludge slurry will then be pumped to the Defense Waste Processing Facility (DWPF) for vitrification. The composition of the sludge feed for the first stage of waste immobilization is shown in Table 1. When Stage 2 begins decontamination of soluble waste salts, the composition of the waste to be vitrified will be slightly altered, due to the addition of the radionuclides present in the salt (Table 2). The feed to the DWPF will then be composed of a blend of these two. Thus, the Stage 2 glass will contain ~10% less sludge components than the Stage 1 glass.

In the DWPF, the waste slurry (either Stage 1 or Stage 2) will be mixed with glassforming chemicals in the form of premelted glass frit. This slurry will be heated to drive off excess water and then fed to a Joule-heated ceramic-lined melter. Here, the slurry will dry and fuses to form a glass at 1150°C. The glass will be poured out of the melter into stainless steel canisters. After cooling to ambient temperatures, the canisters will be decontaminated, welded closed, and then stored onsite on an interim basis. Eventually, the canisters will be shipped to a federal repository for permanent disposal. The composition of the Stage 1 and Stage 2 glass products are shown in Tables 3-5.[5] The major difference between the two is the 20-fold higher concentration of Cs_2O in the Stage 2 glass product. These compositions are based on the current frit composition, Frit 131.

Glass Frit Composition

As noted above, SRP waste will be mixed with glassforming chemicals (in the form of premelted frit) before vitrification. The composition of this frit is important, since it must be able to reliably combine with the waste to form a durable glass. Initial frit composition development at SRL was directed toward demonstrating the feasibility of vitrifying SRP waste.[6,7] A large amount of experimental data was obtained on the properties of simulated and actual waste glasses made with Frit 18 (Table 6). Because of the difficulty of vitrifying high aluminum wastes with Frit 18, a new composition, Frit 21, was developed. This composition replaced 4 wt % of the Na_2O in Frit 18 with 4 wt % Li_2O.[8] Tests with Frit 21 demonstrated its ability to vitrify all SRP wastes in a durable matrix on a laboratory-scale.[8]

In 1977, large-scale vitrification tests began with Frit 21 and simulated waste. These tests demonstrated that a durable product could be made on a large-scale with Frit 21 but that processing was sometimes difficult.[9,10] This motivated a systematic investigation of the effects of glass composition on glass processing and product performance, which has led to the current frit composition, Frit 131 (Table 6).[11]

TABLE 1

Chemical Composition of Stage 1 DWPF Feed

	lb/gal
Soluble Solids	0.0357
Insoluble Solids	1.75
Water	7.61

Soluble Solids, Wt %		Insoluble Solids, Wt %			
NaOH	31.59	$Fe(OH)_3$	37.97	$Zn(OH)_2$	0.3646
NaNO	28.92	$Al(OH)_3$	15.71	$Mg(OH)_2$	0.6288
$NaAlO_2$	16.08	MnO_2	6.414	C	0.1257
$NaNO_2$	11.71	$UO_2(OH)_2$	4.237	Group A*	0.3416
Na_2SO_4	6.550	$Ni(OH)_2$	2.427	Group B**	1.123
Na_2CO_3	4.885	$CaCO_3$	4.992	$SrCO_3$	0.1308
NaCl	0.1980	Zeolite	4.602	Others	0.40
Na[HgO(OH)]	0.0397	SiO_2	7.332		
NaF	0.0128	NaOH	4.086		
Others	0.020	$NaNO_3$	3.521		
		HgO	1.987		
		$CaSO_4$	0.5911		
		CaC_2O_4	0.5030		
		$Ca_3(PO_4)_2$	0.4652		
		CaF_2	0.1257		
		NaCl	0.1257		
		ThO_2	0.7168		
		$BaSO_4$	0.3143		
		$PbSO_4$	0.1760		
		$Cr(OH)_3$	0.4778		
		$Cu(OH)_2$	0.1383		

---

* Tc, Se, Te, Rb, Mo.

** Ag, Cd, Cr, Pd, Th, La, Ce, Pr, Pm, Nd, Sm, Tb, Sn, Sb, Co, Zr, Nb, Eu, Np, Am, Cm.

TABLE 2

Chemical Composition of Feed from Stage 2 DWPF for Vitrification*

Component	Amount (wt %)
HCOOH	53.87
NaHCOO	32.87
SiO_2	7.51
NaOH	3.95
Solids**	0.92
CsHCOO	0.88
$Sr(HCOO)_2$	1.1×10^{-3}
PuO_2	2.4×10^{-8}

---

* This feed will be blended with the composition in Table 1 to produce Stage 2 glass (Table 4).

** Solids composition is that listed as insoluble solids in Table 1.

TABLE 3

Chemical Composition of Stage 1 Glass Waste Form

Compound	Wt %	Compound	Wt %
SiO_2	45.5	BaO	0.0696
Na_2O	15.0	PbO	0.0448
B_2O_3	10.9	Cu_2O	0.0351
Fe_2O_3	6.57	SrO	0.0318
Li_2O	4.23	RuO_2	0.0257
Al_2O_3	3.62	Y_2O_3	0.0188
Fe_3O_4	3.13	CoO	0.0178
MnO	1.81	PuO_2	0.0158
MgO	1.64	RhO_2	0.00544
Zeolite	1.59	Cs_2O	0.00316
UO_2	1.30		
CaO	1.16	TOTAL	100.00
TiO_2	0.743		
NiO	0.677		
B*	0.389		
La_2O_3	0.371		
ZrO_2	0.371		
ThO_2	0.248		
$Ca_3(PO_4)_2$	0.161		
Cr_2O_3	0.122		
A**	0.112		
ZnO	0.103		

---

*B = Ag, Cd, Cr, Pd, Tl, La, Ce, Pr, Pm, Nd, Sm, Tb, Sn, Sb, Co, Zr, Nb, Eu, Np, Am, Cm.

**A = Tc, Se, Te, Rb, Mo.

TABLE 4

Chemical Composition of Stage 2 Glass Waste Form

Compound	Wt %	Compound	Wt %
SiO_2	46.3	Group B	0.349
Na_2O	16.3	ThO_2	0.223
B_2O_3	10.9	$Ca_3(PO_4)_2$	0.144
Fe_2O_3	5.90	Cr_2O_3	0.109
Li_2O	4.25	Group A	0.102
Al_2O_3	3.25	ZnO	0.0927
Fe_3O_4	2.81	Cs_2O	0.0639
MgO	1.63	PbO	0.0402
MnO	1.62	BaO	0.0625
Zeolite	1.43	Cu_2O	0.0315
UO_2	1.17	SrO	0.0285
CaO	1.04	RuO_2	1.0231
TiO_2	.746	Y_2O_3	0.0169
NiO	.607	CoO	0.0160
ZrO_2	.373	PuO_2	0.0141
La_2O_3	.373	RhO_2	0.00489

Group A: Tc, Se, Te, Rb, Mo

Group B: Ag, Cd, Cr, Pd, Tl, La, Ce, Pr, Pm, Nd,
Sm, Tb, Sn, Sb, Co, Zr, Nb, Eu, Np, Am, Cm

TABLE 5

Major Radionuclides in Stage 1 and Stage 2 Glass

Species	Amount (mCi/lb glass) Stage 1	Stage 2
Co-60	62.8	47.1
Sr-90	11157.7	8393.9
Y-90	11160.6	8396.1
Ru-106	545.2	409.3
Rh-106	545.2	409.3
Ag-110	4.6	3.5
Sb-125	309.9	232.4
Te-125M	69.0	54.5
Cs-134	--------	37.1
Cs-137	6.5	7748.7
Ba-137M	6.1	7330.3
Ce-144	3611.5	2708.3
Pr-144	3611.6	2708.4
Pr-144M	43.3	32.5
Pm-147	8849.9	6637.6
Sm-151	86.3	64.8
Eu-152	1.4	1.0
Eu-154	228.8	171.7
Eu-155	181.1	135.8
Pu-238	275.4	207.1
Pu-239	2.6	1.9
Pu-240	1.6	1.2
Pu-241	308.0	231.4
Am-241	4.0	3.0

TABLE 6

Glass Frit Compositions

Component	Amount (Wt %) Frit 18	Frit 21	Frit 131	Frit 165
SiO_2	52.5	52.5	57.9	68.0
Na_2O	22.5	18.5	17.7	13.0
Li_2O	--	4.0	5.7	7.0
B_2O_3	10.0	10.0	14.7	10.0
CaO	5.0	5.0	--	--
MgO	--	--	2.0	1.0
TiO_2	10.0	10.0	1.0	--
La_2O_3	--	--	0.5	--
ZrO_2	--	--	0.5	1.0

The effects of all the major glass components on important glass properties are shown in Table 7. The properties of SRP waste glass are primarily determined by five components: silica (SiO_2), alkali (Na_2O and Li_2O), boric oxide (B_2O_3), alumina (Al_2O_3), and iron oxide (Fe_2O_3).[2] The alumina and iron oxide (which constitute most of the waste) are important determinants of the durability of SRP waste glass.[11] As Table 6 shows, the amount of silica (important for glass durability) has increased significantly from Frits 18 and 21 to the present composition, Frit 131. A new frit, Frit 165, has recently been developed through the joint efforts of SRL and Ferro Corporation. This frit contains much more silica than any of the previous compositions and should increase durability further.

Waste Glass Simulations

The glass compositions in Tables 3-5 represent the average expected compositions over the entire operating lifetime of the DWPF. However, these compositions cannot be conveniently used for process development or product performance testing because of the difficulties associated with handling radioactive materials. For this reason, most of these studies at SRL have been performed using simulated SRP waste glasses.

Three compositions have been used (Table 8): composite, high iron, and high aluminum waste glass. The composite waste glass is a simulation of the compositions in Tables 3-5 and has been used for most of the studies reported here. The high iron and high aluminum waste glass compositions represent the most extreme glass compositions which might be processed in the DWPF.

Physical Properties of Waste Glass

Representative physical properties of the composite waste glass are shown in Table 9. These properties have been measured for several simulated SRP waste glasses and do not vary significantly with variations in simulated waste glass compositions. This is not unexpected since most of the physical properties of industrial glass compositions are not strongly dependent on the glass composition.[12] Properties of the glass waste form (waste glass in its canister) are shown in Table 10, and thermal decay curves are shown in Figures 2 and 3.

EXPECTED REPOSITORY CONDITIONS

The final fate of canisters of SRP waste glass will be disposal in a geologic repository. Currently, four rock formations

TABLE 7

Effects of Waste Glass Components on Processing and Product Performance

Component	Processing	Product
	Frit Components	
SiO_2	Increases viscosity greatly Reduces waste solubility	Increases durability
B_2O_3	Reduces viscosity Increases waste solubility	Low amounts increase, large amounts reduce durability
Na_2O	Reduces viscosity and resistivity Increases waste solubility	Reduces durability
Li_2O	Same as Na_2O, but greater effect Increases tendency to devitrify	Reduces durability, but less than Na_2O
CaO	Increases then reduces viscosity and waste solubility	Increases then reduces durability
MgO	Same as CaO Reduces tendency to devitrify	Same as CaO
TiO_2	Reduces viscosity slightly Increases then reduces waste solubility Increases tendency to devitrify	Increases durability
ZrO_2, La_2O_3	Reduces waste solubility	Increases durability greatly
	Waste Components	
Al_2O_3	Increases viscosity and tendency to devitrify	Increases durability
Fe_2O_3	Reduces viscosity, hard to dissolve	Increases durability
U_3O_8	Reduces tendency to devitrify	Reduces durability
NiO	Hard to dissolve	Reduces durability
MnO_2	Hard to dissolve	Increases durability
Zeolite	Slow to dissolve, produces foam	Increases durability
Sulfate	Antifoam, melting aid	Too much causes foam or formation of soluble second phase

TABLE 8

Composition of Simulated SRP Waste Glasses

Component	Composite	High Iron	High Aluminum
SiO_2	42.2	41.8	42.3
B_2O_3	10.4	10.4	10.4
Na_2O	13.4	14.3	14.0
Li_2O	4.0	4.0	4.0
CaO	1.1	1.2	0.3
MgO	1.4	1.4	1.4
TiO_2	0.7	0.7	0.7
La_2O_3	0.4	0.4	0.4
ZrO_2	0.4	0.4	0.4
Fe_2O_3	14.2	17.7	4.1
MnO_2	4.1	1.2	3.4
Zeolite	3.1	2.9	3.1
Al_2O_3	2.9	0.4	14.8
NiO	1.7	3.0	0.6
Na_2SO_4	0.2	0.2	0.2

TABLE 9

Physical Properties of SRP Borosilicate Waste Glass

Property	Value
Thermal Conductivity at 100°C	0.95 W/(M)(K)
Heat Capacity at 25°C	0.828 J/g-°C
375°C	1.25 J/g-°C
Softening Point	1.37 J/g-°C
Fractional Thermal Expansion	1.09 X 10^{-5}/°C
Young's Modulus	66.9 GPa
Tensile Strength	57 MPa
Compressive Strength*	550 MPa
Poisson's Ratio	0.177
Density at 100°C	2.75 g/cc
Softening Point	502°C

---

* Experimentally determined for Frit 18 glasses. Not expected to vary significantly with glass composition.

TABLE 10

DWPF Glass Waste Form (Glass and Canister) Properties

Canister Material	304L stainless steel
Canister Dimensions	0.61m in diameter by 3.0m in length
Wall Thickness	Nominal 0.375 in. (9.5 mm)
Inside Volume	$0.73m^3$
Weight of Glass	1480 kg.
Weight of Canister	450 kg.
Heat Loading - Average	256 w/canister-Stage 2 224 w/canister-Stage 1
Heat Loading - 1000 Years	<1 w/canister
Total Activity - Maximum	150 kCi/canister-Stage 2 134 kCi/canister-Stage 1

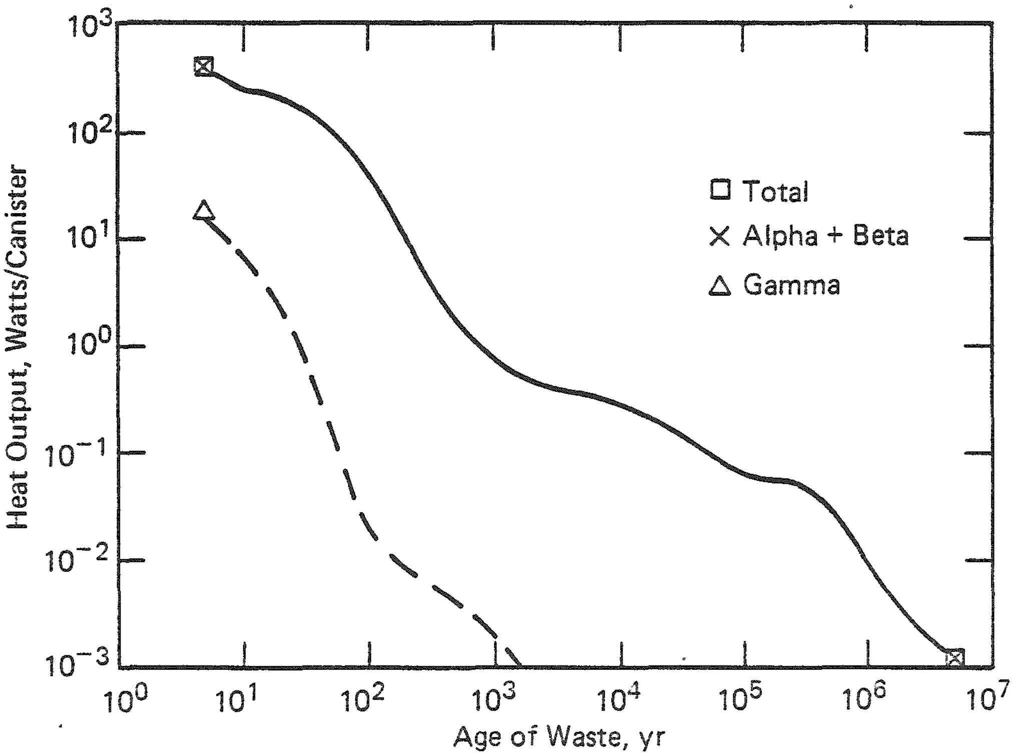


FIGURE 2. Stage 1 Canister Decay Heat

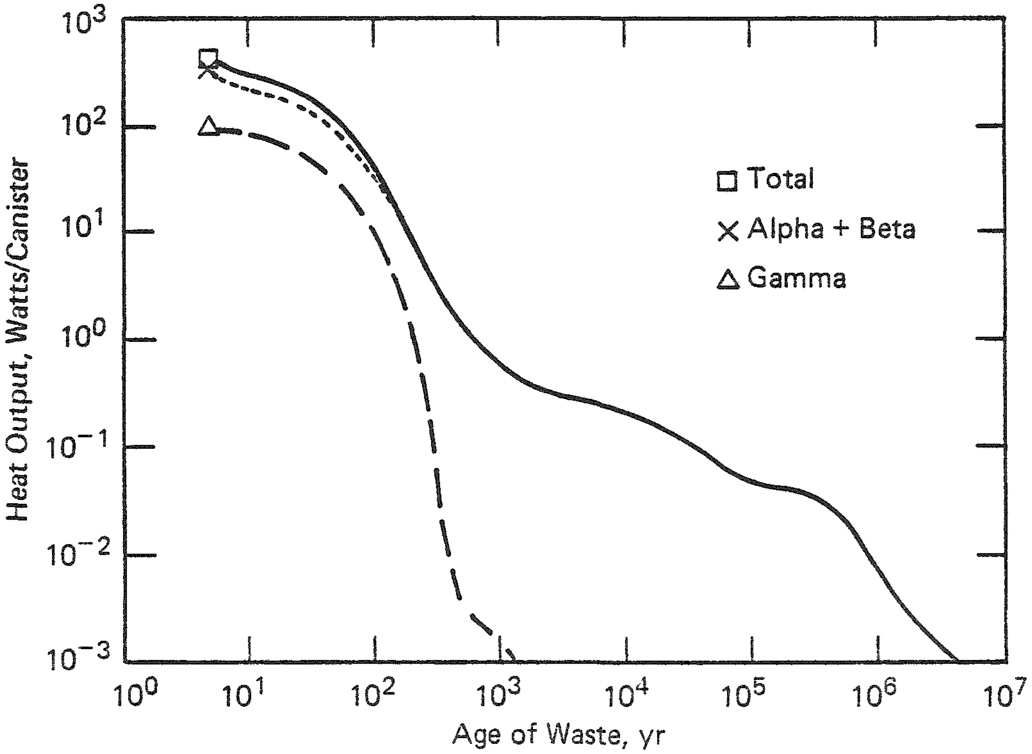


FIGURE 3. Stage 2 Canister Decay Heat

are being intensively investigated as possible repository locations by the Office of Nuclear Waste Isolation (ONWI): salt, granite, tuff, and basalt. A fifth, shale, has been assigned a lower priority and will be studied in detail at a later date. The nuclear waste forms under study by ONWI are SRP waste glass (DHLW), commercial high-level waste glass (CHLW), and spent fuel (SF). Repository conditions for CHLW and SF in all four rock formations have been developed by the Reference Repository Conditions Interface Working Group (RRC-IWG).[13] Because of funding restrictions, conditions for DHLW were developed by that group only for salt and granite.[13-15] Their results show that the long-term (>1000 year) surface temperature of SRP waste glass in salt is expected to be less than 50°C, and in granite is expected to be less than 40°C. The maximum surface temperature in either will be <90°C. In a salt repository only 500 mL of brine is expected to be in contact with each canister of glass. In a granite repository, approximately 1900 L of ground water is expected to be in contact with each canister of glass. Hydrostatic or lithostatic pressures in a repository will be less than 10 MPa.

Reference Repository Design

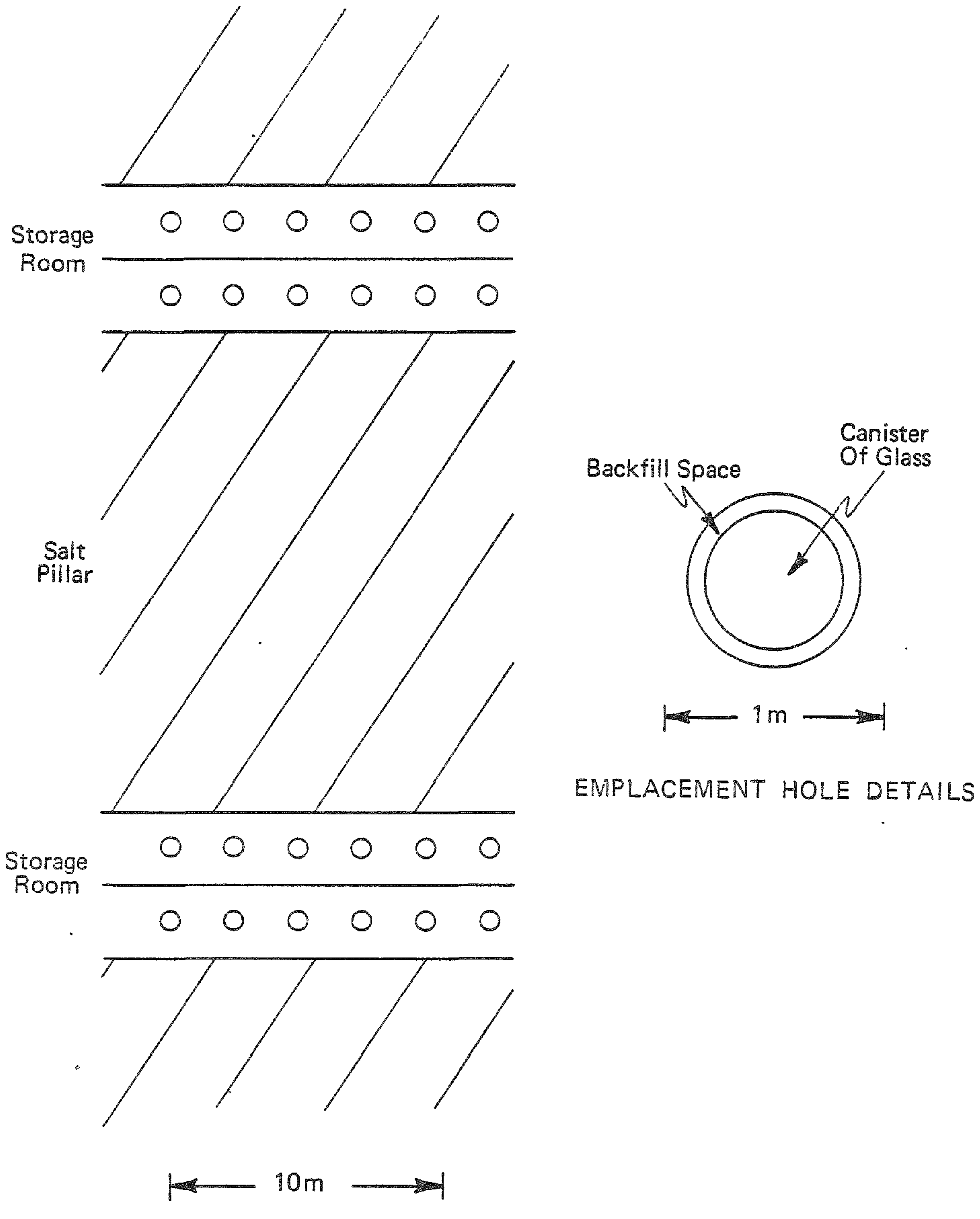
The RRC-IWG developed designs and concepts for both salt and granite repositories. Their reference repository designs utilize the room and pillar mining concept. In this concept, waste storage rooms hundreds of meters below the earth's surface are separated by wide pillars. For example, in the reference salt repository, the storage rooms are 5.5 m (18 ft) wide and are separated by 18 m (59 ft) wide pillars.[14,16] Each storage room contains two rows of emplacement holes for vertical storage of the canisters, as shown for salt in Figure 4. Specific dimensions assumed for the two repositories are in Table 11. In both these instances, the holes and rows are as close together as is practical.[16,17] If closer spacings were attempted, the rock matrix might not be able to support the drilling equipment. The hole diameters for both repositories are slightly larger than the waste canister diameter, 0.61 m (2 ft), so that an overpack and some backfill material can be accomodated. In operation, canisters and their overpacks (if necessary) would be placed in the holes, the holes backfilled and possibly sealed with concrete. Eventually, the entire storage room would be backfilled.

TABLE 11

Reference Repository Characteristics for SRP Waste Glass in Salt or Granite

Repository Characteristic	Repository	
	Salt	Granite
Depth Below Surface	600	1000
Storage Room Width	5.5	7.5
Distance Between Rooms	18.0	22.5
Canister Rows Per Room	2	2
Row Separation	2.28	2.50
Hole Pitch (Along a Row)	2.28	1.85
Hole Diameter	0.76	0.81
Hole Depth	5.5	5.0
Backfill Thickness	0.076	0.010

NOTE: All dimensions in meters.



REPOSITORY LAYOUT

EMPLACEMENT HOLE DETAILS

FIGURE 4. Reference Design for Salt Repository

Temperatures in a Salt Repository

Detailed calculations for the temperature increase in a salt repository have only been performed for canisters with a heat content of 310 watts waste[13] due to funding limitations. In this case the maximum centerline temperature is approximately 100°C and the maximum surface temperature is 90°C (Table 12). These are similar to the temperatures in the granite repository even though the canister heat content assumed was slightly higher than that for a granite repository. Salt, because of its higher thermal conductivity, can accomodate a higher thermal loading. Temperatures during storage of SRP waste glass have been estimated with the data in Table 12 and the thermal decay properties in Table 13. For 15 year old waste, the maximum centerline temperature is 88°C and the maximum surface (leaching) temperature is 84°C. The above temperatures are probably maxima since they assume dry conditions and the canisters as close together as practical.

Temperatures for longer times for SRP waste glass in salt have also been calculated. At 100 years the leaching temperature would be 69°C and at 10^3 years, 51°C. These temperatures are higher than in a granite repository because of the higher ambient temperature of the salt (34°C for salt,[16] compared to 20°C for granite).

Temperatures in a Granite Repository

Detailed calculations have been performed to estimate heat buildup from storage of SRP waste glass in a granite repository. (J. D. Osnes. RE/SPEC, Inc., Rapid City, SD, 1981, private communication).[18] The calculational method was based on a three dimensional superposition technique. In this technique, the thermal response at each point in the repository is calculated by summing the thermal contribution from each canister to that point. The response is calculated in terms of temperature rise above ambient (20°C for granite).

Results of these calculations for Stage 1 and 2 waste are shown in Table 12. In this case, the waste in the glass was assumed to be 15 years out of the reactor when emplaced in the repository. At that time, the thermal output is 256 watts/canister as shown in Table 13. This represents the nominal maximum heat load of the canisters that will be shipped to a repository. As shown in Figure 5, the maximum centerline temperature will be 93°C. The maximum surface temperature will be 90°C (Figure 6). Both occur approximately 20 years after the waste is emplaced.

TABLE 12

Temperatures During Storage of Stage 1 and 2 SRP Waste Glass Canisters in a Salt or Granite Repository

	Temperatures, °C			
	Canister Surface**		Glass Centerline	
Age of Waste, Years*	Salt†	Granite†	Salt	Granite
5	109	135	117	142
10	86	100	95	104
15††	80	89	84	94
100	65	55	65	57
1000	47	40	47	40

---

* This is the time the waste has been out of the reactor.

** This temperature is the maximum temperature for leaching at the various times.

† Ambient salt temperature is 34°C. Ambient granite, 20°C.

†† Assumed average age of waste to be transported to a repository.

TABLE 13

Heat Generation by SRP Waste Glass Canisters

Time Out of Reactor	Watts/Canister Stage 1	Watts/Canister Stage 2
5	414.	422.
10	257.	291.
15	224.	256.
20	198.	227.
25	177.	202.
30	158.	181.
35	141.	161.
40	127.	144.
50	103.	119.
75	62.3	68.8
100	39.2	41.9
200	9.95	7.87
300	4.50	3.50
400	2.61	1.97
500	1.75	1.35
1,000	0.756	0.568
1,700	0.511	0.384
2,000	0.464	0.349
5,000	0.344	0.259
10,000	0.295	0.207
20,000	0.193	0.145
50,000	0.0982	0.0751
100,000	0.0621	0.0466
200,000	0.0521	0.0397
500,000	0.0303	0.0228
1,000,000	0.0102	0.0077

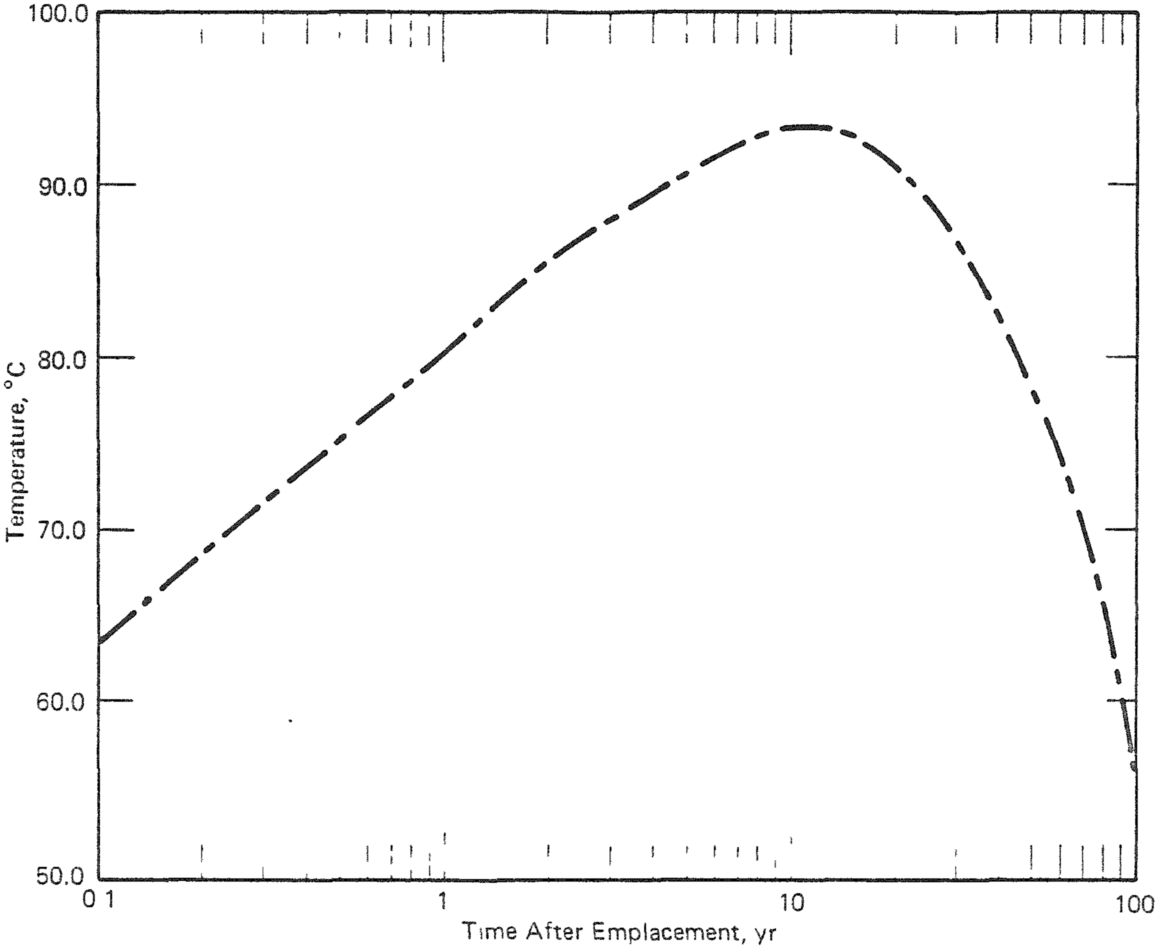


FIGURE 5. Centerline Temperatures of Reference Glass Canister in a Granite Repository

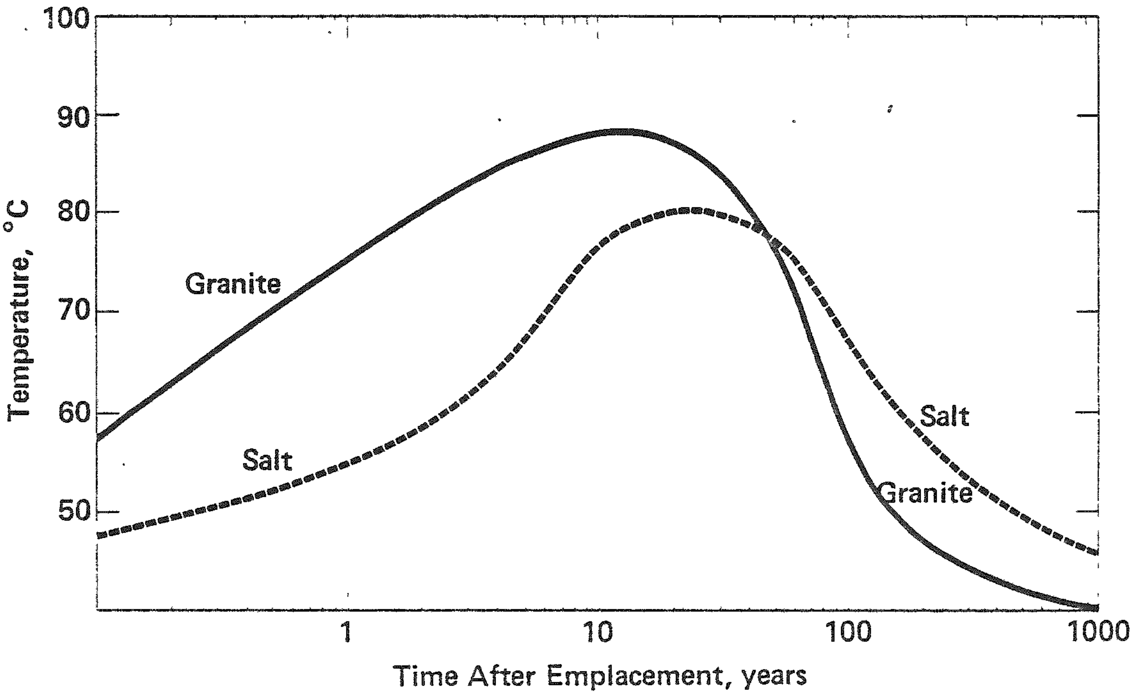


FIGURE 6. Surface Temperatures for a Stage 2 Glass Canister in Granite or Salt

In the repository, the maximum temperature at which leaching could occur will be that of the surface of the glass, i.e. 90°C. Actual maximum temperatures would probably be 2-3°C lower (J. D. Osnes, private communication) because the presence of moisture would raise the thermal conductivity of the backfill. Also, in an actual repository, the canisters might be farther apart, resulting in cooler temperatures. The configuration (Figure 4) used in the calculation, deliberately placed the canisters as close together as practical, for drilling and loading.

Table 12 also shows the calculated decrease in temperature at long times due to decay of the radionuclides. At 100 years the leaching temperature has decreased to 55°C. At 1000 years the estimated temperature is approximately 40°C.[17,18]

Ground Water Compositions

The detailed composition of the ground water that will come in contact with the waste canister in a repository depends on the rock type and on the specific site of the repository. Thus, an exact ground water composition will not be known until the repository site is chosen and characterized. However, reasonable compositions based on analyses of the ground waters in salt, granite and other potential repositories are available. These compositions are given in Table 14.

Two compositions are suggested for a salt ground water. Composition A resulted from analysis of brine inclusions obtained from a bedded salt formation in New Mexico.[16] These inclusions were from a potash zone and thus contained a relatively large amount of potassium. Similar compositions have been obtained from a salt formation in Kansas. Brine B was obtained by saturating an aqueous solution with salt obtained from the 320 m level at the Waste Isolation Pilot Plant (WIPP) site near Carlsbad, New Mexico. The appearance of only small amounts of potassium and magnesium in the solution is in agreement with analyses of the rock salt itself. Composition A has been used by more researchers, since this composition is recommended in the MCC standard leach tests.[19] Because of the presence of potassium and magnesium, this composition is representative of most possible salt repositories. However, composition B should be used for tests specific to WIPP.

The granitic ground water composition in Table 14 is from a granite formation in Sweden.[20] This sample was obtained at a depth of 900 m. Comparison with recent analysis of a granitic ground water obtained at 420 m in the United States shows reasonable agreement.[21] The major cations are Na, Ca, and Si. The major anions are $SO_4^=$, HCO_3^-, and Cl^-.

TABLE 14

Compositions of Ground Water in Potential Repositories

	Concentration, mg/L				
	Salt				
Constituent	A*	B**	Granite†	Basalt††	Tuff††
Lithium	20	---	---	---	0.05
Sodium	42,000	115,000	125	250	51
Potassium	30,000	15	0.4	1.9	4.9
Rubidium	20	1	---	---	---
Cesium	1	1	---	---	---
Magnesium	35,000	10	0.5	0.04	2.1
Calcium	600	900	59	1.3	14
Strontium	5	15	---	---	0.05
Iron	2	2	0.02	---	0.04
Silica	---	---	11	92	61
Fluoride	---	---	3.7	37	2.2
Chloride	190,000	175,000	283	148	7.5
Bromide	400	400	---	---	---
Iodide	10	10	---	---	---
Carbonate	---	---	3	25	---
Bicarbonate	700	10	13	21	120
Sulfate	3,500	3,500	19	108	22
Borate	---	10	---	---	---
Nitrate	---	---	---	---	5.6
pH	6.5	6.5	9.0	9.7	7.1
Eh (Volts)	Mildly Oxidizing	Mildly Oxidizing	+0.17	-0.50	Mildly Reducing

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* Based on analysis of brine inclusions in the Salado formation near Los Medanos, New Mexico (see Reference 14).

** Based on solution results from water saturated with WIPP salt.

† Based on results from Stripa mine in Sweden (see Reference 21). pH value taken from Reference 12.

†† Based on data of Reference 12.

Ground Water Intrusion

After all the canisters are emplaced and the repository is sealed, ground water may intrude into the emplacement holes. The salt is a naturally dry formation and contains very little water - less than 0.55 vol % brine inclusions.[22] A granite repository, however, would probably be below the water table and thus would eventually flood.

In a salt repository, brine inclusions will migrate toward canister. Brine migration results from the temperature difference between the canister and the surrounding salt. The warm canister causes salt to dissolve on the warm side of the inclusion and crystallize on the cooler. The inclusion reaches the canister if it is close enough initially, or if the temperature difference lasts long enough. The amount of brine reaching a canister has been calculated using a single crystal model.[22] In this model, the trapping of water along grain boundaries or in multiphase zones has been neglected. The calculations were performed for a 310 watt canister assuming an initial equilibrium distribution of the 0.5 vol. % inclusions in the salt around the canister.[14,16] The maximum amount of brine reaching the canister was only 0.5 L. This occurred during the first 400 years after emplacment. After 400 years the canister is not hot enough to cause additional flow.

Previous tests have shown that the ability of a glass to withstand aqueous attack depends on the ratio of the glass surface area to the volume of solution in contact with the glass (A/V).[23] The glass surface area will be a function of processing and handling before emplacement, and so will not depend on the specific repository environment. However, since the amount of ground water available will vary for different repositories, A/V will depend on the specific repository environment.

In a salt repository the value of A/V will be large. This is due to the small amount of brine migration to the canister. Since the surface area of an unfractured glass form is 4.86×10^4 cm^2, and assuming that the canister has corroded away, and the 0.5 L of brine is distributed evenly over the cylinder, A/V will be 96 cm^{-1}.* This large value would be difficult to achieve in standard (MCC) leach tests.

In a granite repository, A/V will be much smaller than in salt because of the large amount of ground water that can intrude. A maximum value for A/V can be calculated assuming that the

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* Here cm^{-1} is a convenient shorthand for cm^2 of surface area per cm^3 of solution volume.

ground water fills all available space in the emplacement holes surrounding the glass form and that the canister has corroded away. Using the reference design, the volume of an emplacement hole (from the dimensions in Table 11) is 2.6 m^3. The volume of the glass form is 0.68 m^3. This leaves a total volume for the solution of 1.9 m^3. Some backfill material will be present and reduce this volume. If the backfill occupies 80% of the volume, A/V would be 0.13 cm^{-1}. This is nearly equal to the value of 0.1 cm^{-1} prescribed for standard MCC static leach tests.[19]

Repository Pressures

In a geologic repository there are three possible sources of pressure on the canister and glass. These are pressure in the emplacement hole due to self-heating of the glass, hydrostatic pressure, and lithostatic pressure. The pressure increase due to self-heating is small, but the latter two can cause significant pressure increases due to the depth of the repository.

Gas pressure in the voids of an emplacement hole will increase because of self-heating after the hole is sealed. For SRP waste glass this pressure increase is low because of the low thermal output of the waste glass. Calculations of this increase have been made for a nominal heat content of 310 watts/canister. For salt, the maximum calculated pressure is 0.34 MPa.[14,15] For the granite repository, the value is 0.24 MPa.[19] The pressure is lower in granite because of the larger gas volume in the emplacement hole before flooding occurs.

During flooding, the pressure would rise due to the decreasing volume and increasing hydrostatic head. Noncondensible gases would partially dissolve and also be driven into other fissures in the rock.

Hydrostatic pressure is not significant in a salt repository because of the small amount of water present. In a granite repository the maximum hydrostatic pressure has been calculated to be 9 MPa for a repository at 1000 m below the surface.[13] A previous study has shown that pressures up to 10 MPa at 90°C do not affect the leachability of SRP waste glass in deionized water--a leachant usually more aggressive than a granitic ground water.

Lithostatic pressure results from the rock formation itself. In a salt repository, the salt will creep and eventually completely seal the emplacement holes and backfilled area. One reference suggests that sealing will be completed approximately 250 years after the operational period of the repository.[16] When the emplacement hole is completely sealed, the pressure on the canister and glass will be equal to lithostatic pressure. At a depth of 600 m in salt, the lithostatic pressure is 4-5 MPa.[13] In the granite repository, lithostatic pressures may be reached after very long storage times. For a repository at a depth of 1000 m, the lithostatic pressure will be <7 MPa.[13]

Ground Water Flow

Ground water flow rates are the most poorly characterized parameter of potential repository sites. In salt no further ground water flow is expected after brine inclusions have migrated to the glass. In granite, the water in contact with each canister will be completely displaced once every 500-13000 years.

In salt, as noted earlier, brine will migrate toward the waste glass canister until the temperature gradient between the glass and the salt is too small to cause further appreciable flow. It is likely that no further flow will occur after this, unless the repository is breached and an overlying aquifer intrudes into the salt bed or dome.[12] Thus, brine leaching under static conditions best represents expected conditions in a salt repository.

Currently, a potential granite repository under consideration is in the Climax Stock, on the Nevada Test Site.[21] Tests are underway to characterize the hydrologic properties at this site.[21] Barker and Black[24] found volumetric flows of 0.4-4 ml/year in a British granitic site. Flow through the Stripa site in Sweden is believed to be less than 0.1-0.2 l/m^2-year. Thus, ground water flow through a granitic repository should be less than 1 ml/m^2-day, for a volumetric flow around each canister of approximately 10 ml/day. Using the formalism of Marine,[25] these flows correspond to flush times of 500-13000 years (based on 1900 L/hole).

GLASS LEACHING

The rate of release of radionuclides to the ground water of a potential repository is an important measure of the performance of SRP waste glass. Because potential repository sites are only now being identified,[13] it has been necessary to test SRP waste glass under a wide variety of conditions spanning the range of those expected in potential repositories. These laboratory experiments have shown that leachabilities will be low in the ultimate repository environment, approaching 10^{-4}g/m^2-day (in 1000-day tests using glasses containing actual SRP waste).

The most important determinants of the leachability are the glass composition, the composition of the leachant, the temperature, and the duration of exposure of the glass to aqueous attack. The presence of other waste package components, expected ground water flows, and lithostatic or hydrostatic pressure do not appear to significantly affect leachability.

Terminology

One of the biggest barriers to understanding of leaching data is the rather confusing profusion of nomenclature and conventions. In this report only two terms will be used in presenting leaching data--the leachability and the fraction leached. These will be precisely defined and then used as the quantifiable measures of glass durability.

In a leaching experiment, one starts with a mass of glass, M_T, of a known surface area, A. Normally, only one piece is used, and A is set equal to the geometric surface area. The sample usually contains several species of interest, such as cesium, strontium, or plutonium. The fraction of a species, i, in the sample before leaching is W_i. Normally, W_i is determined by analysis of the glass, but on occasion it has been determined from the composition of the feed used to make up the glass, especially for glasses containing actual waste.[7,8]

The sample is immersed in a volume of leachant, V, for a period of Δt days. One normally monitors the concentration of a species i (for example plutonium) in solution, C_i. In this case, the <u>leachability</u> based on species i, L_i, is defined by

$$L_i = \frac{(C_i)(V)}{(W_i)(A)(\;t)} = \frac{M_i}{(W_i)(A)(\Delta t)}$$

where M_i = the total mass of i removed from the glass = $(C_i)(V)$. In the special case where the leachability is based on the mass loss (the difference in the mass of the sample before and after leaching), $W_i = 1$ and the definition of the leachability is still valid.

Occasionally, especially for radioactive species, the fraction of species i leached from the glass, F_i, will be measured. The fraction F_i is the ratio of the amount of i leached into solution (M_i) to the amount of i originally in the glass (W_i X M_T). Thus the fraction of i leached from the glass is

$$F_i \equiv \frac{M_i}{(W_i)(M_T)}$$

If F_i and L_i have been measured over the same time interval (Δt), then

$$F_i \equiv L_i \left(\frac{A}{M_T}\right) \Delta t$$

Effects of Waste Composition

Since the composition of SRP waste glass may vary from the composite waste glass composition (within the range defined in Table 8), the effects of waste composition on leachability have been determined. In general, adding SRP waste improves the durability of the glass frits, primarily because of the iron or aluminum content of the waste, which form protective surface layers. Leachabilities may vary by up to 5X from that of the composite waste glass, over the expected range of waste glass compositions.

Wicks and Rankin,[26] and Clark and Maurer[27] have both shown glass made from frit and waste has much lower leachability (i.e. is much more durable) than the glass-forming frit alone. Wicks found that the leachability of the composite waste glass was a factor of 30 to 45 lower than that of Frit 131 (Table 15) in static leach tests at 90°C in deionized water (MCC-1 type test). Although both the frit and the waste glass formed surface layers during leaching, the frit layer was much thicker (120 micron) and enriched in silica. The leached layer on the waste glass was thinner (8 micron) and enriched in waste constituents. Wicks concluded that iron and manganese from the composite waste glass formed surface layers which much more effectively protected the glass against subsequent leaching.[28] Clark observed even larger improvements due to the presence of waste (20-500X).[27]

Clark also studied the effect of waste type on leaching in static tests in deionized water. He concluded that the high aluminum waste glass was more durable than either the composite or the high iron waste glass by up to 20X. Stone[29] came to the same conclusion after a series of standard (MCC-1) static leach tests in deionized water, a simulated basaltic ground water, and a simulated brine. The high aluminum glass generally had a lower leachability than the composite waste glass and was up to 12X less leachable than the high iron glass (Table 16).

In 100-day tests with actual SRP waste (waste compositions in Table 17), Wiley[30,31] found that the cumulative amount of cesium, strontium, and plutonium leached* after 100 days varied by a factor

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* Product of the leachability times the duration of the experiment.

TABLE 15

Improvement in Leachability Due to Inclusion of SRP Waste

	Leachability* (g/m^2-day) Based On		
	Si	B	Na
Frit 131**	18.3	31.5	44.3
Composite Waste Glass†	0.61	0.86	0.94

---

* Static test at 90°C in deionized water for 28 days. $A/V = 0.1cm^{-1}$, Teflon vessels.

** For composition, see Table 6.

† For composition, see Table 8.

TABLE 16

Effect of Waste Composition on Glass Leachability

	Leach Rate** (g/m^2-day) Based On		
Waste Glass*	Na	Cs	U
High Aluminum	0.54	0.54	0.040
Composite	0.64	1.54	0.055
High Iron	5.84	3.24	0.084

---

* See Table 8 for compositions.

** Standard (MCC-1) static leach tests, 28 days in 90°C deionized water, $A/V = 0.01cm^{-1}$, Teflon vessels.

TABLE 17

Principal Components of Actual SRP Waste*

Component	Amount (Wt %) Tank 4,6	Tank 5	Tank 13	Tank 15	Tank 16
Fe	32.77	28.90	25.57	5.29	13.91
Al	2.28	1.57	8.70	18.75	16.61
Mn	1.99	5.83	7.85	2.45	2.59
U	9.22	10.81	4.18	3.77	4.49
Na	2.95	5.66	2.58	2.45	2.19
Ca	2.28	0.90	1.76	0.52	2.87
Ni	6.29	6.34	0.45	0.73	0.30

---

* Waste dried at 110°C to remove all free water.

of 4 about an average value, depending on waste type. Invariably, the waste glass with the highest iron content had the lowest leachability (Figures 7, 8, and 9).

Effects of Leachant Composition

Since the composition of ground water in potential repositories varies so widely, the effects of leachant composition on glass leaching have been extensively studied at SRL. Over the range of expected repository ground water compositions, variations in pH will not significantly affect leachability. Laboratory tests have shown that leachants (such as deionized water) which have low pH buffering capacity are generally more aggressive leachants than simulated repository ground waters.

Leachant pH is generally regarded to be the most important variable controlling the durability of a given glass composition.[32] Wicks determined the effect of pH by immersing composite waste glass grains in buffered solutions for 5 days at room temperature and then measuring the Na and Si leached from the glass.[33] The Si results, plotted in Figure 10, are very similar to the Na results and show that over the pH range of 4.5 to 9.5, leachability is independent of leachant pH. As indicated in Figure 10, this range spans the expected pH range for repository ground waters.[13,33] Within this pH range, leaching is primarily by ion exchange, while above the critical pH of 9.5 and below the critical pH of 4.5 leaching is primarily by network dissolution.

In a more detailed study, the leachabilities of composite waste glass were determined in modified static tests at 90°C (Table 18), in pH 3, 7, and 11 buffered solutions. The Si, Na, and Cs in the glass behaved as predicted by Figure 10, i.e. leachability was lowest in neutral pH solution, and high in the extreme pH solutions. However, Mn, Fe, Mg, and Sr in the glass had low leachabilities in both the neutral and alkaline media. Thus, SRP waste glass may effectively immobilize hazardous radionuclides such as Sr over an even wider pH range than Figure 10 would suggest.

In static deionized water, SRP waste glass causes the solution pH to increase and reach or exceed the critical pH within the first three days of leaching (Table 19) at 90°C. Thus, the solution pH is above the upper critical pH for network dissolution (9.5) during most of long-term leaching tests in deionized water. On the other hand, repository ground waters (Table 14) because they contain buffering species such as carbonates or acidic cations such as Mg should tend to remain within the desired pH range for longer periods, and thus attack the glass network less extensively than deionized water.

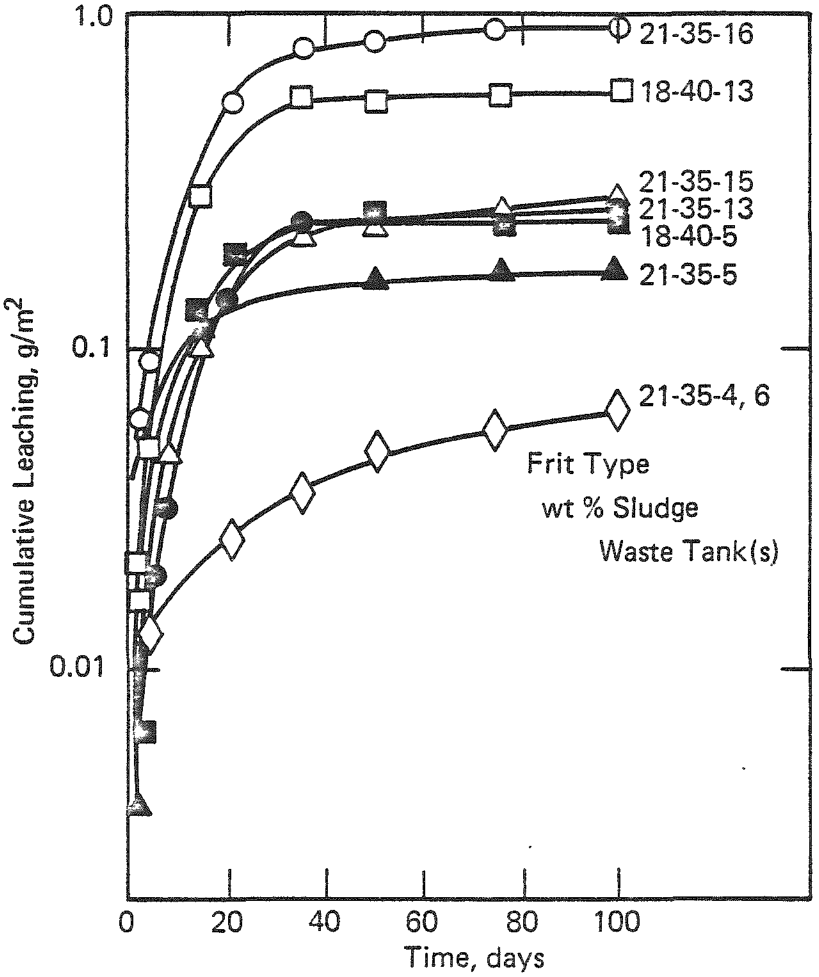

FIGURE 7. Cumulative Leaching of Actual SRP Waste Glass (For Test Details see Reference 32) Based on Cs-137 (Numbers indicate frit type, waste loading and waste type, i.e., 21-35-16 indicates a glass containing 35 wt % Tank 16 sludge in Frit 21.)

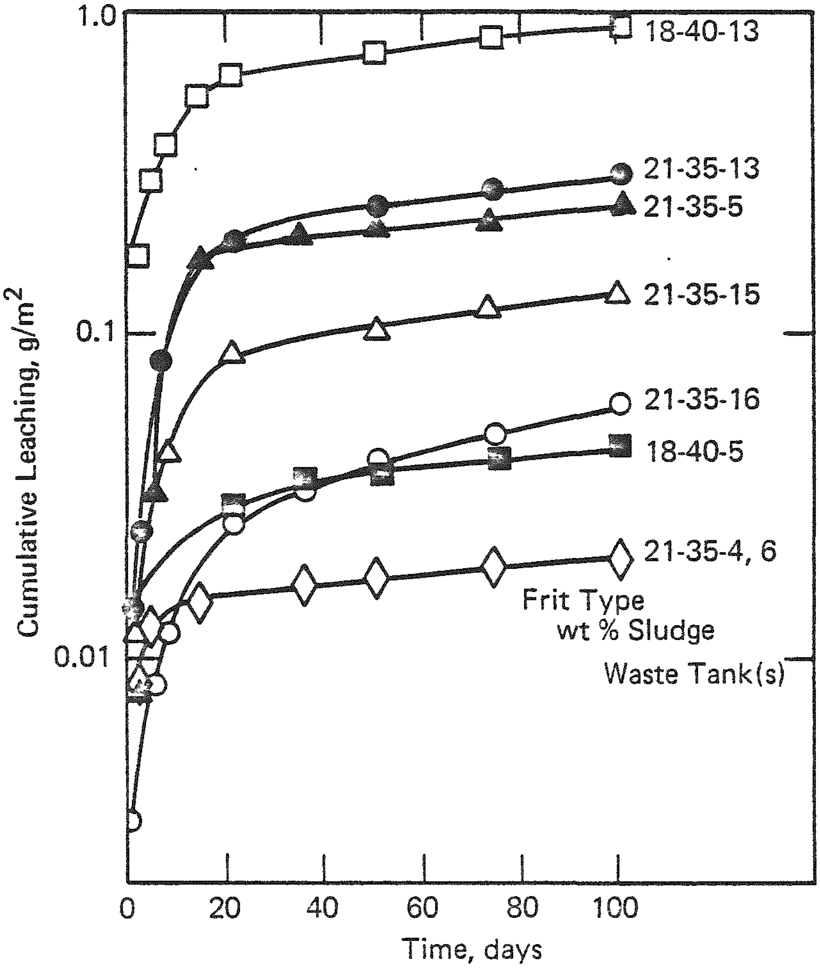

FIGURE 8. Cumulative Leaching of Actual SRP Waste Glass (For Test Details see Reference 32) Based on Sr-90

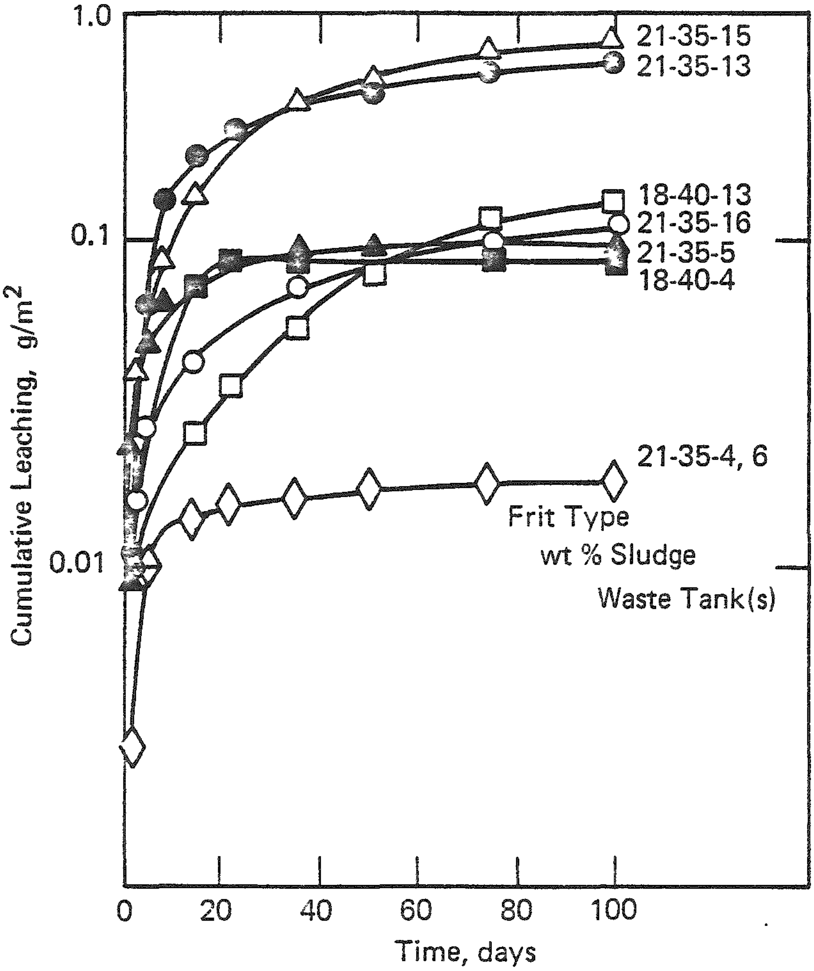

FIGURE 9. Cumulative Leaching of Actual SRP Waste Glass (For Test Details see Reference 32) Based on Pu Analysis

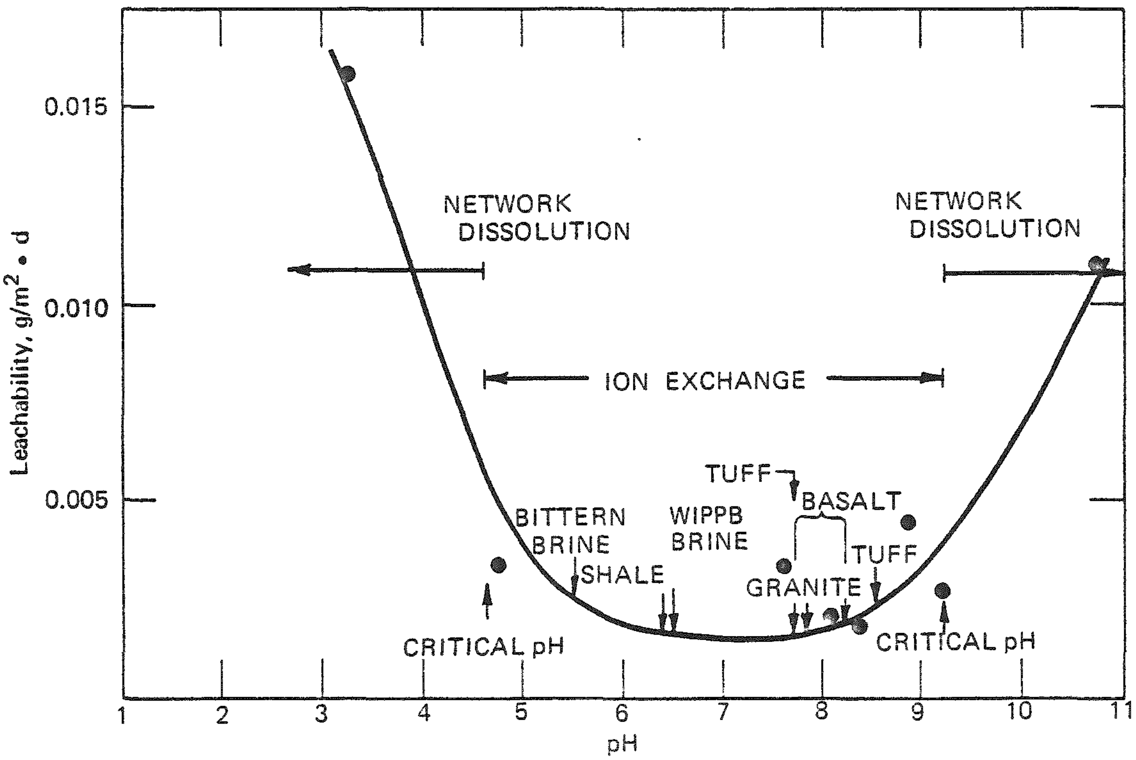

FIGURE 10. Effect of pH on Glass Leachability*

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* Leachability based on Si, 5-day static tests at 23°C. Glass is composite waste glass (Table 8), A/V = 10 cm^{-1}.

TABLE 18

Leachabilities of Composite Waste Glass from Buffered MCC-1 Type Tests*

Leachant Buffered at pH		Leachability (g/m^2-day) Based On							
		Mass Loss	Si	Na	Mn	Fe	Mg	Sr	Cs
3	3	2.21	1.98	2.40	2.43	1.77	1.55	5.89	2.54
7	7	0.17	0.10	0.69	0.51	0.01	0.82	1.07	0.50
11	11	1.60	1.96	3.33	0.05	0.05	ND	0.27	2.42

---

* Tests consisted of 2 samples leached at 90°C for 14 days in buffered solutions.

TABLE 19

Increase of pH During Leaching* in Deionized Water at 90°C

Time (Days)	pH
Before leaching	6.2
3	10.52
7	9.87
14	10.01
28	10.10

---

* Standard (MCC-1) static leach test of composite waste glass (for composition, see Table 8), A/V = $0.1 cm^{-1}$.

This effect was seen by Walker[30,34] and Dukes in leach tests with actual SRP waste glass at room temperature. They compared the leachability in distilled water to those in two types of brine--one with a high content of an acidic cation (Mg) and one with virtually none (Table 20). After 300 days (when steady state was reached) the leachability in the magnesium brine was significantly lower than that in either of the other two (Table 21).

This result has been confirmed in laboratory tests comparing the leaching behavior of composite waste glass in several potential repository ground water simulations (Table 22) to the leaching behavior in deionized water. As Tables 23 and 24 show, the more concentrated leachants simulating a salt repository were as little as one-fifth as aggressive toward the glass than deionized water. None of the simulated ground waters tested attacked the glass more aggressively than deionized water.

However, there may be specific interactions between components of the glass and repository ground waters. In 28-day tests, both Stone[29] and Wicks found such a specific interaction between uranium and the MCC silicate leachant (Table 22). In static leach tests (Table 25) uranium leached much more slowly than silicon or cesium in deionized water or brine. In the MCC silicate leachant, however, the uranium leachability was approximately the same as that of silicon or cesium. As the data in Table 23 show, the leachability in deionized water provides an upper bound to the leachability in repository ground waters of specific glass component.

Effects of Temperature

In a repository the temperature at which leaching of SRP waste glass is expected to occur (after the canister corrodes) will be in the range 25-55°C (Figure 6). Laboratory tests have shown that in this temperature range, initial (28-day) leachabilities are low (0.001-0.1g/m^2-day). As the temperature is increased, initial leachabilities increase as well, but in a complex manner depending on the glass composition and the composition of the leachant.

In 28-day standard (MCC-1) leach tests at 40°C (slightly above ambient in a salt or granite repository), leachabilities of the composite waste glass ranged from 0.001 to 0.1 g/m^2-day, and averaged about 0.03 g/m^2-day (Tables 26-28). Increasing the temperature to 90°C (which represents the maximum glass-water contact temperature in a granite or salt repository) increased the leachability by about 10X. However, even at the peak temperature of 90°C (reached briefly 25 years after emplacement), the leachability is still low. In 28-day tests, leachabilities ranged from 0.05 to 1.0 g/m^2-day and averaged about 0.3 g/m^2-day (Tables 26-28).

TABLE 20

Brine Leachant Compositions

Component	Amount (g/liter of brine)	
	Magnesium Brine	Chloride Brine
$MgCl_2$	213	0.642
$CaCl_2$	132	2.49
NaCl	50	287.
KCl	50	0.028
Na_2SO_4	---	6.2
$Na_2B_4O_7.10H_2O$	---	0.016
$NaHCO_3$	---	0.014
NaBr	---	0.52
$FeCl_3$	---	0.006
$SrCl_2.2H_2O$	---	0.033

---

* After the salts are dissolved the pH is adjusted to 6.5 using dilute HCl or NaOH.

TABLE 21

Effect of Leachant Composition on Leachability of Actual SRP Waste Glass

Leachant*	Type Waste**	Leachability† (g/m^2-day)	
		First Year	Steady State††
Distilled Water	**Tank 13**	4.5×10^{-4}	2.5×10^{-4}
Magnesium Brine	**Tank 13**	4.5×10^{-4}	0.5×10^{-4}
Distilled Water	Tank 16	3.8×10^{-4}	2.1×10^{-4}
Chloride Brine	Tank 16	10.0×10^{-4}	2.9×10^{-4}

---

* Compositions in Table 20.

** Compositions in Table 18.

† Based on Cs-137. Modified ISO room temperature leach test with refreshed leachant. A/V approximately $0.03 cm^{-1}$.

†† Value reached after approximately 300 days.

TABLE 22

Simulated Repository Ground Water Compositions

Component	Granite	Tuff	Shale	Basalt	Salt
$NaHCO_3$	0.0352	0.3304	0.1101	0.0688	1.9276
Na_2SO_4	0.0471		0.2484	0.3178	6.0734
$CaCl_2$	0.3268		10.6278	0.0072	
KNO_3	0.0009		0.0046		
SiO_2	0.08	0.122	0.0038		
CaF_2	0.0148				
NaCl	0.5857		11.78	0.5264	206.094
$MgCl_2$	0.0029		0.329		274.155
$FeCl_2$	0.0001		0.0002		
SrF_2		0.001			
$Ba(NO_3)_2$		0.0001			
$MgSO_4$		0.0208		0.0013	
LiCl		0.0006			0.2444
Na_3PO_4		0.0004	0.0002		
$Al(NO_3)_3$		0.0005			
$FeSO_4$		0.0002			
KF	0.0007	0.0149	0.0037	0.0059	
$NaNO_3$		0.0148			
$CaSO_4$		0.0389			4.0761
$CaCl_2$		0.0459			

TABLE 22 Continued

Component	Granite	Tuff	Shale	Basalt	Salt
$MnCl_2$			0.0334		
NaF				0.1593	
NaH_3SiO_4				0.3601	
NaOH				0.0471	
Na_2CO_3				0.0742	
RbCl					0.0566
NaI					0.0236
NaBr					1.0302
Cs_2SO_4					0.0027
$SrSO_4$					0.0155
$Fe_2(SO_4)_3$					0.0143
KCl					114.374
H_3BO_3					2.5224
(pH)	(7.8)		(6.4)	(7.7-8.2)	(6.5)

MCC Brine Leachant: 4.82g KCl, 90.0g NaCl & 116.0g $MgCl_2$; pH adjusted to 6.5.

MCC Silicate Leachant: 0.179g $NaHCO_3$, 0.058g SiO_3; pH adjusted to 7.5.

TABLE 23

Effect of Leachant Composition on Leachability of Composite Waste Glass*

Leachant	Leachability** (g/m^2-day)
Deionized Water	1.52
Simulated Salt	0.32
MCC Brine	0.34
MCC Silicate	0.75
Simulated Shale	0.96
Simulated Granite	1.00
Simulated Tuff	1.20
Simulated Basalt	1.34

---

* Composition in Table 8.

** Based on Si. Static leach test (MCC-1 type) in 90°C leachant for 7 days, A/V = 0.1 cm^{-1}.

TABLE 24

Leachability in Various Media of Composite Waste Glass

	Leachability* (g/m^2-day)		
Element	Deionized Water	Silicate Water	Brine
Si	0.55	0.21	0.21
B	0.79	0.38	0.31
Cs	1.39	0.83	0.24
Fe	0.007	0.05	0.01

---

* MCC-1 leach tests - 28 days at 90°C.

TABLE 25

Effect of Leachant Composition* on Leaching of Composite Waste Glass

Leachant	Leachability** (g/m^2-day) Based On U	Si	Cs
Deionized Water	0.13	0.96	0.58
MCC Silicate	0.44	0.56	0.49
MCC Brine	<0.019	0.32	0.35

---

* For compositions, see Table 22.

** MCC-1 standard static leach test, 90°C, 28 days, $A/V = 0.1\ cm^{-1}$.

TABLE 26

Effect of Temperature on Leaching of Composite Waste Glass in Deionized Water

Temperature (°C)	Leachability* (g/m^2-day) Based On Mass Loss	Si	Cs	Sr	U
40	0.07	0.05	0.14	ND**	0.018
90	0.63	0.96	0.58	ND	0.13
150	3.11	4.28	1.30	ND	0.24

---

* Standard (MCC-1 or MCC-2) static leach tests, 28 days at temperature, $A/V = 0.1 cm^{-1}$.

** ND = none detected.

TABLE 27

Effect of Temperature on Leaching of Composite Waste Glass in MCC Brine Leachant

	Leachability* (g/m^2-day) Based On				
Temperature (°C)	Mass Loss	Si	Cs	Sr	U
40	0.01	0.007	0.041	ND**	ND
90	0.10	0.32	0.35	ND	ND
150	0.55	1.41	2.65	2.60	ND

---

* Standard (MCC-1 or MCC-2) static leach tests, 28 days at temperature, A/V = 0.1 cm^{-1}.

** ND = none detected.

TABLE 28

Effect of Temperature on Leaching of Composite Waste Glass in MCC Silicate Leachant

	Leachability* (g/m^2-day) Based On				
Temperature (°C)	Mass Loss	Si	Cs	Sr	U
40	0.01	0.040	0.081	ND**	0.018
90	0.30	0.56	0.49	ND	0.44
150	2.31	2.96	1.71	0.006	0.38

---

* Standard (MCC-1 or MCC-2) static leach tests, 28 days at temperature, A/V = 0.1 cm^{-1}.

** ND = none detect.

Leaching tests have also been performed at a higher temperature (150°C). These tests have shown that although the leachability increases to a range of 0.5 to 10 g/m^2-day, the integrity of the waste glass would not be severely compromised by ground water attack at this high temperature.

As the data indicate, the effect of temperature on leachability varies for each element. In general, the leachability increases with temperature, but as the uranium leachability data in Table 28 show, this is not always the case. In addition, the specific glass composition involved may respond differently to increases in temperature. For example, Stone[35] found that the SRP high aluminum simulated waste glass was much more sensitive to temperature than the composite or high iron waste glass (Table 29).

Effects of Pressure

In the repository environment SRP waste glass will be leached under lithostatic and/or hydrostatic pressures. According to the Reference Repository Conditions Interface Working Group, the maximum pressure after emplacement of the canister in the hold would be less than 7 MPa (70 atmospheres).[13] Leaching tests at 10 MPa (102 atmospheres) and 90°C have shown that pressure does not accelerate leaching, but appears to cause a reduction in leachability (Table 30). Wicks, et al., also found that the surface layer formed at high pressure was less cracked and more adherent to the glass surface than that formed at low pressure.[36] Thus, pressure will not degrade the performance of SRP waste glass in the repository environment and may actually reduce the leachability.

Effects of Leachant Flow

It is unlikely that SRP waste glass will be leached under completely static conditions. In most potential geologic repositories (in particular granite, tuff, basalt and shale) ground water will fill the void volume of the canister emplacement holes, reach a steady state with respect to the ground water hydraulic gradient, and then slowly move through the rock mass.[25] Leach tests performed under dynamic conditions indicate that expected ground water flow rates will not significantly increase the leachability of SRP waste glass. The sensitivity of the leachability of individual species to flow rate appears to be related to their role in the surface layer formed during leaching.

Recently, the Materials Characterization Center measured the leach rates of SRP composite waste glass in dynamic tests with flow rates of 2, 15 and 143 ml/day. Since 40 ml of solution were used, these flow rates corresponded to flush times of 20, 2.7 and

TABLE 29

Sensitivity of the Leachability of SRP Waste Glass Compositions to Temperature

Glass*	Temperature (°C)	Leachability** (g/m^2-day) Based On U	Cs
Composite	40	0.011	0.055
	90	0.055	0.15
High Aluminum	40	0.001	0.006
	90	0.040	0.54
High Iron	40	0.017	0.50
	90	0.084	3.24

---

* Compositions in Table 8.

** MCC-1 static leach tests.

TABLE 30

Effect of Pressure on Leachability of Composite Waste Glass

Pressure, MPa	Leachability* (g/m^2-day) Silicon	Sodium
0.1	0.75	1.26
	0.77	1.30
10.	0.45	0.68
	0.44	0.63

---

* Tests run 30 days at 90°C.
(Surface area/leachant volume) = 0.1 cm^{-1}.
Leachant is ultra-pure water.

0.14 days. As shown in the section on expected repository conditions, flush times (in granite) over an individual canister are expected to be on the order of 500 years or less than 1.4 ml/day. Thus, static tests and the 2 ml/day tests should bracket expected repository flow rates. The cumulative amount leached* in static tests and at 2 ml/day flowing tests at 90°C for several species are shown in Table 31. For all elements tested (except Sr), the amount leached at 2 ml/day is less than twice as much that leached in a static test. If the leachability varies linearly with flush time, then the leachability in a granite repository would be <<1% higher than the static leachability.

The complete set of data is shown graphically in Figure 11. As the figure shows, the species analyzed fall into three groups, based on their sensitivity to leachant flow rate.

Group 1: Sr, Ca

The leach rates of strontium and calcium from SRP waste glass show the largest changes with leachant flow rate. The amount of calcium or strontium leached after 28 days at 150 ml/day is at least 250 times greater than that leached in static leach tests. Under low or no flow conditions, both strontium and calcium are much less leachable (approximately 20X) than other species. Under high flow conditions, their leachability is still only half that of Group 3 elements. These species are usually found to be enriched (relative to the bulk glass) in the surface layers formed during leaching of SRP waste glass.[26]

Group 2: U

The amount of uranium leached is relatively insensitive to flow rate. It remains roughly constant at all flow rates. Its role in the surface layer of leached glass has not yet been determined, but it is believed to concentrate in the leached layer as well.

Group 3: Si, B, Al, Cs, Na, Li

The leach rates of these species vary only slightly with flow rate (approximately 4X). For all flow rates, more of these elements are leached than Group 1 or 2. These elements are not enriched (and are often depleted) in the surface layer of leached SRP waste glass.[26]

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* Product of leachability times the duration of the test.

TABLE 31

Effect of Flow Rate on Amount Leached from Composite Waste Glass

Species	Cumulative Leaching (g/m^2) in 28 Days Flow Rate = 0 ml/day*	2.0 ml/day**
Si	17.6	28.6
B	40.0	57.2
Al	7.3	9.0
Cs	16.2	23.8
Na	37.5	59.2
Li	25.9	59.6
U	3.6	0.8
Ca	0.02	0.1
Sr	<0.01	0.1

---

* MCC-1 static test, 90°C, A/V = 0.1 cm^{-1}.

** MCC-4 dynamic test, 90°C, A/V = 0.1 cm^{-1}.

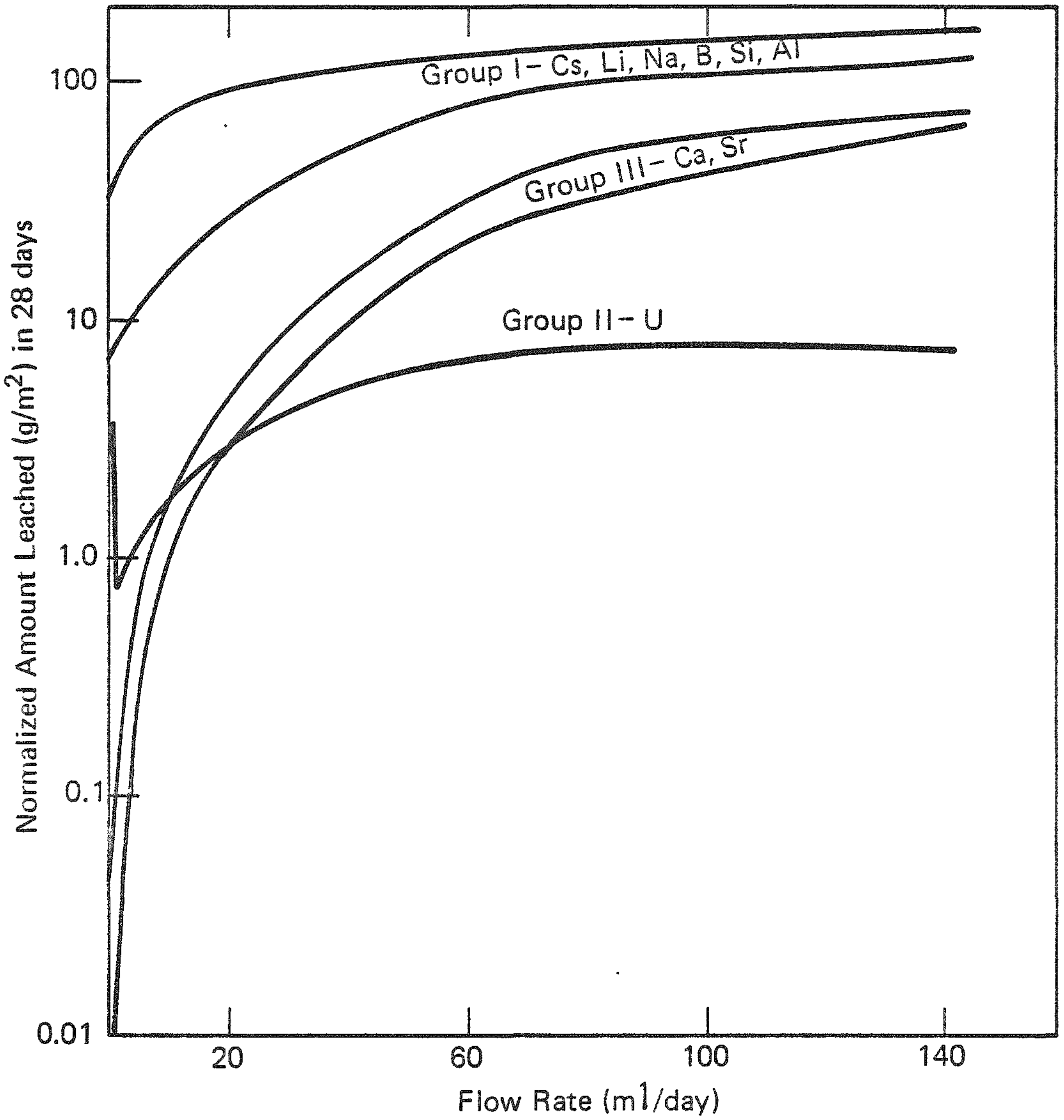

FIGURE 11. Effect of Leachant Flow Rate on Cumulative Cumulative Leaching of Composite Waste Glass. Tests at 90°C in Deionized Water, A/V = 0.1 cm^{-1}

Time Dependence of Leachability

The leachability of SRP waste glass generally decreases as the time of exposure to aqueous attack increases. Realistic assessments of the performance of SRP waste glass in the repository environment must explicitly take into account this time dependence of the leachability. At temperatures in the range of those expected for leaching of SRP waste glass in a repository (25-55°C) steady state leachabilities approach 10^{-4} g/m^2-day. At these temperatures, leachabilities fall sharply from initial values of 10^{-1}-10^{-3} g/m^2-day, then gradually approach steady state values. If the waste package fails prematurely (i.e. within 25 years), so that leaching occurs at 90°C (the maximum temperature the surface of an SRP waste glass canister will reach in a repository) initial leachabilities are approximately 10X higher. Tests are now in progress to define steady-state values under these conditions.

Kelley[7] and Wiley[8,31] both studied the leachability of glasses containing actual SRP waste as a function of time, at room temperature. Kelley measured first day leachabilities of 0.01-0.5 g/m^2-day, falling by 5-200X after 1 week. After 100 days, the leachability was decreasing more slowly, since the leachability at 100 days was only 1/2-1/5 than at 7 days. Wiley observed the same general trend,[8] and found excellent agreement between the data from 7-100 days and a diffusional model, which predicted that the fraction leached would increase as $t^{0.5}$. Both sets of tests were done in distilled water.

Wiley, Walker[30] and Dukes[37,38] extended Wiley's earlier studies to longer times and other leachants. In distilled water and simulated brines, they found that steady state leachabilities (here, steady state means time independent, i.e., constant) were reached after 100-300 days. Steady state leachabilities ranged from 2 to 5 x 10^{-4} g/m^2-day for Cs, Sr, and Pu. From 100 days until steady state was reached, the fraction leached increased by $t^{0.3}$, rather than $t^{0.5}$. Their data are shown in Tables 21 and 32.

If the waste package, in particular the glass canister, were to fail prematurely SRP waste glass might be leached at temperatures as high as 90°C (Figure 6). Although long term data are not yet available, tests have been conducted out to 90 days at this temperature. These tests indicate that the leachability of SRP waste glass has roughly the same time dependence at 90°C as at expected repository leaching temperatures (25-55°C) but is generally about 10 times higher.

In short term tests (up to 25 hours), Bibler, and Clark,[27] showed that the fraction of composite waste glass leached (based on Si and B) was approximately linear in time for the first day of leaching at 90°C. For the first week (days 1-7) the fraction

TABLE 32

Long-Term Leaching Experiments in Distilled Water

Waste	Radionuclide(s)	Leachability* (g/m^2-day)	
		First Year	Steady State**
Tank 13	Cs-137	4.5 X 10^{-4}	2.5 X 10^{-4}
	Sr-90	4.1 X 101^{-4}	2.6 X 10^{-4}
	Pu	5.5 X 10^{-4}	4.6 X 10^{-4}
Tank 16	Cs-137	3.8 X 10^{-4}	2.1 x 10^{-4}
	Sr-90	2.7 X 10^{-4}	1.8 X 10^{-4}
	Pu	2.6 X 10^{-4}	2.2 X 10^{-4}

---

* Room temperature, A/V approximately 0.1 cm^{-1}

** Value reached after approximately 300 days leached increased more slowly ($t^{0.5}$). From 7-91 days Bibler found that the fraction leached increased still more slowly (approximately as $t^{0.2}$). Thus, the same general trend as at lower temperatures was observed. Wicks currently has a series of tests underway at both 40°C and 90°C, which will last for several years. These tests should help clarify both the rate of approach to, and the value of, the steady state leachability as a function of temperature. Results from 3 to 91 days indicate the fraction leached (based on Si) is increasing slightly slower than $t^{0.3}$ at both 40°C and 90°C, and that steady state has still not been reached.

Interactions with the Repository System

In the repository environment SRP waste glass will be leached in the presence of repository minerals and potential multibarrier components. Extensive tests of the interactions between SRP waste glass and other possible components of a repository system demonstrate that SRP waste glass is compatible with current repository concepts. In general, the leachability decreases slightly in the presence of potential repository minerals. Potential canister (304L stainless steel) or overpack (Ticode 12) materials have little effect on the leachability. Potential backfill materials have the largest interactions with SRP waste glass, and materials have been identified which have beneficial effects on glass leaching.

Wicks has extensively tested the compatibility of SRP waste glass with potential repository materials. He first compared the amounts of several glass components extracted from composite waste glass in deionized water in the presence and absence of potential repository minerals. As Table 33 shows, at all values of glass surface area to solution volume tested, the amount of each component extracted from the glass in the presence of repository minerals was the same as or less than that extracted from the glass when leached by itself. When the tests were repeated with the simulated ground waters of Table 22 as leachants, the amount leached in the presence of the appropriate rock type either remained the same or decreased. In all cases the amount extracted was less than that in deionized water in the absence of repository minerals (Table 34).

Wicks also examined the interactions between potential canister/overpack materials or potential backfill materials and SRP composite waste glass. Canister materials will be selected primarily for compatibility with waste processing. However, since they will be present in the repository environment, their effects on glass leaching must be determined. As Table 35 shows the canister/overpack materials tested (304L stainless steel and

TABLE 33

Effect of Repository Minerals on Leaching* of Composite Waste Glass

		Leachability** (g/m^2-day)					
Component	A/V (cm^{-1})	Glass Only	Glass + Salt	Glass + Basalt	Glass + Granite	Glass + Shale	Glass + Tuff
Si	0.5	0.77	0.28	0.62	0.76	0.57	0.61
	0.1	1.83	0.85	1.42	1.79	1.71	1.66
	0.03	2.62	2.43	1.92	2.54	2.64	2.25
Cs	0.5	0.82	0.56	0.16	0.64	0.10	0.14
	0.1	1.64	1.30	ND	0.96	ND	ND
	0.03	ND	3.20	ND	1.32	ND	ND
Sr	0.5	0.03	1.20	0.03	0.02	ND	0.04
	0.1	0.38	ND	0.15	0.38	ND	0.15
	0.03	5.01	ND	0.25	4.51	1.00	0.50

---

* Modified MCC-1 test, 90°C for 7 days in deionized water.

** Corrected for component release of repository mineral by subtracting concentration of component released by rock when leached alone, from concentration released from rock containing system.

TABLE 34

Effects of Potential Repository Minerals on Leaching* of Composite Waste Glass in Simulated Ground Waters

Leachant†	Leachability** Based on Si (g/m^2-day) Repository Minerals Absent	 Repository Minerals Present
Deionized Water	1.52	---
Basalt	1.34	1.02
Granite	1.00	0.80
Shale	0.96	1.06
Tuff	1.20	1.01
Salt	0.32	0.14
MCC Brine	0.34	0.40††
MCC Silicate	0.75	0.45¶

---

* Modified MCC-1 static test, 90°C for 7 days (A/V) glass = ~1; (A/V) rock = 0.1 cm^{-1}, glass composition in Table 8.

** Corrected for rock leaching as in Table 33.

† Composition of leachants in Table 22.

†† Salt from Waste Isolation Pilot Plant (WIPP) used as mineral.

¶ Basalt from Basalt Waste Isolation Program (BWIP) used as mineral.

TABLE 35

Effects of Potential Canister/Overpack and Backfill Materials on Leaching* of Composite Waste Glass

Canister Material	Backfill	Leachability Based on Cs (g/m^2-day)
--	--	1.73
304L	--	1.54
Ticode 12	--	1.43
--	BF1**	0.49
--	BF2**	0.17
--	BF3**	0.73
--	Clinoptilolite	0.21
--	A-51†	0.68
--	IE-95††	0.08

---

* Modified MCC-1 brine leachant. Seven days at 90°C system.

** BF1 = 30% bentonite, 20% cocoanut charcoal, 50% sand;
BF2 = bentonite from Sandia National Lab;
BF3 = bentonite from SRL.

† Linde® A-51 zeolite.

†† Linde® Ion-Siv IE-95 zeolite.

Ticode 12) had little effect on the amount of material leached from the glass. On the other hand, potential backfill materials significantly altered the amount of cesium extracted. However, beneficial materials (ones which reduced the amount of radionuclides such as Cs extracted from the glass) were identified, again showing the compatibility of SRP waste glass with current repository concepts.

THERMAL STABILITY OF WASTE GLASS

SRP waste glass will undergo two types of thermal stress which might affect its performance in the repository environment: self-heating and cooling after melting. Calculations have shown that the heat generation rate of SRP waste glass is negligible and will not affect product performance. Large- and small-scale experiments have shown that normal cooling after melting is rapid enough to prevent devitrification of the glass but causes the glass to fracture, increasing the surface area. This increase in surface area will increase the fractional release rate from a full scale form by approximately a factor of five (compared to a monolithic glass form), under expected repository conditions.

In the very unlikely event of a high temperature excursion (such as a fire), the glass will only devitrify if the temperature is maintained over 500°C for extended periods of time. Since little devitrification will occur, it will not significantly effect the performance of SRP waste glass in the repository environment.

Self-Heating Effects

Calculations performed by members of the Reference Repository Conditions Interface Working Group[12] (set up by the Office of Nuclear Waste Isolation) have shown that SRP waste glass (either Stage 1 or Stage 2) emplaced in a granite or salt repository reaches a maximum centerline temperature of 90-100°C within twenty-five years after emplacement, then slowly decays (Figures 5 and 12). After 100 years, the glass centerline temperature is 55-70°C. At these temperatures, the rates of processes such as devitrification (glass crystallization) are insignificant.[39] Even at 200°C, Macedo[39] has shown that the time required for significant crystallization of waste glass exceeds the expected life of the solar system (5×10^9 years). Thus, self-heating should not cause devitrification of SRP waste glass in a repository environment.

Calculations[5,40] show that the maximum steady state temperature difference from the center to the outside of a waste glass

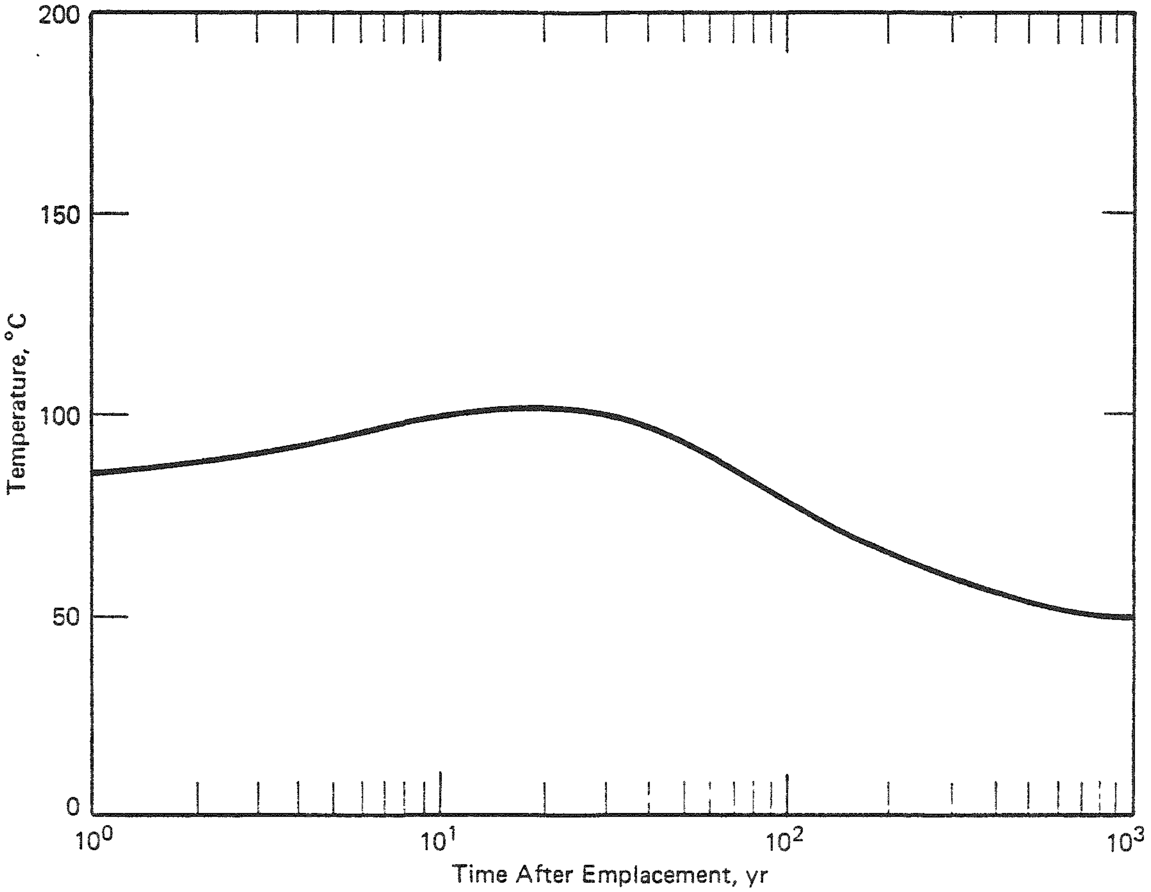

FIGURE 12. Centerline Temperatures of Stage 2 Glass Canister in a Salt Repository

form is 13°C, immediately after processing. Using the equation[41]

$$(\Delta T)_{\text{max.}} = \frac{P(1-S)}{E}$$

where $(\Delta T)_{\text{max.}}$ is the maximum temperature difference the glass can withstand without cracking, P is the tensile strength, E is Young's modulus and S is Poisson's ratio, and the values for these parameters in Table 9, the glass can withstand a maximum temperature difference of 65°C without fracture. Thus, self-heating will not increase the degree of fracture of the waste form.

Effects of Cooling After Melting

SRP waste will be vitrified in a joule-heated melter at 1150°C and then poured into 0.61 m diameter by 3 m long stainless steel canisters.[5] Typical temperature profiles of the glass as a function of position in the canister during filling and subsequent cooling are shown in Figures 13-16. If the glass cools too rapidly, it may crack due to excessive thermal gradients[42,43] which increase the glass surface area. If the glass cools too slowly, second phases may form (liquid-liquid phase separation or devitrification) which reduce the durability of the glass product.

Fracturing during cooling of large glass waste forms during production increases the surface area available for leaching. Acoustic emission and visual analyses have shown that cracking in SRP waste glass begins when the glass has cooled to its softening point, and continues until the glass reaches ambient conditions.[42,43] Experiments have shown that glass fracture can be reduced by:

- Slowly cooling the glass form through the annealing range
- Matching coefficients of expansion of the glass and the canister (use of carbon steel, titanium, or ceramic, as primary canisters or as liners for canisters)
- Use of crushable liners (e.g., aluminosilicate papers)
- Use of liners which allow the glass to slip along the canister wall (e.g., graphite).

The relative increase in surface area observed for canisters of glass filled at rates matching those in Figures 13-16 is a factor of about twenty-five times the area of a similar unfractured glass form. In the repository environment, this increased surface

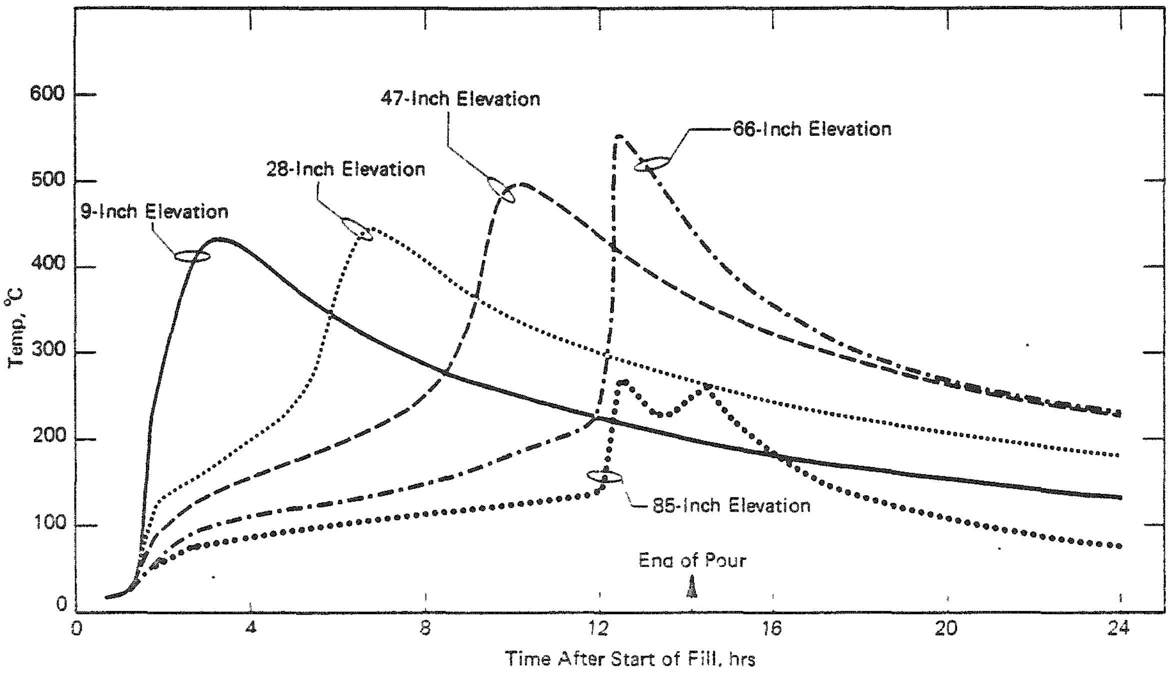

FIGURE 13. Surface Temperature Profiles of Composite Waste Glass Form During Canister Filling

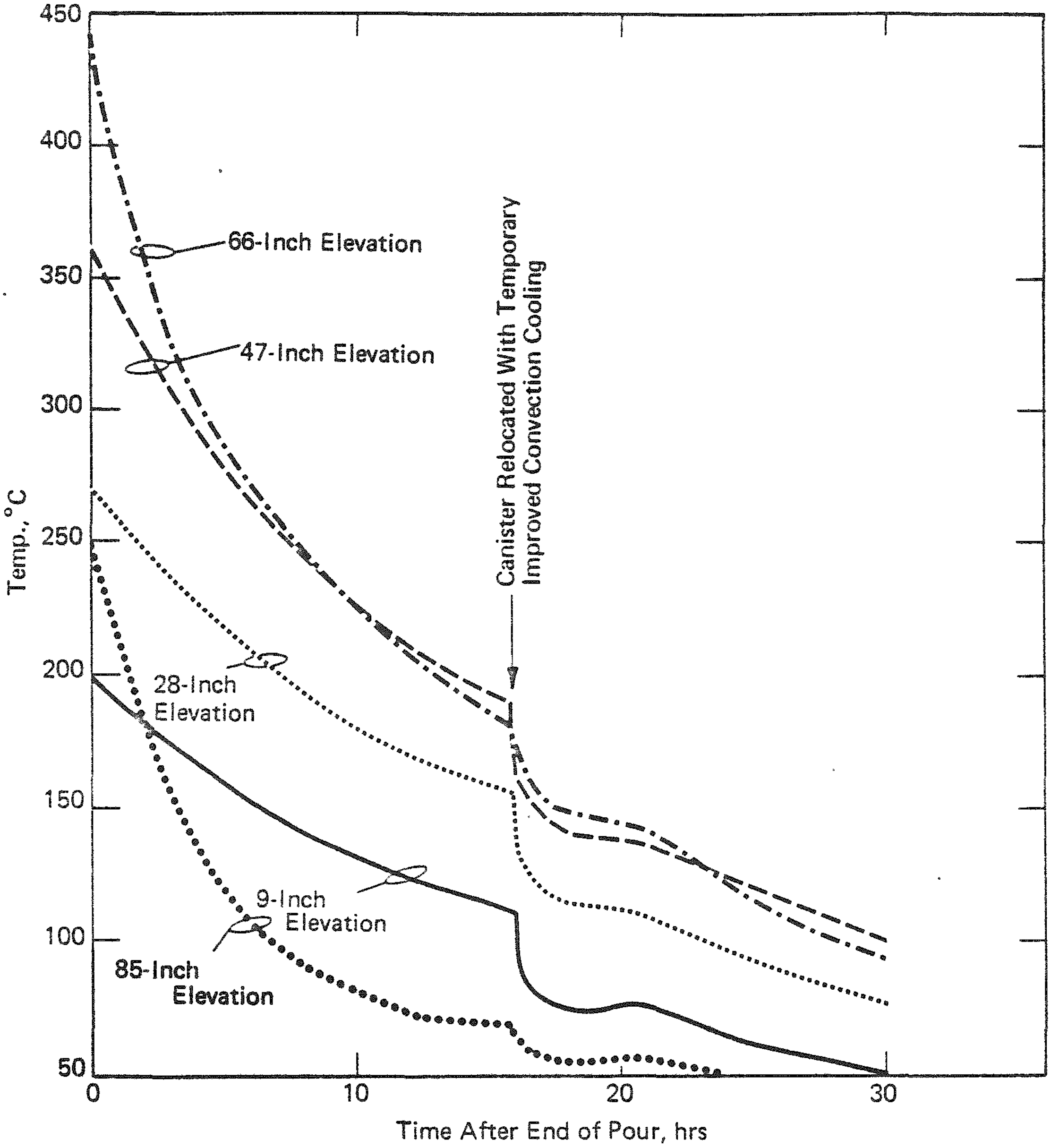

FIGURE 14. Surface Temperature Profiles of Composite Waste Glass Form During Cooling of Canister

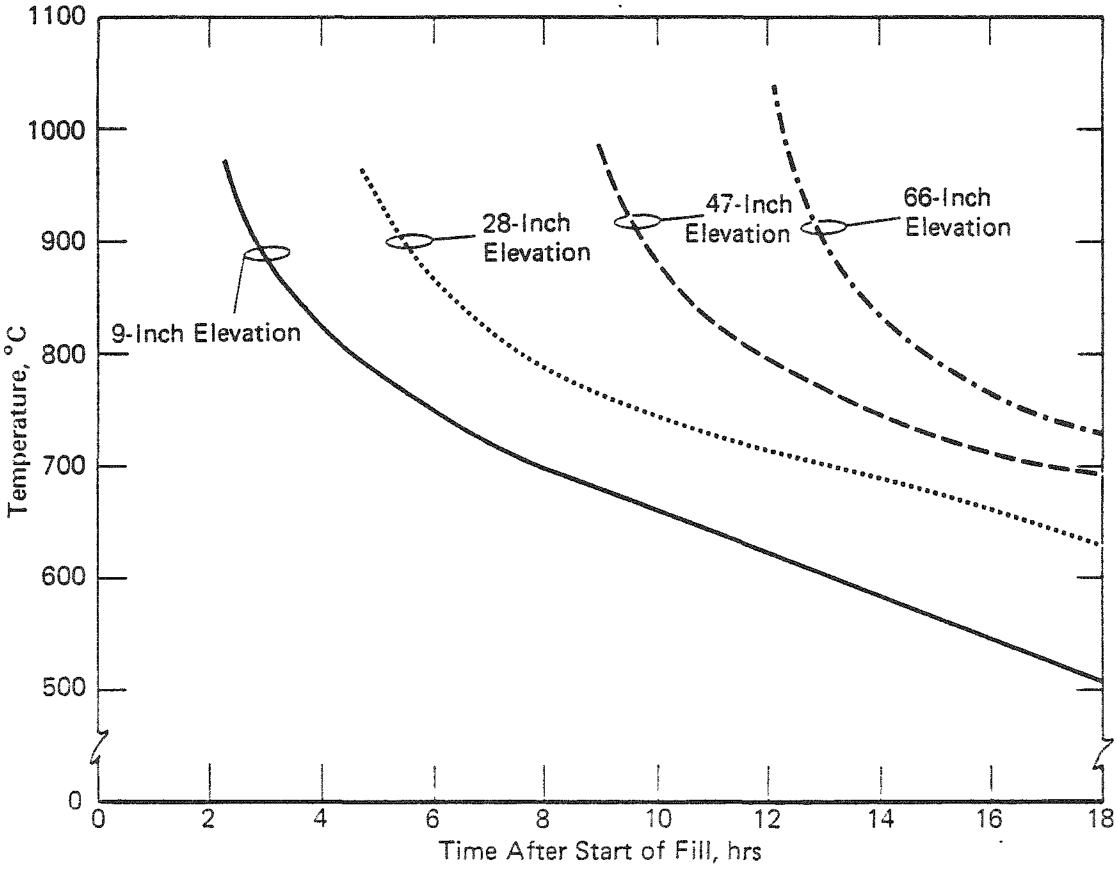

FIGURE 15. Centerline Temperature Profiles of Composite Waste Glass Form During Canister Filling

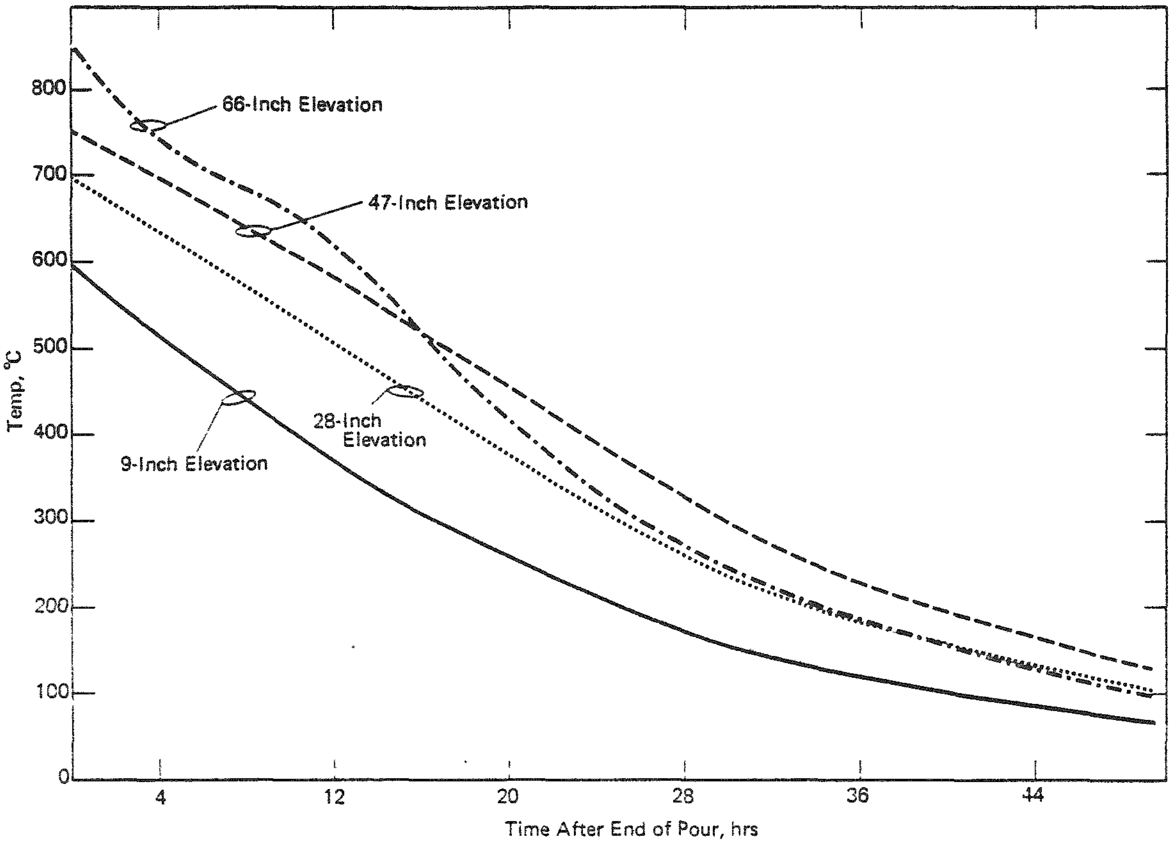

FIGURE 16. Centerline Temperature Profiles of Composite Waste Glass Form During Cooling After Canister Filling

area will also increase A/V, the ratio of glass surface area to leachant volume. As Table 33 shows, the leachability decreases by a factor of approximately 2.2 for a five-fold increase in A/V. Thus, the fraction of radionuclides released from the waste form will not increase proportionally with the increase in surface area, but more slowly due to this reduction in leachability.

As shown earlier, the fraction leached, F, is given by

$$F = L\left(\frac{A}{M_T}\right)t$$

Let F_u be the fraction of an unfractured glass sample leached in t days, and F_b be the same for a fractured glass sample. If the fractured sample has the same mass as the unfractured sample, but 25 times the surface area (i.e. $A_b = 25A_u$),

$$F_b = L_b\left(\frac{A_b}{M_T}\right)t = L_b\left(\frac{25A_u}{M_T}\right)t$$

In the nearly static repository environment, the A/V ratio is proportional to the glass surface area (since the volume is essentially fixed). As noted earlier, the leachability decreases by a factor of 2.2 for an increase in A/V of a factor of 5. Thus, if the surface area increases by 25X due to fracture, A/V will also increase by 25X, and the leachability will decrease by about a factor of 5, i.e.

$$L_b = \frac{L_u}{5}$$

Substituting this value of L_b into the previous equation yields

$$F_b = \left(\frac{L_u}{5}\right)\left(\frac{25A_u}{M_T}\right)t = 5\ L_u\ \left(\frac{A_u}{M_T}\right)t = 5\ F_u$$

Thus, if the surface area increases by a factor of 25, the preceding implies that the fraction of radionuclides leached from the glass will increase by only about a factor of five.

Formation of second phases during cooling of glass canisters might reduce the durability of the glass product. Robnett and Wicks[44] subjected laboratory glass specimens to the most severe cooling schedules expected in full-scale glass forms, similar to those in Figures 15 and 16. They found no changes in leach rate. Tomozawa (personal communication) specifically sought liquid-liquid phase separation and found no evidence of it. He also found no

TABLE 36

Effect of Normal Cooling on Leach Rate of Simulated Waste Glasses

Glass*	Heat Treatment**	7-Day Leachability† (g/m^2-d) Based on Na	Si	B	Al
High Iron	Quenched	5.1	3.8	5.1	††
	Normal Cooling	4.8	3.9	5.9	††
Composite	Quenched	2.9	2.3	††	2.3
	Normal Cooling	2.6	2.3	††	2.3
High Aluminum	Quenched	1.2	1.0	††	1.1
	Normal Cooling	1.0	1.0	††	0.95

---

* Compositions given in Table 8.

** Quenched samples were formed at 1150°C and poured into heated (200°C) graphite molds, then annealed at 400°C. Normal-cooled samples were furnace-cooled at a rate simulating that shown in Figures 16 and 17, for the centerline of a canister of glass.

† MCC-1 static leach test at 90°C in deionized water, A/V = $0.1 cm^{-1}$.

†† Below detection limits.

changes in the leachabilities of simulated waste glasses cooled at a rate simulating centerline cooling of a full-size canister (Table 36). In large-scale tests it was shown that no crystalline material formed in full-size simulated waste glass forms cooled by natural convection.[45,46] Thus, formation of second phases which might occur during normal cooling will have no effect on glass durability and can be ignored in predicting the performance of glass in a repository.

Effects of Unlikely High Temperature Events

High temperature events (such as fires) could cause volatilization, expansion, or devitrification of the glass. Only devitrification could significantly alter glass performance in a repository, and the probability of a high temperature event of sufficient duration to cause devitrification is very low.

Volatility depends on the temperature, the composition of the atmosphere above the glass, and the composition of the glass. SRL has not performed a comprehensive study at intermediate temperatures (<900°C), but at 900°C only 19 mg/hr of volatiles would be released from a canister of SRP waste glass.[47] Since volatility varies exponentially with temperature, at lower temperatures the amount released would be negligible. Similarly, volume changes associated with expansion (alpha = $1.1 \times 10^{-5}\,{}^{\circ}C^{-1}$) would be so small (<1%) that any stress generated in the canister would be negligible.

In recent experiments at SRL, devitrification was investigated by heating various waste glass compositions for one day at temperatures 500 to 900°C. Crystalline phases were identified by x-ray diffraction and SEM microprobe. The amount was quantified by comparing sample x-ray peak heights to those of standards (Table 37). Acmite ($NaFeSiO_4$) and spinels (e.g., $NiFe_2O_4$) were the main crystalline products formed in this temperature range. At 500°C, no crystalline material was found even after a one week heating period. Samples were also heated for 1 week at 550°C and 600°C to examine devitrification in more detail. Under these conditions, a small amount of Li_2SiO_3 also formed. For a waste glass composition high in aluminum, a small quantity of nepheline ($NaAlSiO_4$) was also observed. The formation of the silicate phases increased the leachability (based on Na, Si, Cs, and Sr) but only to about 2-4 g/m^2-day from 0.2-0.8 g/m^2-day for undevitrified glass.* The nonappearance of crystallinity in the samples held at 500°C indicates that severe high temperature events are necessary to cause devitrification.[44]

---

* Leachabilities were measured for glass grains, -40+60 mesh, 30 days at 90°C, A/V = 10 cm^{-1}.

TABLE 37

Crystalline Phases Produced by Heat Treatments of Composite Waste Glass

Temperature, °C Heated One Day	Crystalline Phases Formed
500	None
550	19% Acmite
600	46% Acmite
650	48% Acmite
800	38% Acmite, 14% Spinel
900	27% Spinel
Heated One Week	
500	None
550	54% Acmite, 8% Li_2SiO_3
600	44% Acmite, 6% Li_2SiO_3

This conclusion is substantiated by more detailed microstructural and kinetic studies of SRP simulated waste glasses at Battelle-PNL.[48,49] These studies showed that in the temperature range 500-1000°C, isothermal treatments would have to last at least (in the worst case) four hours before detectable (approximately 1% by x-ray diffraction) crystallization would occur. At most temperatures within this range longer treatments were required to force devitrification to occur.

In tests with glasses containing actual SRP waste, Kelley found that for some waste compositions even one month at 600°C did not induce crystallization.[7,50] Plodinec later showed that waste components such as uranium and nickel greatly reduced the tendency of the glass to devitrify at temperatures less than 850°C.[8] Even in cases where devitrification was forced to occur Kelley found that radionuclide release was not uniformly affected (Table 38). In fact, the leach rate based on alpha-emitting nuclides (actinides) was not affected by devitrification at all. Thus, since high temperature excursions are very unlikely to occur in the repository environment, and since, with actual waste they have little or no affect on the release rate of long-lived alpha-emitting radionuclides, these postulated events will not affect the performance of waste glass in a repository environment.

MECHANICAL STABILITY OF GLASS

The ability to withstand mechanical stresses is a desirable characteristic for waste glass since it limits the effects of impacts or other mechanical events on glass product performance. Upon impact, a fragile waste form could produce fine particles which could be easily dispersed in fluid phases. Although mechanical stability is primarily of importance during transportation to a repository, it will determine the ability of the glass to withstand the increased pressures possible in a repository.

Recently the impact resistance of composite waste glass was measured by Jardine of Argonne National Laboratory.[51] For an impact energy density of 10 joules/cm^3, 0.14 wt % respirable fines (<10 m diameter) were generated. Tests on full-scale canisters have also shown that damage due to impacts would be confined to the region in the immediate vicinity of the point of impact. Thus, the actual fraction of fines generated by an impact event would be much less than that measured in the laboratory even though the latter used a much less sophisticated apparatus. As shown in Table 39, for comparable impacts the predicted fraction of respirable fines produced is the same. For comparison, results on Pyrex (by Jardine[51]) are also included. The data shows that composite waste glass has about the same resistance to impacts (in terms of fine particle generation) as this very common commercial glass.

TABLE 38

Effect of Devitrification on Radionuclide Leaching of Tank 13 Waste Glass*

Radionuclide	Heat Treatment	Fraction Leached**
Gross Alpha (Actinide)	None	1.0×10^{-5}
	One month at 500°C	4.0×10^{-6}
	One month at 600°C	1.8×10^{-5}
^{90}Sr	None	3.5×10^{-5}
	One month at 500°C	4.3×10^{-4}
	One month at 600°C	2.9×10^{-4}

---

* Glass leached in distilled water at 25°C, A/V approximately 0.05. Leachant changed periodically. Glass contained 40 wt % Tank 13 waste (composition of waste is in Table 17).

** Glasses not heat-treated were leached 100 days. Heat-treated glasses were leached 84 days.

TABLE 39

Respirable Fines Produced in Impact Tests

Glass	Impact Energy (J/cm^3)	Respirable Fines (Wt %)
Composite Waste Glass[51]	10 5	0.16 0.087
Frit 18 Waste Glass[52]	5.9	0.12
Pyrex[51]	10 5	0.27 0.11

Kelley also measured the compressive strength of simulated waste glasses.[5] He found that the strength did not seem to depend on the glass composition. This is not unexpected, since compressive stengths of industrial glasses are not very composition-dependent.[53] Since hydrostatic or lithostatic pressures in a repository will be less than 10 MPa, SRP waste glass will be able to withstand these compressive forces without fracture.

RADIATION STABILITY OF GLASS

During long-term storage (10^6 years), the glass waste form will receive a dose of 5 X 10^{10} rads from beta-gamma radiation and 10^{18} alphas/g glass. An extensive experimental program has conclusively shown that radiation will not significantly affect the performance of SRP waste glass in the repository environment.

Density

Radiation-induced density changes have been studied because of their potential effects on the mechanical integrity of the waste-glass or the canister. In several tests at SRL,[54,55] alpha radiation has caused the density to decrease by only about 1%, at doses equivalent to those the glass will receive in $>10^6$ years. This volume increase is not sufficient to cause appreciable canister strain and does not cause fracture of the glass. Gamma radiation has not caused observable density changes in SRP waste-glass, even at doses in excess of those the glass will receive in 10^6 years.

A sample of composite waste glass has been doped with 2 wt % ^{244}Cm. At a total dose of 10^{18} alphas/g (simulating $>10^6$ years storage of actual SRP waste glass), the density has decreased by 1.0% (glass is expanding).[54] The dose response is similar to that predicted from earlier results.[55] The change in density with total alpha dose is shown graphically in Figure 17. Comparing these results to Figure 18, the expansion due to alpha radiation is too small to affect the canister during its expected lifetime (100-1000 years). The higher dose the glass will receive after 10^6 years will cause expansion of the glass, but Bibler and Kelley[54] showed that no fracture would result, even at these high doses.

A sample of composite waste glass was irradiated in the SRL ^{60}Co Irradiation Facility to a dose of 8 X 10^{10} rads ($>10^6$ years storage). There was no change in density.[53] This test and the previous one are summarized in Table 40.

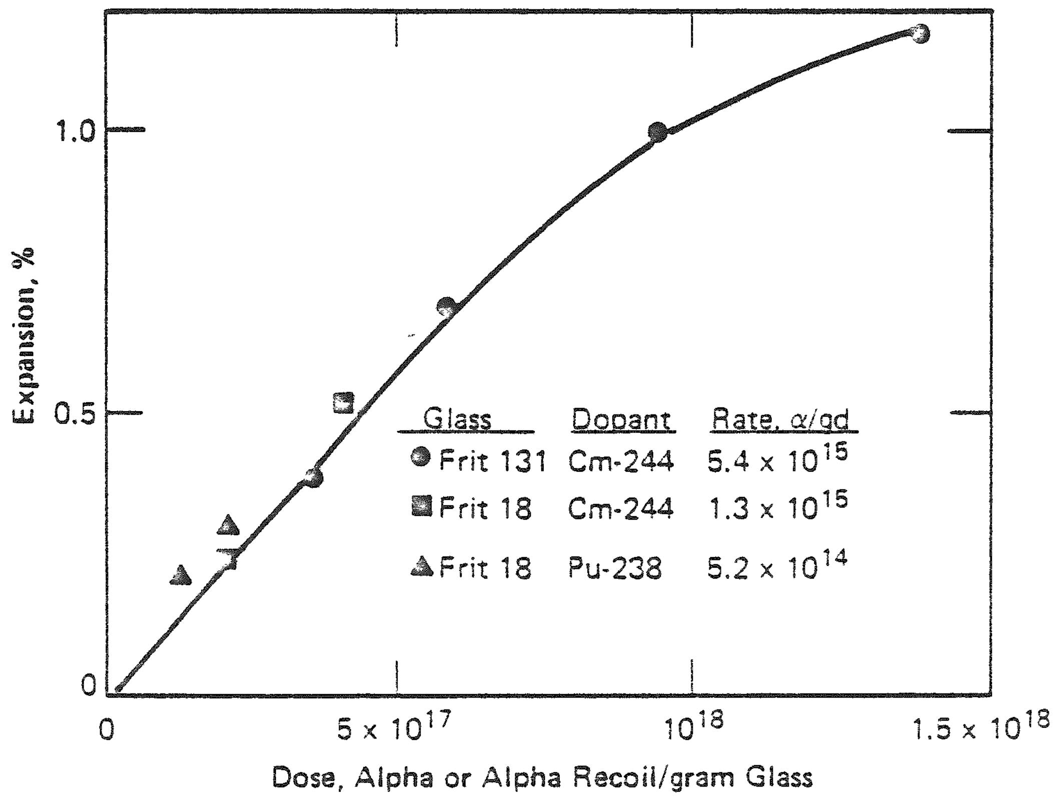

FIGURE 17. Effect of Alpha Radiation on Composite Glass Density

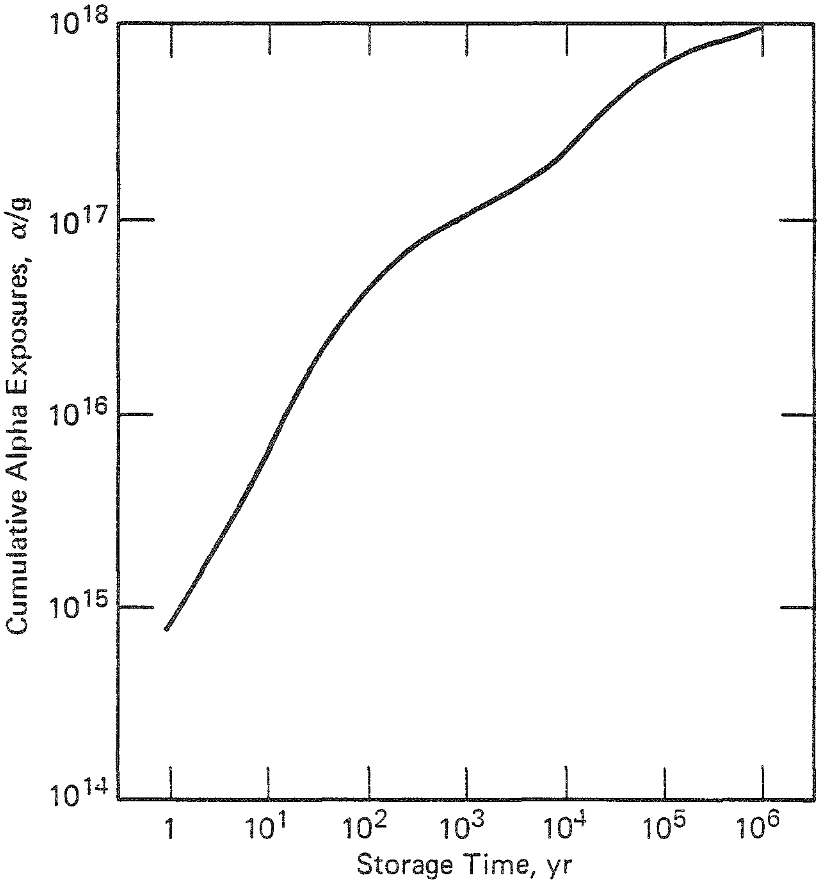

FIGURE 18. Cumulative Alpha Dose to Glass Containing SRP Stage 1 Waste

TABLE 40

Effects of Radiation on the Density of Waste Glass

Radiation	Dose	Equivalent Age	Result
Gamma	6×10^{10} rads	$>10^{6}$ years	No change
Alpha	9.3×10^{17} α/g	9×10^{5} years	Density decreases 1.0%

Leachability

The effects of radiation on the leaching behavior of SRP waste glass have been tested[6,34,53,54] under a variety of conditions (varying pH, time, temperature, surface area to volume ratio, alpha, beta, gamma-radiation, varying dose rates). All of these tests lead to the conclusion that radiation will not affect the leachability of waste glass in the repository environment.

Gamma radiation might affect the leachability of SRP waste glass by forming activated species in the leachant or at the glass surface. Samples of composite waste glass were leached by Bibler at 45°C in deionized water for 25 days, and the leach rate determined. One sample was irradiated in the ^{60}Co Irradiation Facility during leaching, and one was not. As Table 41 shows, gamma-irradiation did not significantly affect the leachability.[34] This is in accord with earlier results of Kelley,[6] who saw no effect for either monolithic or granular samples.

The above tests by Bibler were performed at a dose rate 5 times greater than that possible for SRP waste glass (1.5×10^6 vs. 3×10^5 rads/hr for the reference canister). When the tests were repeated at a dose 20 times greater than expected (5.8×10^6 rads/hr) an increase in leach rate of only 60% was observed. If the increase in leach rate is proportional to dose rate, then the increase expected for actual waste glass would be at most 3%.[34]

Similar leach tests on gamma-irradiated glass samples were performed by the MCC-1 procedures at 90°C in deionized water and brine.[53] These results (Table 42) indicate that the leachability rate of the gamma-irradiated glass was slightly higher than that of the unirradiated glass. Similar results were obtained based on Na, Li, and B leachability. This small increase is within the usual statistical fluctuation of leach rate determinations on different samples of the same glass or even successive tests on the same sample, and thus may not have resulted from the irradiation. Thus, gamma irradiation is not expected to significantly affect the performance of SRP waste glass in the respository environment.

Alpha radiation might affect the leachability of SRP waste glass by structurally damaging the glass and rendering it more susceptible to aqueous attack. To test this, a sample of composite waste glass doped with 2 wt % ^{244}Cm was leached for over 100 days at 25°C according to a leaching procedure specified by the International Standards Organization. The leachability of this high dose rate glass is compared with a low dose rate glass containing ^{239}Pu in Figure 19. Although the dose to the Cm-doped glass is 23000X greater, there is no appreciable difference in the leachabilities of the two glasses. These results are in accord with

TABLE 41

Effect of Gamma-Radiolysis On Leaching of Composite Waste Glass in Deionized Water

1.5×10^6 rads/hr, T = 45°C

Constituent	Leachability* g/m^2-day Unirradiated**	 Irradiated**
Si	1.9×10^{-2}	2.3×10^{-2}
B	2.4×10^{-2}	2.4×10^{-2}
Li	2.3×10^{-2}	2.3×10^{-2}
Na	2.0×10^{-2}	1.8×10^{-2}

---

* Based on aliquots removed during leaching.

** Based on least squares slope of line defined by four data points. A/V = 0.25 cm^{-1}.

TABLE 42

Effect of Co-60 Gamma Radiation (dose ≐ 8.5×10^{10} rad) on the Leachability of Composite Waste Glass Based on Si Leached in Deionized Water or Brine*

Leachant	Leach Time (Days)	Leachability (g/m^2d) Unirradiated	 Irradiated
Deionized Water	3	2.9 ± 0.1**	3.3 ± 0.3**
	7	1.8	2.5
	14	1.3	1.3
	28	0.68	0.92
Brine†	14	0.38	0.52
	28	0.19	0.34

* Static leach tests at 90°C; A/V = 0.1 cm^{-1}; MCC-1 procedure.

** Average and uncertainty of two independent 3-day leach tests.

† For composition, see Table 22.

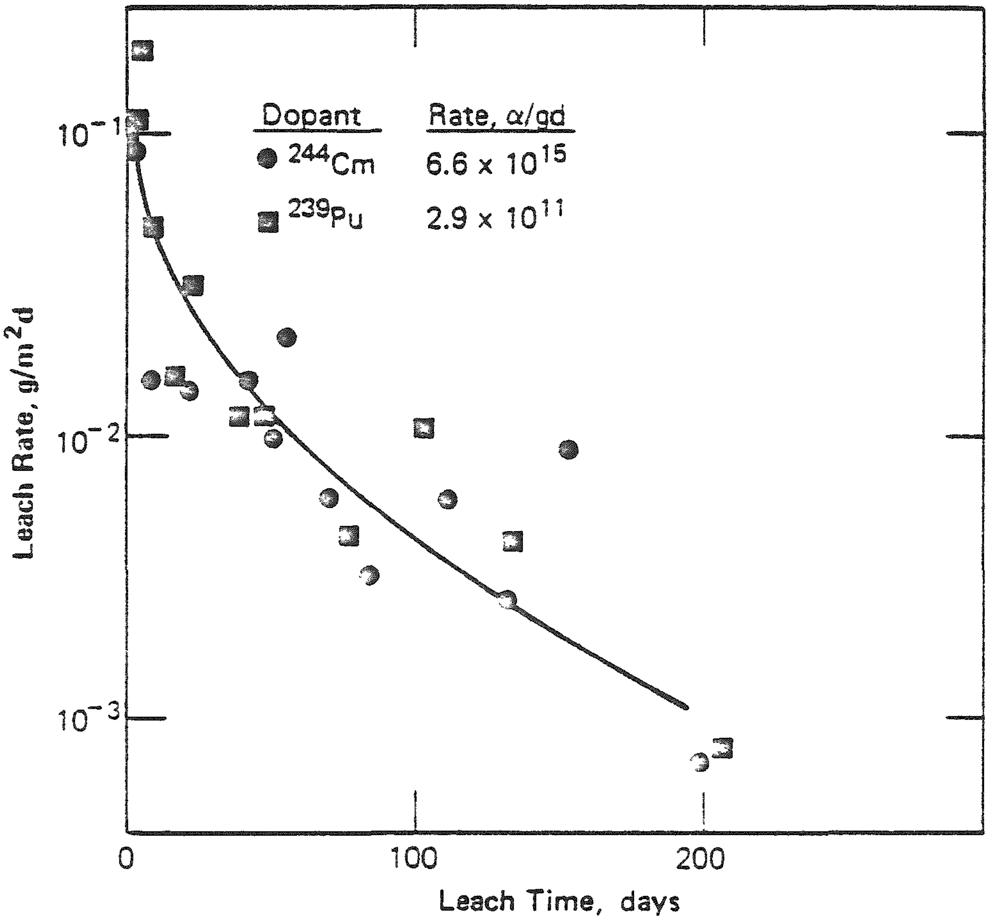

FIGURE 19. Effect of Alpha Radiation on Leaching. Curium Glass Has Received a Dose Equivalent to 10^6 Years Storage of Stage 1 Glass

earlier results of Bibler and Kelley[55], who found no changes in the fraction leached from ^{238}Pu and ^{244}Cm-doped glasses due to irradiation.

Dran and Petit have reported that external irradiation of soda-lime silica glasses by lead ions (simulating alpha-recoil damage) to doses greater than 10^{12} particles/g increased the degree of penetration of the glass by simulated brine solutions.[56] They have postulated that this would mean a great increase (20X) in the release rate of radionuclides into solution; i.e., the leachability of SRP waste glass would be greatly increased. Even though SRP waste glass will not encounter the dose at which this effect has been observed, SRL has investigated this effect. In experiments conducted to date, no significant increase in leachability has been observed in lead or xenon ion-irradiated composite waste glasses, nor in ^{244}Cm-doped glasses at comparable doses (approximately 130 days on Figure 19).[54]

To further examine this potential effect, composite waste-glass samples have been irradiated with xenon or lead ion beams to very high doses (Dran and Petit used lead ions; xenon ion irradiations were performed to look for possible effects specific to lead). Some of the preliminary data for the Xe-irradiated glasses are shown in Table 43. In these tests the glasses were leached for five 5-hour periods, and the leachant analyzed after each period. In 10 hours, the observed leach rate corresponds to complete penetration of the irradiated surface layer by water. In other words, any effect would be most accentuated in these tests. As Table 43 shows, the glass with the highest dose (approximately 6X the threshold dose determined by Dran and Petit - 5×10^{12} ions/cm^2) has a leach rate only about 1.4X that of the unirradiated sample.[54] Since this sample received a dose equivalent to $>5 \times 10^6$ years storage time of SRP waste glass, the effect observed by Dran and Petit probably is not important for the long-term disposal of SRP waste glass. In fact, Dran and Petit have recently concluded a study of French borosilicate waste glasses in which they found amplifications of only 3 or less.[57]

Helium Accumulation

In glass containing alpha-emitting radionuclides, helium will be generated internally by neutralization of the alpha particles. The hypothesis that this helium accumulation would cause damage to the glass or the canister has been examined carefully. Bibler and Kelley, in their tests with ^{244}Cm-doped and ^{238}Pu-doped waste glasses, found no structural damage to the glass due to helium accumulation (or any other cause),[55] even though the glasses had helium concentrations in excess of those expected in the reference glass canister after 10^6 years. Baxter[5] showed that after 1000

TABLE 43

Leachabilities of External-Ion-Irradiated Composite Waste Glass, Based on Si Leached in Deionized Water*

Irradiation	Dose** (Ions/cm)	Leachabilities† (g/m^{2}d)
160 keV Xe Ions	0	0.53 ±0.14
	10^{12}	0.38 ±0.20
	3 X 10^{13}	0.47 ±0.25
250 keV Pb Ions	0	0.76 ±0.31
	10^{12}	1.5 ±0.61
	10^{13}	0.77 ±0.23
	3 X 10^{13}	1.0 ±0.31

---

* Five-hour static leach tests at 90°C; A/V = 0.04 cm^{-1} for Pb-irradiated glass and 0.1 cm^{-1} for the Xe-irradiated glass.

** Dran Petit threshold dose is 5 X 10^{12} ions/cm^2.

† Average and standard deviation of five successive tests.

years the pressure in the void space of the reference canister would have increased by only 0.3 MPa due to helium concentration. Thus, helium accumulation will not affect the long-term performance of SRP waste glass.

ESTIMATING REPOSITORY RELEASE RATES

Laboratory results must be scaled to actual repository conditions to accurately predict glass performance. The surface-area-to-mass ratio of the large glass form is the key factor which transforms laboratory leaching data into release rates.

As shown earlier, the leachability, L_i, of a species, i, from the glass is given by

$$L_i = \frac{M_i}{W_i A \Delta t} \qquad (1)$$

where M_i = the mass of species i leached from the glass; W_i = the mass fraction of i initially in the glass, A = the surface area of the glass, and Δt = the time interval over which the leachability was determined.

The surface area of a monolithic full-scale glass form is $4.86 m^2$ (Table 10). If the glass is fractured, the surface area will increase by a factor, c, the ratio of the surface area of the fractured form to that of a monolith. Thus, the surface area of a fractured form will be $(4.86)(c)m^2$. In practice, c may vary from 1 (a monolith) to a maximum of about 25.[43] If a surface area of $(4.86)(c)m^2$ is used to calculate release rates, then the leachability must be measured at the appropriate A/V ratio as well. For example, in a granite repository the appropriate A/V ratio is $(4.86)(c)/0.38 = (13)(c)m^{-1}$. As shown earlier, the leachability varies with A/V. Thus, L_i will also depend on the factor of c.

The fraction of i leached from the glass, F_i, is the ratio of the mass of i, M_i, in solution to the amount of i initially in the glass, $W_i M_T$,

$$F_i = \frac{M_i}{W_i M_T} \qquad (2)$$

where M_T = the total mass of the glass (1480 kg for a full-scale form - Table 10). Substituting Equation (1) into Equation (2), and rearranging gives

$$F_i = L_i \left(\frac{A}{M_T}\right) \Delta t \qquad (3)$$

If the leachability is in units of g/m^2-day, then the fraction in Δt days

$$F_i = (3.23 \times 10^{-6})(c)(L_i)\Delta t \tag{4}$$

Occasionally, laboratory leaching data is presented in the form of fractional release per unit time. This data can also be scaled to a full-scale form by assuming that the leachability is the same in the laboratory as in a repository environment. Denoting laboratory values by lower case letters, and full-scale values by upper case, and rearranging Equation (3)

$$L_i = \frac{F_i}{(A/M_T)\Delta t} \tag{3A}$$

$$l_i = \frac{f_i}{(a/m_T \Delta t} \tag{3B}$$

By assumption, $l_i = L_i$, which implies Equation (3A) is equivalent to Equation (3B), i.e., or

$$\frac{F_i}{(A/M_T)} = \frac{f_i}{(a/m_T)} \tag{5}$$

$$F_i = f_i \frac{(A/M_T)}{(a/m_T)} \tag{6}$$

Equations (4) and (6) can appropriately be used in any of three situations. If the steady state leachability is known, its value can be substituted in Equation (4) to determine the steady state release rate. If the leachability has not reached steady state, but the leaching experiment has extended over the time period of interest (for example, the first year of leaching) then the fraction leached can be used in Equation (6) to determine an annual release rate. If the time dependence of the leachability is known, then this function of time can be substituted into Equation (4) or (6), and a release rate for the time period of interest determined.

Wiley and Walker's[30,31,34] long-term experiments can be used to demonstrate the use of Equations (4) or (6). For example, the steady state leachability (based on cesium) in a magnesium brine is 0.5×10^{-4} g/m^2 (Table 21). Assuming a value of 5 for the areal increase due to fracture, and substituting these values into Equation (4) gives an annual release rate of

$$F_i = (3.28 \times 10^{-6})(5)(0.5 \times 10^{-4})(365) = 3 \times 10^{-7}/\text{year}$$

Thus, at steady state, 3×10^{-7} (or 0.00003%) of the cesium in a full-scale canister would be released if the glass were leached under the same conditions as in the laboratory.

During the first year, the leachability in the magnesium brine was 4.5×10^{-4} g/m^2-day. In this case, the release rate over the first year is

$$F_i = (3.28 \times 10^{-6})(5)(4.5 \times 10^{-4})(365) = 2.7 \times 10^{-6}/\text{year}$$

Thus, in the first year 2.7×10^{-6} (or 0.00027%) of the cesium in a full-scale canister would be released if the glass were leached under the same conditions as in the laboratory. The results of similar calculations to these for all the data in Tables 21 and 32 are shown in Tables 44 and 45.

FUTURE DEVELOPMENTS

The performance of the glass product has been extensively tested in the laboratory. These results show that the glass product effectively immobilizes SRP waste and thus safeguards the present and future generations. Future efforts related to product performance will be aimed at extending laboratory results to large-scale forms, and at identifying means to optimize the performance of the glass in specific repository environments. Several areas have already been identified for further development. While each of these may be adopted in the future, none of them will affect the design of the DWPF.

Improved Repository System Materials

Several materials are currently being tested for possible inclusion in the waste package. These include soluble salts of aluminum, iron, lead, calcium, or phosphate to either enhance the formation of protective surface layers or act as buffers to slow corrosion. The most promising candidate, however, is metallic lead. Lead was originally tested by Battelle-Pacific Northwest Laboratories,[58] who found large reductions in the amount of material leached from a simulated power-reactor-waste glass. As Table 46 shows, the leachability of SRP waste glass in the presence of lead metal is only about 1% of that of the glass alone.

Improved Glass Composition

As mentioned previously, a new frit composition, Frit 165 (Table 6) has been developed by Ferro Corporation and SRL. This frit was optimized based on both processing properties and product

TABLE 44

Cesium Release Rates Calculated from Long-Term Tests with Actual SRP Waste Glass at 25°C*

Waste**	Leachant	Fraction Released Annually First Year	Steady State†
Tank 13	Distilled Water	2.7×10^{-6}	1.5×10^{-6}
	Magnesium Brine	2.7×10^{-6}	3×10^{-7}
Tank 16	Distilled Water	2.3×10^{-6}	1.3×10^{-6}
	Chloride Brine	6.0×10^{-6}	1.7×10^{-6}

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* Data in Table 21 used in calculation.

** Compositions in Table 17.

† Value reached after approximately 300 days.

TABLE 45

Projected Strontium and Plutonium Release Rates Calculated from Long-term Tests with Actual SRP Waste Glass at 25°C*

Waste**	Leachant	Fraction Released Annually† First Year	Steady State††
Tank 13	Sr-90	2.5×10^{-6}	1.6×10^{-6}
	Pu	3.3×10^{-6}	2.8×10^{-6}
Tank 16	Sr-90	1.6×10^{-6}	1.1×10^{-6}
	Pu	1.6×10^{-6}	1.3×10^{-6}

---

* Data in Table 32 used in calculation.

** Compositions in Table 17.

† Distilled water as leachant.

†† Value reached after approximately 300 days.

TABLE 46

Effect of Metallic Lead on the Leachability of Composite Waste Glass

Sample	Leachability (g/m^2-day) Based on Si
Composite Waste Glass*	0.53
Composite Waste Glass + Lead Metal**	0.007

---

* MCC-1 static leach test. Fifty-six days at 90°C in deionized water. A/V = $0.1 cm^{-1}$. For composition of glass, see Table 8.

** Modified MCC-1 static leach test, in the presence of lead metal. Forty-five days at 90°C in deionized water. A/V = $0.1\ cm^{-1}$. For composition of glass, see Table 8.

performance parameters: leach rate, melt viscosity, waste **solubility, coefficient of** expansion, and tolerance for the large **range of waste compositions.** In short-term static leach tests (Table 47), the leachabilities based on silicon and uranium of a Frit 165 composite waste glass were reduced by approximately an order of magnitude when Frit 165 was substituted for Frit 131. While recent risk assessments show that improvements in leach rate do not significantly reduce the dose to man from the repository under expected repository conditions,[59] such improvements may be desirable side effects of the improved processing characteristics of Frit 165.

TABLE 47

Comparison of Durability of Frit 131 and 165 Waste Glass

Frit*	Leachant**	Leachability† (g/m^2-day) Based On Si	U
131	Deionized Water	0.051	0.011
165	Deionized Water	0.001	0.001
131	MCC Silicate Water	0.040	0.036
165	MCC Silicate Water	0.006	0.051
131	MCC Brine	0.007	<0.02
165	MCC Brine	<0.02	0.001

---

* Frit 131 glass is composite waste glass in Table 8. The Frit 165 glass is its analogue based on Frit 165.

** Composition of leachants are given in Table 22.

† Based on 28-day MCC-1 static leach test. A/V = $0.1\ cm^{-1}$.

Increased Waste Loading

In laboratory tests, the feasibility of increasing the waste content in glass from 28 wt % waste oxides to 35 wt % has been demonstrated. This could reduce the cost of operating the DWPF and could also have a large impact on repository costs. Since SRP waste improves the durability of the waste glass product,[18] increasing the waste content beyond its present level may also improve the product performance.

Improved Understanding of Glass Leaching

A large body of data attests to the fact that borosilicate glass effectively immobilizes SRP waste. However, these data also are being used to develop a more fundamental understanding of the leaching process which should allow tailoring of the glass and the waste package to the repository environment.

To develop this understanding, a model for glass leaching is being developed at SRL. This model describes the leaching of waste glass as a three-stage process: interdiffusion, matrix dissolution, and surface layer formation. Interdiffusion and matrix dissolution rapidly reach a steady state, and diffusion through the surface layers becomes the dominant process. This quantitative model predicts that the amount of material extracted from the glass initially increases linearly with time, then changes to $t^{0.5}$, and finally approaches a constant value as saturation is approached. In cases where saturation does not occur (for example, in a leaching experiment with a high leachant flow rate), the model predicts that the linear time dependence should change to $t^{0.5}$, and then remain constant. The model is quantitative with respect to silica and is in better agreement with experimental data than models which consider only the first two stages of corrosion. It is being further refined and will be published soon.

In addition, a program is underway to study the leaching behavior of long-lived isotopes such as Tc-99. These are present in small quantities in SRP waste, but have never been detected in leachate solutions. Since species such as technetium may well dominate the long-term hazard associated with SRP waste in a repository, these experiments will attempt to quantify their release from the glass.

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