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Annual Report on the Characteristics of High-Level Waste Glasses

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ANNUAL REPORT ON THE CHARACTERISTICS
OF HIGH-LEVEL WASTE GLASSES

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SUMMARY

Processes are being developed to immobilize high-level radioactive wastes in glass for increased safety during handling, storage and final disposal. A concurrent program is the characterization of the waste-containing glasses produced by these processes, particularly in relation to their expected long-term behavior as affected by thermal and radiation-induced alteration of the glass.

A compilation of characterization data is presented for low-melting ($<1100^{\circ}\text{C}$) borosilicate waste glasses, which may contain 33 wt% or more waste and which can be melted in situ in their stainless steel storage canisters. The data demonstrate that these low-melting glasses are relatively unaffected by the radiation doses to which they are exposed. The data also show that thermally-induced devitrification and phase separation can be minimized by proper selection of glass composition.

CONTENTS

SUMMARY	ii
INTRODUCTION	1
GLASS FORMULATION	3
REFERENCE GLASS	5
NFS GLASS	10
AGNS GLASS	11
EXXON GLASS	13
COST OF PRE-PREPARED GLASS FRITS	14
RADIATION HISTORY PROJECTIONS	15
CUMULATIVE RADIATION DOSE IN HIGH-LEVEL WASTE	15
CUMULATIVE RADIATION DOSE IN HIGH-LEVEL WASTE GLASS	18
THERMAL HISTORY PROJECTIONS	21
HIGH-LEVEL WASTE TEMPERATURE	22
CANISTER DESIGN	23
WASTE SOLIDIFICATION	27
CANISTER CLOSURE	28
INSPECTION	30
DECONTAMINATION	31
INTERIM STORAGE	31
FEDERAL REPOSITORY - SALT MINE	32
BULK PROPERTIES OF WASTE GLASSES	35
GENERIC PROPERTIES	35
COMPOSITIONALLY SPECIFIC PROPERTIES	39

ENVIRONMENTAL REACTIONS OF WASTE GLASS	43
LEACH TEST METHODS	43
LEACH RATE CALCULATIONS	46
REFERENCE GLASS LEACH DATA	47
NFS GLASS LEACH DATA	55
AGNS GLASS LEACH DATA	55
EXXON GLASS LEACH DATA	56
PHASE BEHAVIOR	57
REFERENCE GLASS	57
NFS WASTE GLASS	68
EFFECTS OF RADIATION ON WASTE GLASS	71
ACCELERATED ALPHA EFFECTS EXPERIMENTS	71
FULL-LEVEL RADIOACTIVE GLASS EXPERIMENTS	81
PREPARATION OF FULL-LEVEL WASTE CALCINE	81
PROCEDURE FOR PREPARING FULL-LEVEL GLASS	81
VOLATILIZATION DURING GLASS PREPARATION	83
MACROSTRUCTURE OF FULL-LEVEL GLASS	84
MICROSTRUCTURE OF FULL-LEVEL GLASS	86
LEACH RATES OF FULL-LEVEL GLASS	88
REFERENCES	97

FIGURES

1	Range of Composition of HLW Glasses	2
2	The Effect of PW-8a-1 Calcine Content on Viscosity at 1050°C and Leachability at ph 3.9 for Frit 76-101	10
3	The Effect of PW-7a-1 Calcine Content on Viscosity at 1050°C and Leachability at ph 3.9 for Frit 76-199	12
4	The Effect of PW-4b-1 Calcine Content on Viscosity and Leachability for Frit 77-62	14
5	Alpha Dose to Wastes	17
6	Neutron Dose to Wastes	17
7	Beta Dose to Wastes	17
8	Build-up of Alpha Dose in Reference Waste Glass	18
9	Thermal Histogram of 12-Inch Diameter Finned Canister - Short-Term for ICM	25
10	Thermal Histogram for 12-Inch Diameter Finned Canister - Short-Term for Ceramic Melter	26
11	Thermal Histogram of 12-Inch Diameter Finned Canister - Long-Term for All Canisters	26
12	Thermal Effects of Glass Cracking, 12-Inch Finned Reference Canister in Air	28
13	Temperature Distribution, 12-Inch Diameter Reference Canister in Water	29
14	Thermal Performance of 12-Inch Diameter Reference Canister	29
15	Effects of Ambient Air Temperature 12-Inch Finned Reference Canister	30
16	Effects of Surface Emissivity, 12-Inch Finned Reference Canister in Air	31
17	Temperature Distribution for 12-Inch Canister, with 16-Inch Overpack and Suspended Fins, in Air	32
18	Surface Temperature of Canister in Maximum Heat Density Array in Salt Mine	33

19	Fraction Increase in Geometric Surface Area	36
20	Prediction Curves for Sub-10 μ Fine Generation	36
21	Effect of Cooling Rate on the Generation of Increased Surface Area in 6 in. Diameter Glass Castings	36
22	Effective Thermal Conductivity of In-Can Melting Process Borosilicate Glass	38
23	Closed Porosity Distribution in In-Can Melted Glass	39
24	Electrical Conductivity of Molten Waste Glass 72-68 [PW-4b-2 (3.1) 73-1] at 40 and 1000 Hz	41
25	Corrosion of 304L Stainless Steel by 72-68 Type Glass	41
26	Volatility From a 72-68 [PW-4b-6 (2.8) 73-1] Glass in 4 hr	42
27	Soxhlet Leach Test Apparatus	44
28	Paige Leach Test Apparatus	45
29	Soxhlet Leach Rate for the Reference Glass Stored 2 Months	48
30	Leach Rate vs Leachant Temperature for the Reference Glass	50
31	Leachability of Simulated HLW Glass, Normalized to Cesium Behavior	51
32	Leachability of Simulated HLW Glass, Normalized to Strontium Behavior	51
33	Cumulative Penetration of Vitreous and Devitrified Glass, Based on Cesium	54
34	Cumulative Penetration of Vitreous and Devitrified Glass, Based on Strontium	54
35	Outline of Phase Behavior Studies	58
36	Concentration of Selected Elements in Devitrified Glass 72-68	59
37	Micrograph of Glass 72-68 Showing Crystalline Phases After Annealing One Year at 700°C	60
38	X-Ray Diffraction Patterns of As-Prepared (Vitreous) and Devitrified Glasses	61

39	Observed Crystallization Behavior of Zn_2SiO_4 for the Reference Glass	63
40	Observed Crystallization Behavior of the Molybdate Phases for the Reference Glass	64
41	Ingrowth of Calcium-Containing Apatite Phase and Corresponding Change in (Ca, <u>Sr</u> , Ba) MoO_4	65
42	Fractional Ingrowth and Estimates of Heats of Crystallization for Zn_2SiO_4 and (Ca, <u>Sr</u> , Ba) MoO_4	66
43	Short Time Ingrowth of Zn_2SiO_4 Phase	67
44	Times Required for 50% Fractional Ingrowth of Zn_2SiO_4	68
45	X-Ray Diffraction Traces Comparing Devitrified 76-68 Glass and 72-68 Glass	69
46	Stored Energy Buildup (72-68 Glass)	72
47	Stored Energy Buildup (Lead Glass)	73
48	Stored Energy Buildup (European Glass)	73
49	Stored Energy Release Rates	74
50	Stored Energy at Various Glass Storage Temperatures	75
51	Density Changes in Alpha Irradiated Glasses	76
52	Leachability of ^{244}Cm -Doped Zinc Borosilicate Waste Glass	77
53	Full-Level Glass Sectioning	84
54	High-Level Waste Glass Dose Rate as a Function of Depth	85
55	Micrographs of Fully-Radioactive Devitrified Waste Glass	89
56	Leach Rate of Full-Level Waste Glass at 25°C in Demineralized Water, Based on Cesium Behavior	92
57	Leach Rate of Full-Level Waste Glass at 25°C in Demineralized Water, Based on Plutonium Behavior	93
58	Leach Rate of Full-Level Waste Glass at 25°C in Demineralized Water, Based on Curium Behavior	94
59	Leach Rate of Full-Level Waste Glass at 25°C in Demineralized Water, Based on Strontium Behavior	95
60	Comparison of Isotopic Leach Rates from Full-Level Waste Glass at 25°C in Demineralized Water	96

TABLES

1	Parameters For Glass Development	3
2	Waste Compositions, Kgs Oxide/MTU	7
3	Glass Frit Compositions	8
4	Zinc Borosilicates Glass Flowsheet Flexibility	8
5	Typical Waste Glass Compositions	9
6	Beta and Alpha Activities in High-Level Waste from One Metric Ton of UO_2 Fuel	16
7	Alpha Doses for Waste Glasses From UO_2 and Plutonium Recycle Wastes	19
8	Representative Conditions to Which High-Level Waste Glass May Be Subjected	21
9	Thermal Power in Typical High-Level Waste	22
10	Thermal Properties for Steady-State Analysis	24
11	Thermal Conductivity of Waste Glass 72-68	37
12	Compositionally-Dependent Properties for Four Glasses	40
13	Acid-Base Leach Rates for the Reference Glass	47
14	Reference Glass Soxhlet Leach Rates for Laboratory and Engineering-Scale Melts	48
15	Soxhlet Leach Data for the Reference Glass	49
16	Long-Term Leach Data Based on Cesium Behavior for the Reference Glass	52
17	Long-Term Leach Data Based on Strontium Behavior for the Reference Glass	52
18	NFS Glass Leach Data	55
19	AGNS Glass [PW-7a-1 (2.0) 76-199] Leach Data	55
20	EXXON Glass [PW-4b-1 (2.0) 77-62] Leach Data	56

21	Crystalline Phases in Glass 72-68	61
22	Long-Term Leach Data for the Reference Glass	78
23	Relative Leachability of Elements	78
24	HLW Glass Runs	82
25	Glassmaker Off-Gas Data for 100 g Batch of PW-Zorita (3.0) 73-1 . .	83
26	Microprobe Elemental Analyses of HLW Glass, wt%	87
27	High-Level Waste Glass Leach Solution Sampling Schedule	90

INTRODUCTION

A Program Plan for Comprehensive Characterization of Solidified High-Level Wastes⁽¹⁾ was issued in December 1975. This plan was prepared as part of the larger Commercial Waste Fixation Program being conducted by Pacific Northwest Laboratories (PNL) for the U.S. Energy Research and Development Administration (ERDA). This annual report is the first of a series of yearly reports dealing with the implementation of this characterization plan. The goal of comprehensive characterization is to provide such an understanding of the behavior and properties of solidified waste forms that it will be possible to convert waste representative of any reprocessing plant flowsheet into a form safe for both interim and long-term storage. As part of its effort to achieve this degree of understanding, PNL has been conducting in-depth studies of low-melting (1000-1150°C) borosilicate glasses used to immobilize high-level liquid wastes (HLLW) from the LWR fuel cycle. This report deals exclusively with the comprehensive characterization of these borosilicate glasses. Somewhat similar characterizations are being done, or will be done, at PNL for glasses designed to immobilize defense wastes, and for "advanced" forms for solidifying LWR wastes. This latter category comprises solid waste forms other than the glass type. The processes used to produce waste glasses are also being developed at PNL, and are described elsewhere.^(2,3,4)

There is not one specific type of waste glass suited to the immobilization of all LWR high-level wastes. Waste glass compositions must be adapted to account for many variables, including:

- reprocessing plant operating mode - which affects the amount of U and Pu in HLLW
- frequency of plant shutdowns - which affects the amount of sodium and other inerts in the waste
- waste vitrification process used - which affects restraints placed on allowable glass viscosity, electrical conductivity, redox potential, etc.

- fuel type and burnup
 - which affects the ratio of fission product to inerts in HLLW, the amount of transplutoniums, and possible presence of fluoride
- reprocessing plant flowsheet
 - which affects the amount and type of inerts in HLLW (e.g. presence or absence of soluble poisons, ILLW, Pu reductants).

The general compositional range for borosilicate waste glasses is shown on the ternary diagram in Figure 1.

For the purpose of this study, PNL has selected four different borosilicate waste glasses for comprehensive characterization. The discussion which follows is essentially devoted to the findings relative to these four glasses.

FIGURE 1. Range of Composition of HLW Glasses

GLASS FORMULATION

The formulation of high-level waste glasses involves combining waste with a glass frit, melting the combined materials, and allowing the molten substance to cool and solidify. Since the composition of waste is set by the reprocessing operations, the significant variable in waste glass formulation is the glass frit. Table 1 lists some of the considerations and limits central to the development of glass frits:

TABLE 1. Parameters For Glass Development

<u>Characteristic</u>	<u>Description or Value</u>
Melting temperature	1050 - 1150°C
Viscosity	<200 poise at melting temperature
Leach Rate	Minimum possible in acid, basic and neutral solutions
Homogeneity	No visible separations

Resistance to radiation damage and to devitrification are also important considerations in the development effort.

Because of the interrelationships of many glass properties, about 1500 melts have been prepared and tested at PNL in formulating the study glasses. Three basic waste compositions, PW-4b, PW-7a, and PW-8a, are presently included in the glass development program. These compositions are detailed in Table 2. The PW-4b composition corresponds to reprocessed waste from an optimized reprocessing plant operation, in which little uranium or plutonium is lost to the waste stream. The composition of the PW-4b is also low in inert materials or reprocessing chemicals. We have taken PW-4b to be representative of GE's Midwest Fuel Recycle Plant (if vitrification had been the selected solidification method there), and to be a suitable stand-in for the HLW expected to be generated by the Exxon fuel reprocessing plant.

The PW-7a waste is representative of the Allied General Nuclear Services (AGNS) plant in Barnwell, SC. The waste from this plant is a combination of

high-level waste (HLW) and intermediate-level waste (ILW). The addition of ILW is responsible for the higher Na_2O and P_2O_5 content in PW-7a. Unlike the operation which yields PW-4b, Gd_2O_3 is added during reprocessing at the AGNS plant for criticality control. PW-7a also differs from PW-4b in that it has higher expected uranium and plutonium concentrations due to lower expected separation efficiencies (99% vs. 99.9%).

Had it resumed commercial operation, the Nuclear Fuel Services Plant in West Valley, New York would most likely have produced a waste with the composition of PW-8a. Like PW-7a, PW-8a also results from a combined HLW-ILW waste stream, but higher Na_2O levels have been anticipated for the latter. A high Fe_2O_3 content would result from the use of thin mild steel basket liners, which contain the chopped fuel for transfer to the dissolvers. The mild steel dissolves along with the fuel in the nitric acid, and becomes part of the waste stream.

While specific waste compositions are given for each plant considered, these compositions are expected to vary from the reference given. One of the reasons for the variation is that the fission product content is based on a burn-up at 33,000 MWD/MTU. Both higher and lower burn-ups will be encountered with specific fuels. A second reason is that the reprocessing plants will be required to start up and shut down periodically for inventory and accountability purposes in accordance with government regulations. The startup and shutdown periods will generate larger quantities of intermediate-level waste. Regulations can affect waste composition in other ways as well. The quantity of gadolinium required for criticality control at the AGNS plant, for example, has recently been increased significantly over that shown in the PW-7a composition. The selection of other chemicals for the reprocessing operation will also affect the type and quantity of inerts in the waste. To account for these types of changes in the planned operation of the subject plants, additional waste compositions have been defined.^(5,6,7,8)

A standardized nomenclature⁽⁸⁾ has been used to identify characterization samples in order to avoid confusion of different waste composition and mixing ratios. This nomenclature is illustrated in the following example:

		As Defined:fined			
		PW-4b	-8a	PW-8a-1	PW-8a-2
<u>Inerts</u>	Na ₂ O	--	17	14.057	14.057
	Fe ₂ O ₃	1.511	15	27.225	29.008
	Cr ₂ O ₃	0.345	31	1.151	1.151
	NiO	0.141	36	1.471	1.471
	P ₂ O ₅	0.672	12	1.342	1.342
	Gd ₂ O ₃	--		--	--
<u>Fission Products</u>	Rb ₂ O	0.354	14	0.354	0.178(K)
	SrO	1.059	19	1.059	1.059
	Y ₂ O ₃	0.598	18	0.027(RE)	0.043(RE)
	ZrO ₂	4.944	4	4.944	4.944
	MoO ₃	5.176	16	6.375	6.375
	Tc ₂ O ₇	1.291	11	---(Mo)	---(Mo)
	RuO ₂	2.972	12	2.972	---(Fe)
	Rh ₂ O ₃	0.480	10	0.304(Co)	0.304(Co)
	PdO	1.483	13	---(Ni)	---(Ni)
	Ag ₂ O	0.088	18	0.088	0.088
	CdO	0.097	17	0.097	0.097
	TeO ₂	0.725	15	0.725	0.725
	Cs ₂ O	2.880	10	2.880	0.963(K)
	BaO	1.567	17	1.567	1.567
	La ₂ O ₃	1.480	10	3.213(RE)	5.114(RE)
	CeO ₂	3.323	13	6.426(RE)	10.228(RE)
	Pr ₆ O ₁₁	1.482	12	0.669(RE)	1.065(RE)
	Nd ₂ O ₃	4.522	12	2.276(RE)	3.622(RE)
	Pm ₂ O ₃	0.123	13	---(RE)	---(RE)
	Sm ₂ O ₃	0.924	14	0.402(RE)	0.639(RE)
	Eu ₂ O ₃	0.200	10	0.107(RE)	0.170(RE)
	Gd ₂ O ₃	0.137	17	0.268(RE)	0.426(RE)
<u>Actinides</u>	U ₃ O ₈	1.169	19	12.772	---(RE)
	NpO ₂	0.865	15	---(U)	---(RE)
	PuO ₂	0.010	14	---(U)	---(RE)
	Am ₂ O ₃	0.181	11	---(RE)	---(RE)
	Cm ₂ O ₃	0.040	10	---(RE)	---(RE)
Total		40.8		92.8	84.6

a. Where used, chemical substitutes are used.
If no value shown the weight included.

b. RE + a commercial rare earth mixture
17.0 Nd₂O₃, 3.0 Sm₂O₃, 0.8 Eu₂O₃ and

72-68 [PW-4b-1 (2.8) 73-1]

While a glass may be identified as simply 72-68, it is necessary to include the terms in the brackets to fully define the composition.

For experimental use, waste compositions must be modified for cost and availability. The elements Ru, Pd, Rh, Ag, Cs, and rare earths are omitted or replaced by other elements in large-scale tests for cost reasons. The actinides and Tc are also replaced by other elements, or omitted, for handling reasons. The wastes selected for this study have been identified with an additional number to reference the substitutions in that particular waste (i.e., PW-4b-3). Generally, -1 denotes glasses used in laboratory melt development studies. A -2 denotes the formulation used in engineering-scale tests. Special compositions, prepared for specific tests, such as the detailed thermal effect characterization tests or accelerated alpha studies, are indicated by -3 to -6. Table 2 gives the compositions for the three basic wastes under consideration (PW-4b, PW-7a and PW-8a), and for modifications of those wastes.

REFERENCE GLASS

A reference glass 72-68 was defined so that detailed characterization work could proceed. This glass is not characteristic of a specific reprocessor, but utilizes the clean PW-4b type waste.

Frit and Glass Composition

The 72-68 waste glass is formed with 73-1 frit. The composition of the 73-1 frit is shown in Table 3 along with other major frits. The 73-1 frit composition was developed early in the program when most leach testing was conducted in distilled water. These tests indicated that the high ZnO content in this frit was beneficial to leach rate. The 73-1 frit also showed low

viscosity and an ability to accept a wide range of waste concentrations, as shown in Table 4. Primarily for these reasons, it was selected for more detailed study.

TABLE 3. Glass Frit Compositions

	Weight Percent			
	<u>73-1</u>	<u>76-101</u>	<u>76-199</u>	<u>77-62</u>
SiO ₂	37.0	59.7	53.0	52.2
B ₂ O ₃	15.1	14.2	14.0	19.4
Na ₂ O	5.5	11.2	12.0	7.5
K ₂ O	5.5	---	3.0	6.0
ZnO	28.9	7.45	---	7.5
CaO	2.0	3.0	3.0	3.0
MgO	2.0	---	---	---
SrO	2.0	---	---	---
BaO	2.0	---	---	---
TiO ₂	---	4.45	9.0	4.5
Al ₂ O ₃	---	---	1.5	---
CuO	---	---	4.5	---

TABLE 4. Zinc Borosilicate Glass Flowsheet Flexibility

<u>Frit/PW-4b Calcine Ratio</u>	<u>Homogeneity</u>	<u>Viscosity</u>	<u>Leach Rate^(b)</u>
14.1:1	Homogeneous	<500 Poises	0.74
6.5:1	↓	↓	1.06
4.1:1			0.43
2.8:1 ^(a)			0.57
2.0:1			0.44
1.5:1			0.83

^(a) Nominal Flowsheet

^(b) 72 hour Soxhlet test, % weight loss

Various PW-4b wastes have been used in the program, but the most detailed characterization work has involved glass 72-68 [PW-4b-6 (2.8) 73-1]. The composition of this glass is shown in Table 5, along with the other three glasses undergoing detailed characterization.

TABLE 5. Typical Waste Glass Compositions

	Weight Percent			
	<u>72-68</u>	<u>76-68</u>	<u>76-183</u>	<u>76-375</u>
SiO ₂	27.3	40.0	35.5	35.0
B ₂ O ₃	11.1	9.5	9.5	13.0
Na ₂ O	4.0	7.5	8.0	5.0
K ₂ O	4.0	---	2.0	4.0
ZnO	21.3	5.0	---	5.0
CaO	1.5	2.0	2.0	2.0
MgO	1.5	---	---	---
SrO	1.5	---	---	---
BaO	1.5	---	---	---
TiO ₂	---	3.0	6.0	3.0
Al ₂ O ₃	---	---	1.0	---
CuO	---	---	3.0	---
Waste	26.3	33.0	33.0	33.0
(Type)	(PW-4b)	(PW-8a)	(PW-7a)	(PW-4b)

Sodium Molybdate (Na₂MoO₄) Solubility

One problem that has occurred in some engineering-scale runs with 72-68 compositions was the separation of a sodium molybdate phase from the glass. Since this phase also contains some cesium and strontium and is water soluble, its separation has been judged undesirable. Tests have been conducted to determine the interrelationship between Na₂O and MoO₃ content and the phase formation and separation. The data from these tests, which are reported elsewhere, indicate a maximum amount of sodium which can be used in the glass to avoid separation of Na₂MoO₄.⁽⁹⁾

NFS GLASS

From the detailed characterization work with the reference glass, two major areas for glass formulation improvement have been identified. The first of these is acid durability and the second is the elimination of the Zn_2SiO_4 devitrification phase. These improvement goals have apparently been achieved with glass 76-68, for which detailed characterization work has just been initiated.

Frit and Glass Compositions

The 76-101 frit and 76-68 glass compositions are shown in Tables 2 and 3, respectively. Note that the ZnO content has been significantly reduced from that of 72-68 glass and additions of TiO_2 have been made. The alkaline earths have also been reduced and consolidated as CaO .

Allowable Waste Content

Because the NFS waste has a high concentration of Na_2O , the frit used with it for waste glass formulation must have a low sodium content and, consequently, a high viscosity. As waste is added to the frit the viscosity decreases, as shown in Figure 2. Since a glass viscosity of less than

FIGURE 2. The Effect of PW-8a-1 Calcine Content on Viscosity at 1050°C and Leachability at pH 3.9 for Frit 76-101

200 poise is desirable, the minimum amount of calcine for this glass would be 22%. The increased alkali content, resulting from a higher calcine content, can also lead to increased leachability of the glass. Initial leachability versus calcine content is also shown in Figure 2. A major increase in acid leachability occurs with large calcine additions. While firm limits on leachability do not exist, it would seem prudent to limit calcine additions to near 44% waste. This would then allow a working range from 22-44% calcine for these compositions.

Use of Reducing Agents

As noted earlier, sodium molybdate separation can be a problem. The use of reducing agents, however, has been demonstrated in both laboratory and engineering-scale tests to be an effective method of control in NFS glass formulation.⁽¹⁰⁾ The way in which reducing agents, such as powdered silicon metal or powdered silicon carbide, eliminate the phase separation is shown by the following reaction:

This reaction shows complete reduction of molybdate to metal. Reduction to lower oxides also appears to be effective in eliminating separation. The reducing agents affect other species as well, such as rhodium, palladium, nickel and ruthenium, which are reduced to metal. The CeO_2 is reduced to Ce_2O_3 , which increases the solubility of cerium in the glass.

AGNS GLASS

The glass for PW-7a waste was developed concurrently with the NFS glass. Though some similar concepts were incorporated, the major differences involve the alkali content and the use of reducing agents. Reducing agents can, if added in excess, reduce ZnO to zinc metal, which has a boiling point lower than typical melting temperatures. The result is a zinc fume which burns over the glass melt. To prevent zinc loss, ZnO was replaced by CuO in the composition of AGNS glass. Copper has a boiling point of 2595°C and is, therefore, stable in the glass. CuO was found to have an effect on leach rate similar to that of ZnO , i.e., decreased leachability in neutral solutions.

Unlike the NFS glass, the AGNS glass alkali content has been divided between K_2O and Na_2O . The use of K_2O results in a lower viscosity through the "mixed alkali" effect. It is also reported to lower the potential for liquid-liquid phase separation in simple glasses.⁽¹¹⁾ These separations are difficult to quantify since they can only be observed by qualitative measures such as opalescence and increased leaching rates, and with high magnification transmission electron microscopes.

Frit and Glass Composition

The frit composition for the 76-183 [PW-7a-1 (2.0) 76-199] is shown in Table 2 and the glass composition in Table 3. The major differences from 76-101 have been noted above. The other differences resulted from the need to have a lower viscosity frit, since the alkali content of the PW-7a waste is much lower than PW-8a.

Allowable Waste Content

The range of calcine content that can be tolerated from a viscosity and leachability standpoint is indicated in Figure 3. The acid leachability increases rapidly above 40% calcine content. The viscosity, however, does not

FIGURE 3. The Effect of PW-7a-1 Calcine Content on Viscosity at 1050°C and Leachability at ph 3.9 for Frit 76-199

increase until nearly 50% waste is added. A conservative upper limit would be 40% calcine. Additional tests for thermal and radiation effects will be required to confirm the wide calcine content allowable with this composition. The wide range results from a balance in alkali content between glass and calcine so that the alkali content remains nearly constant regardless of waste content. This balance would appear to be a very desirable factor in waste glass.

EXXON GLASS

The glass identified as Exxon glass in this study is made with PW-4b waste and not with a waste formulated by Exxon itself. Work with this pseudo-Exxon waste composition is in the early stages and can be expected to change as the waste composition is better defined. The development to this point has emphasized composition control of sodium molybdate, since the PW-4b standard waste has a high fission product loading. The current selected process is the ceramic melter, which cannot accept the use of reducing agents for molybdate control.

Glass Composition

On the basis of present information, the glass composition which would be selected for the Exxon waste is 76-375 [PW-4b-1 (2.0) 77-62]. Comparison of this composition to others in Table 3 shows that the Exxon glass has a higher B_2O_3 content. This results from efforts to increase the solubility of the molybdate phase in the glass.

Allowable Waste Content

The changes in leach rate and viscosity corresponding to changes in calcine content for this glass can be noted in Figure 4. Its viscosity at 1050°C is higher than that of previous glasses, but the ceramic melter can operate at higher temperatures. This glass also appears to be quite flexible, and can tolerate PW-4b waste loadings of up to 50 wt%. Further tests will be made with actual Exxon composition during the next year.

FIGURE 4. The Effect of PW-4b-1 Calcine Content on Viscosity and Leachability for Frit 77-62

COST OF PRE-PREPARED GLASS FRITS

As has been noted in the previous sections and in Table 2, glass additives can be premelted and homogenized as a glass frit. This premelt process increases subsequent melting rates and glass homogeneity. These speciality frits can be readily obtained from the glass and enamel industry at quite a low cost. Frits purchased for engineering-scale demonstration in lots of 20,000 lb have been obtained for less than forty cents per pound. To put things into perspective, it is estimated that the waste canister will cost ten to thirty times more than the glass frit for respective amounts. Frit costs, therefore, are not seen to be a major criteria in glass development.

RADIATION HISTORY PROJECTIONS

The radioactive components of LWR high-level wastes consist of fission products, transplutonium elements (americium and curium), and uranium, plutonium and neptunium not recovered during reprocessing. The amount of neptunium reaching the waste is dependent on the flowsheet, but current processes are designed to force all the neptunium into the high-level waste. Uranium and plutonium losses to the waste are expected to be 0.5-1.0%, and can vary within this range in accordance with actual plant designs and operating practices. Only a small fraction of the activation products from the fuel cladding reach the high-level wastes, and contribute to the wastes only an insignificant amount of radioactivity in terms of thermal or radiation effects. The same is true for the small amounts of radioactivity from activation of the impurities in the fuel.

The decay of the fission products is the main source of beta and gamma radiation. Since most of the fission products have relatively short half-lives, the major portion of the beta and gamma radiations will have taken place within 1000 years of reactor discharge. A few fission products (e.g., ⁹⁹Tc) over long periods of time contribute slightly to the accumulated beta dose, as do certain daughter products of the long-lived actinides. In general, the actinides in the waste decay by alpha emission and, to a lesser extent, by spontaneous fission, which results in the generation of neutrons and fission fragments. A relatively small number of neutrons are produced by (α , n) reactions.

Table 6 lists the activity, in curies, of beta and alpha emitters in the high-level waste from processing a metric ton of a typical UO₂ fuel, with a burnup of 33,000 MWd/T and at several cooling times (assumes 99.5% recovery of uranium and plutonium).

CUMULATIVE RADIATION DOSE IN HIGH-LEVEL WASTE

The amount of radioactivity in aqueous high-level waste depends on reactor design, reactor exposure history, reprocessing conditions, fuel cooling time from reactor discharge to separation of uranium and plutonium, and the length of time the waste is stored prior to solidification.

TABLE 6. Beta and Alpha Activities in High-Level Waste from One Metric Ton of UO_2 Fuel

Cooling Time, y	β Curie	α Curie
2	1×10^6	3×10^3
10	3×10^5	2×10^3
$10^{0.2}$	3×10^3	290
10^3	21	64
10^4	20	16
10^5	15	2.2
10^6	4	2.4

The ingrowth of ^{241}Am from the decay of ^{241}Pu after reactor discharge is an important factor in estimating the alpha activity in the solidified waste. The fuel cooling times prior to plutonium separation determine the amount of ^{241}Am from this source. (Increasing the fuel cooling time results in increased alpha activity.)

The cumulative doses of alpha, neutron and beta radiations in the waste for a reference case are shown in Figures 5-7. The bases for the estimate include:

- 3.3% enriched UO_2 fuel
- One ton heavy metal
- 33,000 MWd/MT average burnup
- 26.4 MW/MT power
- 150 d cooling time prior to separation and solidification
- 0.5% loss of plutonium and uranium to the high-level waste.

Figures 5 and 6 also show the alpha and neutron doses for wastes from mixed PuO_2 - UO_2 fuel resulting from plutonium recycle in LWRs. The estimated doses are for the plutonium fraction with the same reactor exposure and processing conditions listed above. The case shown assumes a fuel containing 4 wt% PuO_2 with 24% ^{240}Pu isotopic content (not equilibrium case).

FIGURE 5. Alpha Dose to Wastes

FIGURE 6. Neutron Dose to Wastes

FIGURE 7. Beta Dose to Wastes

As is evident from the figures, plutonium recycle will result in waste with much higher alpha activities. In practice, the waste from the plutonium fraction will probably always be mixed with the wastes from the UO_2 fraction, and the resulting alpha dose will be a factor of three lower than shown.

CUMULATIVE RADIATION DOSE IN HIGH-LEVEL WASTE GLASS

The concentration of the radioactive components in the solidified waste depends on the fuel reprocessing flowsheet and on the additives included in the solidification step. Both of these factors can vary over considerable ranges and, thus, have a significant effect on the actual radiation dose to the solidified waste.

The calculated buildup of the alpha dose for the reference waste glass, 72-68, is shown in Figure 8. The estimate uses the same assumed reactor history and reprocessing conditions as in Figures 5-7. The amount of waste glass for this case is 170 kg per metric ton of heavy metal in the fuel.

FIGURE 8. Build-up of Alpha Dose in Reference Waste Glass

Table 7 compares the alpha doses for glasses containing wastes from plutonium recycle fuel with those containing nonrecycle fuel wastes. Two cases are shown, one for wastes from the plutonium fraction only, and the other for wastes from the entire reactor core (assuming that 25% of the core is plutonium fuel).

TABLE 7. Alpha Doses for Waste Glasses From UO_2 and Plutonium Recycle Wastes

Cumulative Alpha Dose, Alpha Decays/g Glass

<u>Time Since Vitrification, y</u>	<u>UO_2 Fuel Waste</u>	<u>Plutonium Recycle Fuel Waste</u>	
		<u>Pu fraction only</u>	<u>Average of entire mixed oxide case</u> ^(a)
2	1.1×10^{17}	15.4×10^{17}	4.71×10^{17}
6	1.9×10^{17}	26×10^{17}	7.9×10^{17}
10	2.5×10^{17}	38×10^{17}	11.3×10^{17}
10^2	7.1×10^{17}	109×10^{17}	32.6×10^{17}
10^3	14.6×10^{17}	174×10^{17}	54.5×10^{17}
10^4	29.5×10^{17}	333×10^{17}	105×10^{17}
10^5	61.3×10^{17}	601×10^{17}	196×10^{17}
10^6	195×10^{17}	815×10^{17}	350×10^{17}

(a) Assumes a reactor core containing
25% Pu fuel

The case representing wastes from the entire reactor core is the most likely mode of waste handling. The accumulated dose for this case is about four times larger than for the nonrecycle case during the first ten thousand years of storage.

THERMAL HISTORY PROJECTIONS

The conditions to which the high-level waste glass may be exposed in a typical handling sequence have been reported by J. E. Mendel et al.,⁽¹⁾ and are shown in Table 8. The authors indicate that some of the steps in the sequence shown in the table, including retrievable storage and perhaps transportation, may be omitted as procedures for high-level waste handling are finalized. Retrievable storage and terminal storage, for example, may turn out to be one and the same.

A considerable amount of the engineering required in the handling of high-level waste is concerned with assuring that provisions are available for properly controlling the temperature of the waste at all times. The maximum allowable temperatures during processing and storage are still being defined. Results of the waste glass characterization program are assisting in this definition.

TABLE 8. Representative Conditions to Which High-Level Waste Glass May Be Subjected⁽¹⁾

	Potential Handling Sequence	Potential Temperature Range, °C(a)	Probable Time Span	Probable Environment
Processing	Processing	50-1400	<1 week	Dynamic heating and cooling (hot cell)
Conditions	Post-processing ^(b)	50-800	<1 month	Dynamic heating and cooling (hot cell)
Storage and	Interim Storage	50-800	<30 years	Dynamic cooling (waster basin)
Transport	Transportation	50-800	<6 weeks	Shipping cask
Conditions	Retrievable Storage	20-600	<100 years	Static cooling (air convection)
Accident	Accident/Recovery ^(c)	50-1000	<8 weeks	Uncontrolled, in man's biosphere
Conditions	Nonretrievable Debris ^(c)	Ambient	∞	Uncontrolled, in man's biosphere
Disposal	Transportation	0-100	<6 weeks	Shipping cask
Conditions	Terminal Storage	0-300	∞	Uncontrolled, remote from man

(a) Includes surface and centerline extremes.

(b) Includes weighing canister, welding on canister lid, canister decontamination, and nondestructive testing, such as ultrasonic scanning, leak checking, radiation profilometry and calorimetry.

(c) Nonroutine, included for safety analysis.

HIGH-LEVEL WASTE TEMPERATURE

The temperature of high-level wastes at any given time is influenced by many factors, including:

- type of fuel elements reprocessed
- irradiation history of fuel elements
- time since reactor discharge
- efficiency of solvent extraction (determines actinide loss to waste)
- composition and physical state of waste form (determines waste loading thermal conductivity)
- canister design (diameter, cooling fins, if any, etc.)
- degree of contact between waste form and canister
- environment (engineered and natural cooling).

The temperature of high-level waste is also a combined function of self-heating due to radioactive decay and engineered cooling provided to counteract this effect. Self-heating information for the fission product waste stream from irradiated fuel elements can be obtained from computer codes such as ORIGEN.⁽¹²⁾ Self-heating sufficient to make cooling requirements a significant consideration will persist for a long time. Table 9 shows the calculated heat generation for a typical high-level waste.⁽¹⁾

TABLE 9. Thermal Power in Typical High-Level Waste

<u>Age, Years</u> <u>After Reprocessing</u>	<u>Waste from Reprocessing</u> <u>1 Metric Ton of Irradiated Fuel^(a)</u>
	<u>Watts</u>
1	8,090
10	1,090
100	115
500	4.3
1,000	2.72
10,000	0.785
100,000	0.0696
1,000,000	0.0299

^(a) Reactor power = 30 MW/MT, exposure = 33,000 MWd/MT,
0.5% fuel loss to waste, reprocessed 150 days out of reactor.

The following sections describe the control temperatures of the waste solidification process and present predicted product temperatures. These predictions were accomplished by subjecting proposed canister designs to thermal modeling, using the HEAT 4 computer program. HEAT 4 is a modified version of the HEATING program developed at Oak Ridge National Laboratory.⁽¹³⁾ The program solves steady-state and transient heat conduction problems. It features three-dimensional Cartesian and cylindrical coordinate systems, temperature-dependent properties, time- and position-dependent functions, and variable boundary conditions. The great flexibility and easy data input features of this code make it an extremely useful tool. HEAT 4 allows the use of variable thermal properties, such as thermal conductivity, density, specific heat, and internal heat generation as functions of position, temperature, and time. The thermal properties used in the model are listed in Table 10.⁽¹⁴⁾

CANISTER DESIGN

The data included in the sections which follow do not consider the effects of convection heat transfer within the canister. Due to this heat transfer effect, when the product softens and becomes mobile, actual centerline temperatures will be lower than those presented in this section. For finned canisters, the convection-type heat transfer effect is retarded until a significant portion of the glass reaches a temperature greater than 900°C.

A 12-inch diameter canister, with eight internal fins of 1/4 inch thickness each, is used for illustration in this phase of the project. A thinner fin can be used for waste greater than one year old. Eighth-inch (1/8") fins in a 12-inch diameter finned canister give a centerline temperature of 800°C in an air storage, when used with year old waste. The reference canister will not have an overpack. (Overpacking is discussed briefly in the "Interim Storage" section of this chapter.) Schedule 40 pipe is used in the canister. Other wall thicknesses may be used with little change in the overall thermal behavior of the canister. Thermal performance would be minimally changed by selecting a high-temperature metal other than the 304L stainless steel used for the computer modeling.

TABLE 10. Thermal Properties for Steady-State Analysis (14)

A. Thermal Conductivity

	BTU/hr-in-°F	W/m-°C
Glass	0.04466 at 212°	0.927 at 100°
	0.07974 at 1600°	1.655 at 871°
Stainless Steel (304L)	0.6666 at 0	13.835 at -17°
	1.0000 at 800°	20.755 at 426°
	1.1666 at 1200°	24.213 at 648°
Air	0.002050 at 500°	0.0430 at 260°
	0.002525 at 800°	0.0520 at 426°
	0.002808 at 1000°	0.0580 at 538°
	0.003450 at 1500°	0.072 at 815°

B. Boundary Conditions

Ambient air	70°F
Radiation Coefficient	0.833×10^{-11} BTU/hr-in ² -°F ⁴ ($\epsilon = 0.7$)
Convection Coefficient	$1.319 \times 10^{-3} (\Delta T)^{1/3}$ BTU/hr-in ² -°F
Storage water temperature	130°F

C. Heat Generation Rates of Simulated PW-4b Waste Glass (72-68)

BTU/hr-in ³	W/l	Approximate Age ^(a)
15.6663	280	150 days
8.3926	150	1 year (Reference)
4.3082	77	2 years
2.6856	48	3 years
1.9583	35	4 years
1.4547	26	5 years
1.2309	22	6 years
1.0071	18	7 years
0.8952	16	8 years
0.8561	15.3	9 years
0.8393	15.0	10 years

(a) Waste age reflects a reference scale assigned to a particular waste composition and is used strictly for comparative purposes.

The heat generation used for most of the illustration is 150 watts per liter, and represents the maximum heat load expected. During the first 10 to 15 years, the actual vitrification process will be conducted with relatively low-heat waste because of the backlog of stored fuel and the low burnup of early reactor cores.

Thermal histograms of the canisters are presented in Figures 9, 10 and 11. Figure 9 is a short-term (one week) graph for an in-can-melted canister. Figure 10 is a short-term graph for a canister filled from a ceramic melter. Figure 11 is a long-term, interim storage graph for all canisters after the first week. The various parts of the histograms will be described sequentially in the following sections.

FIGURE 9. Thermal Histogram of 12-Inch Diameter Finned Canister - Short-Term for ICM

FIGURE 10. Thermal Histogram for 12-Inch Diameter Finned Canister - Short-Term for Ceramic Melter

FIGURE 11. Thermal Histogram of 12-Inch Diameter Finned Canister - Long-Term for All Canisters

WASTE SOLIDIFICATION

The two waste solidification process systems included in this section are the spray calcination/in-can melter (SC-ICM)⁽¹⁵⁾ and the joule-heated ceramic melter.⁽¹⁶⁾

Melting

In the SC/ICM process, the HLW and glass formers are melted in the canister at a current design temperature of 1050°C. The moving-zone heating technique allows the cooling of the melted portion of the rising level of glass after equilibration and homogenization of the product.

In the joule-heated ceramic melter, the glass formers and HLW are equilibrated and homogenized at about 1150°C before pouring into a canister. This process does not require a finned canister for process engineering. A finned canister, however, is desirable for the storage of the young waste (one year old) modeled in this section.

Intermediate Holding Temperature

For ICM canisters, the plans are to force-gas cool the melted zone down to 900°C after turning off the heater. This temperature will be maintained until the canister is completely filled.

The ceramic melter product will be poured into canisters at ambient air temperature. The surface temperature of the filled portion of the canister will be kept below the devitrification temperature by cooling with forced gas or water. The maximum surface temperature will probably be 200°C.

Quenching

All the ICM canisters will be forced-gas quenched from 900°C to about 400°C, and then placed in water at 80°C. This cooling will result in the fracturing of some of the glass product. The thermal effects of these cracks has been investigated analytically by modeling a complete 360° glass fracture, with a gap of less than 5 mil, across which only radiation heat transfer can occur.⁽¹⁴⁾ The effect of such a crack for a 12-inch canister might be a 12°C temperature drop at the crack and 6°C rise in centerline temperature as shown in Figure 12. This analysis would represent young waste where radiation would be controlling across cracks.

FIGURE 12. Thermal Effects of Glass Cracking, 12-Inch Finned Reference Canister in Air⁽¹⁴⁾

CANISTER CLOSURE

The canister closure will be welded with the canister submerged in water to the product-fill level. The temperature distribution of the vitrified product when the reference canister is stored in water at 54°C is illustrated in Figure 13.⁽¹⁴⁾ If the canister is removed from the water storage environment and allowed to equilibrate in air at a reference ambient temperature of 21°C, the centerline temperature will increase by about 50%, as indicated in Figure 14.⁽¹⁴⁾ Increases in temperature of the ambient air above the reference temperature will increase the canister temperature by approximately 1/2°C per degree increase in air temperature, Figure 15.⁽¹⁴⁾ This latter effect, illustrating the axial thermal gradient at the canister outer surface due to convection, is not expected to be a major product degradation problem.

An alternate procedure would be to weld the canister in air. Surface emissivity is the controlling heat transfer variable for air cooling. The emissivity may vary from a low value of 0.2, representing non-oxidized surfaces, to a value of 0.7, assumed for the oxidized reference canister.⁽¹⁴⁾

FIGURE 13. Temperature Distribution, 12-Inch Diameter Reference Canister in Water⁽¹⁴⁾

FIGURE 14. Thermal Performance of 12-Inch Diameter Reference Canister⁽¹⁴⁾

FIGURE 15. Effects of Ambient Air Temperature
12-Inch Finned Reference Canister(14)

Figure 16 shows the effect of surface emissivity on air-stored canister temperature. For one year old waste and low surface emissivity, the centerline temperature of a 12-inch finned canister would be 750°C when the canister surface is cooled by 21°C air.

INSPECTION

The canister closure will be vacuum leak checked with the canister partially submerged in water. The vacuum environment will be applied at the closure weld area only. Leaks will be detected by monitoring for helium escaping from the canister, the helium having been added during welding. The welds will be inspected underwater by ultrasonic testing.

Some quality assurance measurements, i.e., dimension checking, weighing, calorimetry, etc., may be done in air. Surface emissivity and age of waste will determine the canister centerline temperature.

FIGURE 16. Effects of Surface Emissivity, 12-Inch Finned Reference Canister in Air(14)

DECONTAMINATION

The two decontamination procedures currently being appraised are high pressure water-steam and electropolishing. In the water-steam process the canister will be in an ambient air environment during the decontamination. This process will clean the canisters of smearable contamination. In the electrochemical process the canister will be electropolished in a cooled electrolyte and rinsed in an ambient temperature water tank. This process will clean the canisters of total surface contaminants.

INTERIM STORAGE

The interim storage shall be water storage. During water storage it is assumed that the canister surface can be maintained at 54°C.

The performance of the canister-overpack option is seen in Figure 17. The glass centerline temperature is higher by 100°C for the overpacked canister than for the reference canister because of the large temperature

drop occurring between the canister and overpack surfaces. The overpack surface temperature is lower than the reference canister because of the larger surface area. By using other than standard size pipe for the overpack, these temperature differences can be adjusted slightly. Since the principal heat transfer modes across the canister-overpack gap are radiation and convection, the centerline temperature of the overpack design is relatively insensitive to the dimensions of this gap.

FIGURE 17. Temperature Distribution for 12-Inch Canister, with 16-Inch Overpack and Suspended Fins, in Air

FEDERAL REPOSITORY - SALT MINE

As related at the National Waste Terminal Storage Program Information Meeting: "The salt and waste criteria stipulate that, in the 10-ft-thick horizontal layer of salt in which the waste cylinders are buried, no more than 1% of the salt will be allowed to have a temperature in excess of 200°C".⁽¹⁷⁾ By this criteria, the maximum surface temperature of the canisters may exceed 250°C. An estimate of the maximum surface temperature of a waste canister in a salt mine repository is shown in Figure 18. The

maximum centerline glass temperature will be about 490°C in a 12-inch canister. As shown in the figure, about 10 years may be required to reach this temperature. Then, the temperature will gradually decrease at a rate governed primarily by the 30 year half-lives of ^{90}Sr and ^{137}Cs .

FIGURE 18. Surface Temperature of Canister in Maximum Heat Density Array in Salt Mine(17)

BULK PROPERTIES OF WASTE GLASSES

Bulk properties of waste glass are important considerations from the engineering point of view. Knowledge of these properties is required to determine waste handling and process requirements, and the design of the waste package.

GENERIC PROPERTIES

Many of the bulk properties are not highly sensitive to composition and, therefore, can be determined on a generic basis rather than for specific compositions. Those properties that can be dealt with generically are impact behavior, thermal shock resistance, and thermal conductivity. Other properties, such as density and viscosity, are more compositionally dependent and will be discussed later in this chapter.

Impact Behavior

A detailed report⁽¹⁸⁾ has been prepared on impact behavior of annealed canisters of waste glass. Two of the report's most important results are illustrated in Figures 19 and 20. Figure 19 shows the effects of impacts on the surface area of one-half and one-sixth scale canisters, as a function of impact velocity. Figure 20 shows the effects impacts have on generation of $<10\mu$ particles.

Future tests will attempt to verify that impact behavior can be treated in a generic sense, and will specifically try to determine how impact behavior is affected by composition and residual crystalline material in the glass.

Thermal Shock Resistance

Thermal shock is expected for canisters of glass during their cooling. The effect of thermal shock on a 72-68 [PW-4b-2 (3.0) 73-1] waste glass in a 6 inch diameter canister has been determined,⁽¹⁹⁾ and is shown in Figure 21. This figure indicates that surface area will increase by about a factor of 10 due to air cooling.

FIGURE 19. Fraction Increase in Geometric Surface Area

FIGURE 20. Prediction Curves for Sub-10μ Fine Generation

FIGURE 21. Effect of Cooling Rate on the Generation of Increased Surface Area in 6 in. Diameter Glass Castings

A secondary thermal cracking of the glass will occur with time. This cracking is due to the thermal gradient decrease in the canister, which results from decay of the major heat producers. This decrease in gradient will generate sufficient stress to crack the glass. The cracking can be expected to be a function of initial thermal power in the canister, the fin and canister design, the storage conditions, and the position of the glass within the canister. Since the temperature distribution within a cylinder of uniform heat generation is parabolic, the major stress would be expected to occur near the canister walls, where the glass is already cracked from thermal shock. Additional cracking will, therefore, be limited. Further tests of this behavior are planned for the next year.

It is recognized that the thermal shock sensitivity of a waste glass will be dependent on the thermal expansion coefficient, thermal conductivity and heat capacity of the glass. Variations in these properties for different waste glasses, however, have been quite small.

Thermal Conductivity

Thermal conductivity measurements for representative waste glasses have been quite limited. A set of data for a 72-68 [PW-4b-2 (3.0) 73.1] glass is shown in Table 11. These data correspond to typical glasses at low temperature. Unlike commercial glasses, however, the waste glasses have very poor radiant heat conductivity at higher temperatures. This is because the waste glasses contain a large amount of transition metal oxides, which make the glasses opaque. Higher temperature data for high-level waste canisters from the WSEP program⁽²⁰⁾ is shown in Figure 22. The rapid increase in conductivity above 700°C is due to convection in the melts and can be expected to be a function of the viscosity of each specific glass. The data in Table 11 and Figure 22 agree within 10%.

TABLE 11. Thermal Conductivity of Waste Glass 72-68

<u>Temperature °C</u>	<u>Thermal Conductivity (W/m °C)</u>
25	0.84
211	1.05
403	1.21

FIGURE 22. Effective Thermal Conductivity of In-Can Melting Process Borosilicate Glass

Homogeneity

Detailed examination of engineering-scale melts has indicated that canisters of in-can melted glass are not completely homogeneous. Principal inhomogeneities include porosity, insoluble materials, and, on occasion, Na_2MoO_4 . (Sodium molybdate control was discussed earlier in "Glass Formulation Development.") Bubbles rise to the top of the melt and, as they do, insoluble particles often attach themselves to the bubbles and rise with them, even though the particles may have a higher density than the glass.

The porosity distribution (residual bubbles) in two in-can melted canisters is shown in Figure 23. The ICM-16 composition [PW-7a-2 (2.0) 75-75 + 1.5 wt% Si]] and the ICM-18 composition [PW-8a-2 (2.0) 75-75 + 1.5 wt% Si]] represented in this figure are not reference compositions.

FIGURE 23. Closed Porosity Distribution in In-Can Melted Glass Canisters

The residual insoluble particles have made the top 2 to 3 1/2 inches of the ICM-18 rich in Mo, Sr, Zr, and Fe. Residual materials have also been observed to settle to the bottom of canisters. Because CeO_2 has limited solubility when reducing agents are not used, it is present in higher concentrations (see Table 1 in the Glass Formulation chapter), and therefore has been observed to settle in engineering-scale melts. When reducing agents are used, the CeO_2 is reduced to Ce_2O_3 , which has greater solubility, and settling does not occur. Oxidized stainless steel spall has also been noted on the bottom of ICM-16. With all separations noted and tested, however, the leach rate of the material in question has not been significantly higher, and in the case of CeO_2 -rich regions, is actually lower.

COMPOSITIONALLY SPECIFIC PROPERTIES

Property data for the four study glasses is shown in Table 12. As indicated, 72-68 is considerably different from other glass types. Its higher

density results from the high ZnO content. The glass volume is lower for 76-68 and 76-375 since the inert and actinide content is much lower in the PW-4b waste than in other wastes. The 72-68 also has two ranges of thermal expansion coefficient. Though not yet determined, the specific heat of the other glasses is expected to be slightly higher than that of 72-68, due to their lower density.

TABLE 12. Compositionally-Dependent Properties for Four Glasses

	<u>72-68</u>	<u>76-68</u>	<u>76-183</u>	<u>76-375</u>
Density (°/cc)	3.4	3.0	3.1	3.1
Glass Volume (ℓ/MTU)	43	93	73	39
Melting Temp.* (°C)	935	1050	1040	ND
Softening Point (°C)	543	566	568	ND
Transition Point (°C)	512	513	ND	ND
Thermal Expansion } Coefficient (10 ⁻⁷ /°C) }	79 (30-33°C) 100 (330-500°C)	90 (30-400°C)	93 (30-400°C)	ND
Specific Heat	.16-.185	ND	ND	ND

* Temperature at which viscosity is 200 poise.

N.D. - Not Determined

Electrical Conductivity

Electrical conductivity is most important for design of the ceramic melter system, which uses the conductivity of the glass for self-heating. As expected, conductivity proved to be a strong function of temperature. The data for the 72-68 [PW-4b-2 (3.0) 73-1] glass are shown in Figure 24. Data are not yet available on other glasses.

Canister Corrosion

Consideration of canister corrosion by molten glass and vapor is important to the in-can melting process, since corrosion rates are approaching values which could be significant. Typical values for corrosion of 304L stainless steel by 72-68 type waste are shown in Figure 25. More details on corrosion are available in a recent report.⁽²¹⁾

FIGURE 24. Electrical Conductivity of Molten Waste Glass 72-68 [PW-4b-2 (3.1) 73-1] at 40 and 1000 Hz

FIGURE 25. Corrosion of 304L Stainless Steel by 72-68 Type Glass

Volatility

Some waste elements, particularly alkalis, can be vaporized at higher temperatures. The volatility of glass components from a melted glass have been determined.⁽²²⁾ Typical results are also shown in Figure 26 for a 72-68 [PW-4b-5 (2.8) 73-1] glass. The results, reflecting a total of 4 hours at temperature, show that Cs is the major volatilized species and that total volatility increases exponentially with temperature.

FIGURE 26. Volatility From a 72-68 [PW-4b-6 (2.8) 73-1] Glass in 4 hr

ENVIRONMENTAL REACTIONS OF WASTE GLASS

Conditions under which glass might be in contact with environments other than the canister include breach of the canister in an accident, leakage of the canister during storage in a water basin, or deterioration of the canister while in geologic storage. Water and aqueous solutions are the most potentially harmful substances with which the glass could come in contact in each of these situations. Water leaches the radioactive species from the glass, increasing the chance of dispersal to the biosphere. It is therefore necessary to measure the resistance of glass to chemical attack by water and aqueous solutions. This measurement is typically made by leach testing.

LEACH TEST METHODS

Four leach tests are used at PNL to evaluate the chemical durability of waste glasses. These include an acid-base test,⁽²³⁾ the Soxhlet^(24,25) and Paige⁽²⁵⁾ tests, and a long-term test modeled after the proposed IAEA Standard Leach Test.⁽²⁶⁾

Acid-Base Leach Test

Naturally occurring ground waters have pH's which rarely exceed a range from 4 to 9. The acid-base leach test examines glass durability at the extremes of this pH range. With this test, glass crushed to -42 + 60 mesh is leached 19 hours in an ammonium hydroxide buffer of pH 9, followed by an additional 19 hour leach in an acetate buffer of pH 3.9. Both solutions are at ambient temperature. After exposure to the buffered solutions, the glass is leached 24 hours at 99°C in the Soxhlet apparatus. Weight loss is measured after each phase of the test and the results are reported as percent weight loss.

Standard Soxhlet Leach Test

In the standard Soxhlet leach test, crushed glass screened to -42 + 60 mesh is exposed for three days to continuously distilled water at 99°C. The Soxhlet apparatus is diagrammed in Figure 27.

FIGURE 27. Soxhlet Leach Test Apparatus

The high temperature used in the Soxhlet test is more typical of the temperatures waste glasses will experience in early storage than is room temperature. This test gives an indication of leachant temperature effects on glass durability. The leach rates are reported as percent weight loss in 72 hours.

Paige Leach Test

The Paige test is used to predict the long-term leaching behavior of waste glasses. It is also used to measure the effects of leachant temperature on glass leach rates. Figure 28 shows the Paige apparatus. Crushed or bulk glass is leached in recirculating distilled water. Temperature is maintained using heating mantles. The leachant is changed daily or weekly during the first portion of the test, and at longer time intervals thereafter. The solutions are analyzed for chemical elements leached from the glass. These data are used to calculate leach rates in weight percent and in grams glass leached per square centimeter per day ($\text{g}/\text{cm}^2\text{-d}$).

FIGURE 28. Paige Leach Test Apparatus

Long-term Leach Test

To predict the chemical durability of waste glasses in geologic storage, long-term leach rates must be determined. This is achieved at PNL using a long-term leach test modeled after the proposed IAEA leach test procedure.⁽²⁶⁾ Crushed (-42 + 60 mesh) or bulk glass samples are leached in deionized water at room temperature. The leachant is changed daily for the first week, weekly for the following eight weeks, once a month for six additional months, a semi-annually thereafter. The leachant is analyzed for constituents of the glass and the leach rates are reported as grams glass leached per square centimeter per day ($\text{g}/\text{cm}^2\text{-d}$).

LEACH RATE CALCULATIONS

Leach rates are reported either as percent weight loss per unit time, or as grams glass leached per unit surface area per unit time. Percent weight loss is calculated in accordance with the following formula:

$$\% \text{ weight loss} = \frac{W_o - W_f}{W_o} \times 100$$

where W_o = initial weight of the glass

W_f = the final sample weight

Leach rates expressed in grams/cm²-d are calculated from the equation:

$$\text{leach rate} = \frac{A_t}{A_o} \frac{W_o}{St}$$

where

A_t = amount of ion removed in time t

A_o = initial amount of ion

S = surface area of specimen (cm²)

t = leach period (days)

Leach rates expressed as percent weight loss for samples crushed to -42 + 60 mesh may be converted to leach rates expressed as grams/cm²-d by using the relationship:

$$\begin{aligned} \text{Leach Rate (g/cm}^2\text{-d)} &= \text{Leach Rate (\% wt loss)} \times 3.85 \times 10^{-5} \\ &\times 1/\text{leach period (days)} \end{aligned}$$

The conversion is based on a BET surface area measurement of one gram of -42 + 60 mesh glass. The surface area was measured to be 260 cm²/gram.

A method of expressing long-term leach data is cumulative penetration, i.e., the theoretical thickness of glass from which the ion of interest has been leached completely away. Cumulative penetration is calculated from the equation:

$$\text{cumulative penetration} = \frac{\sum A_t}{A_o} \frac{V}{S}$$

where V is the volume of the glass sample.

REFERENCE GLASS LEACH DATA

The reference glass (72-68) has undergone extensive leach testing. Both laboratory and engineering-scale preparations have been characterized. Additional leach data have been obtained through the accelerated alpha effects study and the thermal effects study.

Acid-Base Leach Test Results

Table 13 lists the results of the acid-base leach test for reference glass [PW-4b-6 (2.8) 73-1], indicating its poor acid-base durability. More durable glasses have been since developed, as will be described later in this chapter.

TABLE 13. Acid-Base Leach Rates for the Reference Glass

	<u>% Weight Loss</u>	<u>g/cm²-d</u>
pH 9.0	3.59 in 19 hours	1.74×10^{-4}
pH 3.9	93.4 in 19 hours	4.53×10^{-3}

Soxhlet Leach Test Results

Table 14 lists Soxhlet leach test results for laboratory⁽²⁷⁾ and engineering-scale⁽¹⁰⁾ glass melts. Within the precision of the measurements, there is no difference between the two glasses yielded by these melts. The high leach rate for the top sample of ICM-3 is related to the formation of a leachable molybdate phase which collected on top of the melt.

Extensive Soxhlet data has been generated in the thermal effects studies.⁽²⁸⁾ Devitrification and phase separation effects due to extended storage at temperatures between 300 and 900°C cause Soxhlet leach rates to increase by a factor of ten. Figure 29 illustrates this effect. Leach rates are plotted as a function of the storage temperature for the reference glass stored two months. Data obtained for other storage periods are listed in Table 15. The values in the table are averages of three measurements. Maximum leach rates for a given thermal storage period result from changes in the glass matrix caused by the formation of (Ca, Sr, Ba) molybdate and Zn_2SiO_4 in the glass (see the following chapter).

TABLE 14. Reference Glass Soxhlet Leach Rates for Laboratory and Engineering-Scale Melts

	<u>% Weight Loss</u> <u>72 hours</u>	<u>g/cm²-d</u>
Laboratory-Scale		
PW-4b-1 (2.8) 73-1	0.57	7.30×10^{-6}
Engineering-Scale		
PW-4b-2 (3) 73-1		
ICM-2	1.17	1.50×10^{-5}
ICM-3 Top	2.66	3.40×10^{-5}
Middle	0.93	1.19×10^{-5}
Bottom	0.79	1.01×10^{-5}
ICM-4 Middle	0.69	8.83×10^{-6}
Bottom	0.62	7.94×10^{-6}

FIGURE 29. Soxhlet Leach Rate for the Reference Glass Stored 2 Months

TABLE 15. Soxhlet Leach Data^(a) for the Reference Glass

Storage Temperature °C	Storage Period				
	2 Hours	1 Day	1 Week	2 Months	1 Year
1100	0.78				
1050	0.66				
1000	0.72				
900		0.92	1.20	0.46	
800		1.09	0.89	0.96	
750		0.47	2.30	2.37	
700			2.33	4.30	4.50
600			2.43	3.60	7.50
500				0.69	0.74
400				0.45	0.53
300				0.20	0.42

(a) Leach rate in % weight loss in 72 hours.

Paige Leach Test Results

The Paige test was used to measure leach rates for the reference glass as a function of the leachant temperature.⁽²⁹⁾ Figure 30 shows average leach rates for the reference glass and for a bottle glass. For comparison, the Soxhlet leach rates for both glasses are included in the graph. From the data it may be concluded that the reference glass leachability is not as temperature-dependent as that of the bottle glass. Though not a linear relationship, the leach rate of the reference glass increased by a factor of 15 from 25° to 100°C leachant temperature.

Long-Term Leach Test Results

Reference glass preparations used in the thermal effects study⁽²⁸⁾ and the accelerated alpha effects study⁽³⁰⁾ have been leached for extended periods using the long-term leach test.

FIGURE 30. Leach Rate vs Leachant Temperature for the Reference Glass

Cesium and strontium behavior have been monitored to obtain long-term leach rates for the reference glass samples used in the thermal effects studies. Leach rate curves for the as-formed glass (1000°C for 2 hours) and for devitrified reference glass (700°C for 2 months), based on cesium and strontium measurements, are shown in Figures 31 and 32 respectively. In concurrence with data obtained from the Soxhlet test, the curves illustrate that devitrification effects at 700°C increase the leachability of the reference glass by a factor of ten. The two figures also show that after an initial drop, the leach rates remain relatively constant with time. Tables 16 and 17 list average long-term leach rates over a period from 28 to 203 days.

FIGURE 31. Leachability of Simulated HLW Glass, Normalized to Cesium Behavior

FIGURE 32. Leachability of Simulated HLW Glass, Normalized to Strontium Behavior

TABLE 16. Long-Term Leach Data^(a) Based on Cesium Behavior for the Reference Glass

STORAGE TEMPERATURE °C	STORAGE PERIOD			
	2 HOURS	1 DAY	1 WEEK	2 MONTHS
1100	2.90×10^{-7}			
1050	3.12×10^{-7}			
1000	2.00×10^{-7}			
900		1.51×10^{-7}	1.35×10^{-7}	1.62×10^{-7}
800		2.04×10^{-7}	1.96×10^{-7}	2.13×10^{-7}
750		2.13×10^{-7}	3.17×10^{-7}	4.07×10^{-7}
700			2.46×10^{-7}	2.44×10^{-6}
600			2.40×10^{-7}	3.66×10^{-7}
500				2.61×10^{-7}
400				1.40×10^{-7}
300				1.88×10^{-7}

(a) Leach rate in $\text{g/cm}^2\text{-d}$

TABLE 17. Long-Term Leach Data^(a) Based on Strontium Behavior for the Reference Glass

STORAGE TEMPERATURE, °C	STORAGE PERIOD			
	2 HOURS	1 DAY	1 WEEK	2 MONTHS
1100	2.35×10^{-7}			
1050	2.38×10^{-7}			
1000	1.61×10^{-7}			
900		1.23×10^{-7}	1.10×10^{-7}	1.30×10^{-7}
800		1.22×10^{-7}	1.22×10^{-7}	1.29×10^{-7}
750		1.51×10^{-7}	1.85×10^{-7}	3.19×10^{-7}
700			1.45×10^{-7}	1.15×10^{-6}
600			2.29×10^{-7}	2.83×10^{-7}
500				2.02×10^{-7}
400				1.18×10^{-7}
300				1.59×10^{-7}

(a) Leach rate in $\text{g/cm}^2\text{-d}$

When long-term leach data are calculated as cumulative penetration, and are plotted as a function of the total time leached, curves similar to those shown in Figures 33 and 34 are generated. Figure 33 shows the cumulative penetration of vitreous and devitrified glass based on cesium; Figure 34 shows the results based on strontium. The linear relationships demonstrated in these figures gives an indication of the mechanism involved in the leaching process and may be used to make long-range estimates of the amount of material leached from the glass.

For a log cumulative penetration vs log time line, a slope of one indicates a corrosion mechanism, while a slope of one-half suggests a diffusion-controlled leaching of the glass. Slopes between these extremes indicate that both mechanisms are in operation. Thus, Figures 33 and 34 show that devitrification changes the glass such that it "leaches" mainly by corrosion, while attack of the vitreous glass is mainly by a true leaching mechanism.

Extrapolation of the lines shown in these same two figures to 1000 years gives an estimate of the depth of leaching over that time period. Based on cesium, it is estimated that the equivalent of one millimeter of the diameter of the glass would have been leached from the devitrified glass over 1000 years, and the vitreous glass would have been penetrated less than a tenth of a millimeter. Extrapolation of cesium data beyond 1000 years is not appropriate since in actual high-level waste glass the cesium will have decayed away by that time.

Because the frit used to make the reference glass contains stable strontium, the cumulative penetration data can be extrapolated to time periods longer than 1000 years. After 100,000 years, the devitrified glass is estimated to have been penetrated one centimeter, and the vitreous glass less than a millimeter. These extrapolations are given only as indications of the apparent long-term durability of the waste glass in a situation in which the glass comes in contact with very slowly moving water at 25°C. Many complexities are involved in such extrapolations and much more analysis will be required before the extrapolations can be made with confidence.

FIGURE 33. Cumulative Penetration of Vitreous and Devitrified Glass, Based on Cesium

FIGURE 34. Cumulative Penetration of Vitreous and Devitrified Glass, Based on Strontium

NFS GLASS LEACH DATA

Table 18 lists the leach data obtained for the NFS glass. While this glass has a higher Soxhlet leach rate than the reference glass, it is significantly more resistant in the acid-base test. In the long-term test, the reference and NFS glasses have similar leach rates.

TABLE 18. NFS Glass Leach Data

	<u>% Weight Loss</u>	<u>g/cm²-d</u>
Soxhlet Leach Test		
PW-8a-3 (2.0) 76-101	5.80 in 72 hours	7.42×10^{-5}
Acid-Base Leach Test		
PW-8a-1 (2.0) 76-101		
pH 9.0	0.11 in 19 hours	5.34×10^{-6}
pH 3.9	0.03 in 19 hours	1.46×10^{-6}
Soxhlet	1.61 in 24 hours	6.18×10^{-5}
Long-Term Leach Test		
PW-8a-1 (2.0) 76-101		
Based on Cesium		2.04×10^{-7}
Based on Strontium		1.84×10^{-7}

AGNS GLASS LEACH DATA

Table 19 lists the acid-base leachability for the AGNS glass (76-183). This composition has high acid and base durability.

TABLE 19. AGNS Glass [PW-7a-1 (2.0) 76-199] Leach Data

	<u>% Weight Loss</u>	<u>g/cm²-d</u>
Acid-Base Leach Test		
pH 9.0	0.15 in 19 hours	7.28×10^{-6}
pH 3.9	0.15 in 19 hours	7.28×10^{-6}
Soxhlet Leach Test	1.38 in 24 hours	5.30×10^{-5}

EXXON GLASS LEACH DATA

Acid-base leach rates of the EXXON glass (76-375) are shown in Table 20. Similar to the AGNS and NFS glasses, the EXXON glass has excellent acid-base durability.

TABLE 20. EXXON Glass [PW-4b-1 (2.0) 77-62] Leach Data

	<u>% Weight Loss</u>	<u>g/cm²-d</u>
Acid-Base Leach Test		
pH 9.0	0.10 in 19 hours	4.85×10^{-6}
pH 3.9	0.61 in 19 hours	2.96×10^{-5}
Soxhlet Leach Test	1.45 in 24 hours	5.57×10^{-5}

PHASE BEHAVIOR

Two characteristics which distinguish nuclear waste glasses from commercial glasses are:

- Waste glasses must incorporate an unusually large number of elements.
- Because of the radioactive decay of some elements, waste glasses are self-heating.

These two characteristics can lead to heterogeneity in waste glass. Calcine constituents such as Pd and RuO_2 , for example, are difficult to dissolve in silicate melts, and remain suspended in the glass as micron-sized particles. As a result of prolonged self-heating at certain temperatures, other phases may separate as crystalline or liquid species, with corresponding changes in the chemical and physical properties of the glass.

In the phase behavior task of the waste glass program, both as-formed and devitrified (i.e. partially crystallized) glasses are examined. All discrete phases, as outlined in Figure 35, are identified with respect to stoichiometry, crystal structure, and concentration, as functions of time and temperature. These data are useful in defining the time and temperature limits that should be maintained during and after vitrification. The data also contribute to an understanding of factors such as leach behavior and the effects of radiation damage.

REFERENCE GLASS

The results reported here for the reference glass (72-68) show that ingrowth kinetics and the establishment of "steady-state" phase concentrations follow expected trends. Major devitrification products are a Zn_2SiO_4 and a Sr-molybdate phase. Zinc silicate (Zn_2SiO_4) crystals cause some micro-cracking of the glass because of a mismatch of the thermal expansion with the glass matrix. The molybdate, $(\text{Ca}, \text{Sr}, \text{Ba}) \text{MoO}_4$, is found to have a greater water solubility than the glass. Other phases present appear to have a smaller impact on reference glass properties.

FIGURE 35. Outline of Phase Behavior Studies

The annealing schedule used in the present work includes temperatures of 300-1000°C and annealing times up to one year. Leaching data for the glasses studied is reported in the previous chapter. Table 21 lists the observed phases in glass 72-68, and gives maximum concentrations for each phase after one-year anneals, along with other pertinent data.

The major devitrification products are Zn_2SiO_4 , $(\text{Ca}_{0.25}\text{Sr}_{0.50}\text{Ba}_{0.25})\text{MoO}_4$, and an apatite phase, $\text{Ca}_2(\text{RE}^{3+})_8(\text{SiO}_4)_6\text{O}_2$. Typical x-ray fluorescence maps of a devitrified glass are shown in Figure 36, where major constituent elements are correlated to microstructure. Figure 37 shows a 400X micrograph of a devitrified glass, with each of the phases present clearly identified. Microprobe analyses of all crystalline species are being performed, as well as qualitative analyses of the glass matrix for elements known, or expected to participate as devitrification products. In general, x-ray diffraction has

TABLE 21. Crystalline Phases in Glass 72-68

	wt% in Melt, 1000°C	wt% After 1 Year, 700°C	Structure/Lattice Constants	Maximum Crystal Size, μm
RuO_2	1.4	1.4	tetragonal $a_0 = 4.50 \text{ \AA}$ $c_0 = 3.10 \text{ \AA}$	1
Pd	1.0	1.0	cubic $a_0 = 3.90 \text{ \AA}$	10
$(\text{Zr, Ni})(\text{Fe, Cr})_2\text{O}_4$	trace	trace	cubic ---	50
$(\text{Ce, Zr, RE}^{3+})\text{O}_{2-x}$	5	5.0	cubic $a_0 = 5.39 \text{ \AA}$	5
Zn_2SiO_4	0	14	hexagonal $a_0 = 13.97 \text{ \AA}$ $c_0 = 9.30 \text{ \AA}$	500 x 100
$(\text{Ca, Sr, Ba})\text{MoO}_4$	0	6.0	tetragonal $a_0 = 5.38 \text{ \AA}$ $c_0 = 12.03 \text{ \AA}$	100 x 2
$\text{Ca}_2(\text{RE}^{3+})_8(\text{SiO}_4)_6\text{O}_2$	0	3.0	hexagonal $a_0 = 9.54 \text{ \AA}$ $c_0 = 7.16 \text{ \AA}$	500 x 100

proven to be the most reliable and sensitive measure of phase concentrations after behavior is qualitatively understood. Figure 38 shows typical x-ray diffraction patterns of as-prepared and devitrified glasses. With the exception of one very small peak, all of the diffraction pattern can be accounted for. In this figure, patterns for "vitreous" and devitrified glasses have not been normalized. As a point of reference, both samples contain 1.4 wt% RuO_2 . Reflections indexed for the vitreous glass are left unlabeled for the devitrified glass.

Long-Term Anneals (72-68)

The matrix indicating times and temperatures for long-term isochronal anneals is presented as Tables 15 - 17 in the preceding chapter, and is the basis of the work described here. From this time-temperature matrix, data have been generated showing the rate at which all phases present in the reference glass approach steady-state concentrations.

FIGURE 36. Concentration of Selected Elements in Devitrified Glass 72-68

100 μm

① Zn_2SiO_4	④ $\text{Ca}_2(\text{RE}^{3+})_8(\text{SiO}_4)_6\text{O}_2$
② SrMoO_4	⑤ Pd metal
③ $\text{RuO}_2; \text{CeO}_2$	⑥ Rh

FIGURE 37. Micrograph of Glass 72-68 Showing Crystalline Phases After Annealing One Year at 700°C

FIGURE 38. X-Ray Diffraction Patterns of As-Prepared (Vitreous) and Devitrified Glasses

From free energy considerations, it is expected that some phases may partially crystallize at temperatures below their liquidus temperatures. Liquidus temperature, which varies for each compound, is that temperature above which the compound completely dissolves in the glass. Figure 39 shows the observed crystallization behavior of Zn_2SiO_4 for glass 72-68. At 800°C, equilibrium concentrations of Zn_2SiO_4 are established in about a day. It is clear that temperature is particularly important to crystal formation near the glass softening temperature (543°C), below which kinetics become very slow. No crystallization occurs in this glass at temperatures of 500°C and lower even after one year of annealing.

FIGURE 39. Observed Crystallization Behavior of Zn_2SiO_4 for the Reference Glass

Figure 40 shows similar data for the molybdate phase, plotted as wt% versus temperature for the various isochronal periods. In this case, crystallization behavior is not as regular, since molybdate concentrations for the 2 month and the 1 year periods are lower than those for the shorter periods. The concentration decreases result from competition for calcium by the late formation of a calcium-containing, rare-earth apatite phase. This is clearly seen by the x-ray diffraction pattern shown in Figure 41. The molybdate reflection decreases in intensity and moves to lower angles (larger lattice constants) as the stoichiometry shifts in the direction of higher Sr and Ba content (i.e., larger cations). This figure also shows that the CeO_2 and RuO_2 phases remain invariant with time.

FIGURE 40. Observed Crystallization Behavior of the Molybdate Phases for the Reference Glass

FIGURE 41. Ingrowth of Calcium-Containing Apatite Phase and Corresponding Change in (Ca, Sr, Ba) MoO_4

Figure 42 plots fractional ingrowth data (estimated from equilibrium concentration) against temperature curves ($\ln F$ versus $1/T$) for both the silicate and molybdate short period phases. The slope is approximately $\Delta H^\circ/2R$ in both cases, yielding heats of crystallization that are of expected magnitude. The liquidus temperatures ($\ln F = 0$) are 1000°C and 890°C for the zinc silicate and molybdate phases, respectively.

FIGURE 42. Fractional Ingrowth and Estimates of Heats of Crystallization for Zn_2SiO_4 and $(\text{Ca, Sr, Ba})\text{MoO}_4$

Kinetics (72-68)

Figure 43 shows that, in general, the growth rate for zinc silicate crystals follows regular sigmoidal ingrowth curves; Zn_2SiO_4 equilibrium concentrations reached in the laboratory are in reasonable agreement with those established in the longer-term annealing studies. The details of sample preparation, such as vitrification temperature, crucible type, and sample morphology, however, have significant influence on data obtained. The present equilibrium data must, therefore, be regarded as qualitative with respect to full-scale (as opposed to laboratory-scale) melts.

FIGURE 43. Short Time Ingrowth of Zn_2SiO_4 Phase

Figure 44 compares several sets of data on 50% fractional ingrowth for frit 73-1 and for waste glass 72-68. The slopes, which give the effective activation energy for nucleation and growth, are reasonably constant ($E \sim 40\text{Kcal/mole}$) for three of the four lines drawn. When extrapolated to lower temperatures,

FIGURE 44. Times Required for 50% Fractional Ingrowth of Zn_2SiO_4

the data suggests that a period of 2 years or more would be required to form measurable quantities of Zn_2SiO_4 at 500°C . At 200°C , which is admittedly a very long extrapolation, about 10^6 years could yield measurable concentrations. At higher temperatures (700 - 900°C) significant crystal yields are observed in a day.

NFS WASTE GLASS

As work is now nearing completion on the reference zinc-borosilicate waste glass (72-68), characterization has begun on NFS waste glass (76-68).

Figure 45 compares the x-ray diffraction pattern for devitrified 72-68 glass to that of 76-68 glass prepared under comparable conditions. The new glass appears to have good devitrification stability, with only small crystals of simple oxides (RuO_2 , Fe-spinel, $(\text{Ce,U})\text{O}_2$, and Pd) having formed. These crystals are expected to resist radiation damage and have low leachability. The as-prepared 76-68 glass has low concentrations of Pd, RuO_2 , and the M_3O_4 spinel. The fluorite-type phase, $(\text{Ce,U})\text{O}_2$, which may also concentrate other actinides (causing nonhomogeneous radiation damage), appears to be dissolved in 1050°C melts, in contrast to glass 72-68 where a temperature of 1200°C was required for dissolution. The limited data now available for anneal times up to two months continues to show comparatively low crystal yields. The undesirable Zn_2SiO_4 and SrMoO_4 phases observed in the reference glass have not been detected in the NFS glass. No microcracking has been observed, nor have any phases been identified which might be expected to have an increased water solubility. With respect to thermal behavior, glass 76-68 clearly demonstrates improved stability.

FIGURE 45. X-Ray Diffraction Traces Comparing Devitrified 76-68 Glass and 72-68 Glass

EFFECTS OF RADIATION ON WASTE GLASS

Theory and experimentation concur that the most damaging radiation in nuclear waste results from alpha recoil-nuclei. Alpha particles contribute to radiation damage to a lesser, but significant, extent. Beta and gamma radiation produce relatively small amounts of damage. Neutrons and fission recoils, because of their low fluxes in the waste, are also relatively non-damaging. Therefore, our experiemntal studies on the effects of radiation on waste glasses focus mainly on alpha damage.

ACCELERATED ALPHA EFFECTS EXPERIMENTS

Radiation effects are produced in test specimens that incorporate ^{244}Cm , an alpha emitter with a half-life of 18.1 years. This testing allows us to simulate in a few months or years the damage that would be produced in actual waste glasses over thousands of years. The net accumulation rate for radiation-induced defects in waste glass depends on defect formation rates and rates of defect recombination or stabilization reactions. These rates are affected by temperature, dose rate and type of radiation. Through the use of ^{244}Cm in accelerated tests, simulation of all these factors except dose rate can be attained. The effect of dose rate can only be approximated since very high dose rates must be used in accelerated tests.

Stored Energy

Radiation-induced defects in waste glass can be eliminated by annealing the glass. This annealing process results in a net release of energy commonly referred to as stored energy. Stored energy is a concern in the management of high-level wastes because of the potential hazards associated with its uncontrolled release in the form of heat. Therefore, the magnitude, rate of buildup, and release characteristics of stored energy in waste glasses need to be known and understood so that the safety of transportation, interm storage and final disposal of solidified waste may be fully evaluated. Stored energy is also a measure of radiation damage and, as such, is a useful indicator of the stability of various glass forms under study in the characterization program.

Experiments have been carried out to determine the rate of buildup of stored energy as a function of alpha dose, the effect of temperature on that buildup, and the rate of the energy's release on heating. Alpha decay was selected as the radiation for these studies because it is expected to be the main source of damage in actual waste glasses. Three glasses have been included in the accelerated alpha effects study to date, 1) glass 72-68 (a zinc borosilicate glass), 2) a lead borosilicate glass, and 3) a high-silica glass typical of some European formulations. The irradiations of the specimens were carried out by incorporating ^{244}Cm in the melt and storing the specimens for the times required to accumulate the desired alpha doses. The amount of stored energy released was measured by differential scanning calorimetry. Details of the experimental approach are described in another report.⁽³¹⁾

The buildup of stored energy with increasing alpha doses is shown for the three glasses in Figures 46, 47 and 48. These glasses behave similarly. In each case the buildup increases rapidly up to 17-20 cal/g, and then begins to level off. As indicated in Figure 46, although the damaging effects appear to be approaching saturation at high alpha doses, the stored energy is still increasing slowly at alpha doses of 2.5×10^{18} alphas/g.

FIGURE 46. Stored Energy Buildup (72-68 Glass)

FIGURE 47. Stored Energy Buildup (Lead Glass)

FIGURE 48. Stored Energy Buildup (European Glass)

The alpha dose rates used in the experiments are much higher than the dose rates projected for actual waste glasses. Because the rates of formation and combination of the radiation-induced defects may be related to dose rates, efforts were made to observe differences in the buildup of stored energy at two greatly different dose rates. The buildup was measured with specimens of 72-68 containing 1% and 8% ^{244}Cm . As is seen in Figure 46, no significant differences are apparent.

Figure 49 shows the stored energy released by heating five specimens of 72-68, each irradiated to a different level. The energy release begins in each case at slightly over 100°C and is complete at about 600°C . It is important to note that the absence of sharp peaks in the release curves indicates that a sudden complete release is highly unlikely.

FIGURE 49. Stored Energy Release Rates

The amount of stored energy accumulated in glass decreases as the temperature is increased. As seen in Figure 50, the stored energy decreases nearly linearly with increasing storage temperature, reaching a negligible value at 350°C. The self-heating of actual wastes will therefore reduce the amount of stored energy, particularly during the first 50-100 years after vitrification.

The stored energy in 72-68 will not likely exceed 50 cal/g. If this amount were released adiabatically, temperature rises in the glass would not be expected to exceed 200°C. Such temperature rises, although significant, are not expected to have serious consequences.

FIGURE 50. Stored Energy at Various Glass Storage Temperatures

Effect of Alpha Radiation on Density of Glass

Damage resulting from alpha radiations on glasses produces small but measurable changes in density. The changes, which can be positive or negative, are characteristic to the given glass formulation. Figure 51 shows the effects of alpha radiation on the density of the glasses under study.

The thermal treatment given the glass prior to irradiation has a significant effect on the density change, as seen in the pronounced difference in behavior between the vitreous and devitrified specimens of 72-68. As with stored energy buildup, the dose rate appears to play an insignificant role

in density change. The difference observed between specimens containing 8% ^{244}Cm and 1% ^{244}Cm are small, and are within the expected experimental uncertainties. The changes in density of vitreous 72-68 glass reach a maximum at approximately 10^{18} alphas/g, and then perceptively decrease. The observed density change is 1%, which may possibly be large enough to affect the design of waste canisters.

FIGURE 51. Density Changes in Alpha Irradiated Glasses

The behavior of the three types of glasses studied suggests that the effects of alpha radiation on density can readily be controlled, if necessary, by adjusting glass compositions.

Effect of Contained Alpha Radiation on Leachability of Glass

Reference glass leach rates determined by following curium and potassium behavior in samples used in the accelerated alpha experiments are shown in Figure 52. Doses and average long-term leach rates from 21 to 140 days are listed in Table 22. The average leach rate values shown are from seven different specimens of Cm-doped glass. Alpha doses ranged from 2.4×10^{17} to 5.1×10^{17} α/g at the beginning of the test to 5.3×10^{17} to 8.3×10^{17} α/g at the end of the test. Leach rates based on curium were a hundred times less than leach rates based on potassium. Comparing the nonirradiated and the irradiated data for potassium-based leach rates, the high alpha doses caused only a slight increase in the leachability of the reference glass. Since no significant differences in leach rates were observed for samples with different doses, it was concluded that radiation effects exceeded a saturation point at the doses used in this experiment.

FIGURE 52. Leachability of ^{244}Cm -Doped Zinc Borosilicate Waste Glass

TABLE 22. Long-Term Leach Data for the Reference Glass

	<u>g/cm²-d</u>
Based on Curium	1.25×10^{-7}
Based on Potassium	
Nonirradiated	8.4×10^{-6}
Irradiated	1.79×10^{-5}

Data from the alpha effects study and the thermal effects study appear to give conflicting long-term leach rates for the reference glass. These discrepancies result from the differences in the ions used to monitor the glass leach rates. Typically, elements with low valences and small ionic radii leach fastest. Table 23 shows data from several studies on the subject.⁽²⁵⁾ The alkali elements including cesium and potassium will leach faster than cesium because of the latter's larger ionic radii. The overall effect is that a glass leach rate based on an ion that leaches fast will be higher than a leach rate calculated from the behavior of a slow-leaching ion.

TABLE 23. Relative Leachability of Elements

<u>Solid Type</u>	<u>Relative Leachability</u>
Silicate Glass	Cs > Sr > Fe > Zr
Asphalt	Cs > Sr > Ce
Alumina Calcine	Cs,Sr > Ru,Ce,Al
Lead Glass	Cs > Al > Pb,Sr,Ce
Phosphate Ceramic	Na,Cs > Sr > Zr-Nb > Ru,Ce
Borosilicate Glass	Cs,Na > Zr-Nb > Ru,Ce
Borosilicate Glass	Na > Si > B > Cs > Sr > Ce,Tb
Borosilicate Glass	Na > B > Si
Phosphate Glass	Cs > Na,Sr > Ru > Ce

Helium Behavior in Waste Glass

As a result of alpha decay of the actinides, generated helium must either be incorporated within the glass structure, or diffuse to the surrounding atmosphere. With a sealed canister, there is a potential for helium pressurization and a possibility of glass swelling due to the formation of helium bubbles. To provide a basis for examination of these factors, a study of helium diffusion in curium-doped glass (72-68) was undertaken and has been reported in detail.⁽³²⁾

Some major conclusions from this work are given below. The samples studied contained $1-2 \times 10^{18}$ helium atoms/cm³ glass. Equivalent self-radiation damage and helium concentrations would be achieved after about 100 years of storage for glass made from LWR fuel wastes.

- At short times and low fractional helium inventory, diffusion follows Arrhenius behavior typical of undamaged, "normal" glass, as given by the equation $D_U = 2.1 \times 10^{-3} \exp(-15,000/RT) \text{ cm}^2/\text{sec}$.
- At long times and higher fractional helium inventory, an Arrhenius temperature dependence is not observed, due to the effects of trapping at radiation-induced defects. The apparent diffusion coefficient is lower than at short times by about one order of magnitude, and is approximated as $D_T = 1.7 \times 10^{-4} \exp(-15,000/RT) \text{ cm}^2/\text{sec}$.
- A helium solubility value (730 Torr He, 400°C) was measured as $S = 1.5 \times 10^{16} \text{ atoms/cm}^3$.
- Assuming a canister with a 10 vol. % plenum, even if the glass is not monolithic, pressures exceeding 15 lbs/in² will not likely be reached for UO₂ fuel wastes until times on the order of 10⁴ years are reached.

Other Radiation Effects

Mechanical strength, and visible surface changes are also being studied in the radiation effects task. Preliminary work to date indicates that no marked changes in these properties occur after alpha irradiation.

FULL-LEVEL RADIOACTIVE GLASS EXPERIMENTS

In order to have full confidence in our understanding of waste glass behavior, the measurements made on simulated waste glass specimens must be corroborated with measurements made on fully radioactive glasses prepared from actual HLLW. HLLW from commercial LWR fuel is not yet available so it has been necessary to prepare HLLW in the laboratory. After the HLLW is prepared, it is batch calcined, combined with the proper amount of glass frit, and melted. Specimens of this full-level glass are now being stored and subjected to various tests.

PREPARATION OF FULL-LEVEL WASTE CALCINE

To prepare the full-level waste for these experiments, enriched UO_2 fuel rods, which had been irradiated to an average burnup of 54,500 MWd/MTU and discharged from the Zorita reactor in October 1973, were obtained. The fuel pellets (2,810 g of oxide) were dissolved in 14 L of 8N HNO_3 . The dissolver was held at 95°C for over 24 hr to complete dissolution. This solution, with a terminal acid concentration of 6M, was diluted to 4M HNO_3 , and filtered first through a 5 μ filter and then through a 0.65 μ filter to remove the solids. A total of 29.3 g of undissolved solids were recovered, representing 1.04 wt% of the oxide charged to the dissolver.

The U and Pu were extracted from the dissolver solution with a mini-centrifugal extraction contactor. Then, the extracted waste solution was evaporated to dryness before transferring it to the glassmaking facility. Preparation of this calcine, termed PW-Zorita, resulted in the loss of about 30% of volatile ruthenium. Other losses during this evaporation were due to entrainment and were uniform for all constituents.

PROCEDURE FOR PREPARING FULL-LEVEL GLASS

Glass specimens (100 g each) were made in a laboratory-scale in-can melter. Crucibles of 304L stainless steel were filled with a mixture of PW-Zorita calcine and glass frit before loading into a melting chamber.

The melting chamber was then heated in an electric furnace. The melting chamber was continuously purged with air. Vacuum applied to the end of the off-gas system acted as the driving force for the air which passed over the crucible, through an effusion hole, across a chill plate, through a series of scrubber solutions, and finally through a wet-test gas meter.

Eight batches of glass, weighing about 100 g each, were made with a composition designated PW-Zorita (3.0) 73-1. Table 24 lists the glassmaker operation data for the various glass runs. All the glasses made were furnace cooled.

TABLE 24. HLW Glass Runs

<u>Run No.</u>	<u>Time To Reach T Max (1050°C), hr</u>	<u>Time at T Max, hr</u>	<u>Cooling Time</u>	<u>Off-Gas ℓ/hr Flow Rate</u>	<u>Bubble Size & Number Observed in Cross Section 1/4-inch Below Top Surface</u>	
CW-2	1.83	3	3 hr to 350°C	25.5	0.05"	(20)
					0.02"	(100)
CW-3	2.25	3	3 hr to 350°C	11.8	0.26"	(3)
					0.15"	(12)
					0.05"	(20)
CW-5	1.50	3	3 hr to 350°C	11.8	0.16"	(10)
					0.05"	(20)
CW-6	2.17	6	3 hr to 350°C	32.8	0.24"	(2)
					0.11"	(15)
					0.03"	(50)
CW-7	3.25	3	3 hr to 350°C	78.4	0.01-0.03" (150)	
CW-9	3.83	3	3 hr to 350°C	124.5	0.05"	(10)
					$\leq 0.02"$	(200)
CW-10	5.00	6	3 hr to 350°C	245.5	0.40"	(4)
					0.16"	(10)
					0.05"	(10)
CW-11	5.00	5	3 hr to 350°C	177.4	none	

VOLATILIZATION DURING GLASS PREPARATION

The volatile material from the in-can glass melter was collected for chemical analyses. A water-cooled platinum chill plate was placed directly over an effusion plate to collect all of the readily condensable fraction. A 20 wt% NaOH scrubber and a water scrubber in series captured the remaining fraction of volatiles. After run CW-9, the number of scrubber solutions was increased to three with the addition of a 20 vol% nitric acid solution at the head end of the bubble train. The data presented in Table 25 is for the chill plate and two-scrubber system.

TABLE 25. Glassmaker Off-Gas Data for 100 g Samples

<u>Element Volatilized</u>	<u>Conc. in Calcine(a)</u>	<u>Chill Plate</u>	<u>Caustic Scrub</u>	<u>Water Scrub</u>	<u>% Volatilized</u>
• Run CW-6 ^(b)					
Te	$3.12 \times 10^5 \mu\text{g}$	100 μg	<400 μg	10 μg	0.16
Se	$2.23 \times 10 \mu\text{g}$	232 μg	156 μg	16 μg	18.1
Sb	$5.42 \times 10 \mu\text{g}$	17 μg	<40 μg	4.4 μg	11.3
Tc	$5.83 \times 10^{-4} \text{Ci}$	$1.25 \times 10^{-5} \text{Ci}$	$1.66 \times 10^{-6} \text{Ci}$	$2.70 \times 10^{-6} \text{Ci}$	2.89
Cs 137	17.9 Ci	$2.72 \times 10^{-2} \text{Ci}$	$3.16 \times 10^{-2} \text{Ci}$	$4.33 \times 10^{-3} \text{Ci}$	0.35
Cs 134	15.47 Ci	$1.74 \times 10^{-2} \text{Ci}$	$2.03 \times 10^{-2} \text{Ci}$	$3.06 \times 10^{-3} \text{Ci}$	0.26
Ru 106	6.73 Ci	$2.12 \times 10^{-3} \text{Ci}$	$1.41 \times 10^{-3} \text{Ci}$	---	0.05
• Run CW-8 ^(c)					
Te	$1.25 \times 10^6 \mu\text{g}$	60 μg	<400 μg	2.8 μg	0.004
Se	$8.92 \times 10^3 \mu\text{g}$	45 μg	108 μg	3.84 μg	1.76
Sb	$2.17 \times 10^3 \mu\text{g}$	7.5 μg	80 μg	3.2 μg	4.18
Tc	$2.33 \times 10^{-3} \text{Ci}$	$4.39 \times 10^{-8} \text{Ci}$	$2.88 \times 10^{-8} \text{Ci}$	$3.60 \times 10^{-8} \text{Ci}$	0.005
Cs 137	71.61 Ci	$1.07 \times 10^{-4} \text{Ci}$	$8.73 \times 10^{-4} \text{Ci}$	$3.19 \times 10^{-4} \text{Ci}$	0.002
Cs 134	61.89 Ci	$7.66 \times 10^{-5} \text{Ci}$	$5.92 \times 10^{-4} \text{Ci}$	$2.17 \times 10^{-4} \text{Ci}$	0.001
Ru 106	26.92 Ci	$7.78 \times 10^{-4} \text{Ci}$	$9.94 \times 10^{-4} \text{Ci}$	----	0.006

(a) Concentration in calcine is not corrected for decay and represents concentration at separation.

(b) Run CW-6, melting PW-Zorita (3.0) 73-1 glass, 70 min heat up time, 6 hr at 1050°C.

(c) Run CW-8, calcining PW-Zorita waste, 1 hr at 500°C.

MACROSTRUCTURE OF FULL-LEVEL GLASS

The crucibles containing the glass were sectioned into wafers as shown in Figure 53. Selected wafers from Run CW-2 were used for the leaching studies discussed later in this chapter. Examination of the wafers showed the presence of some bubbles in the glass, particularly toward the top. The amount of bubbles observed in the sixth wafer from each of the runs is shown in the last column of Table 24.

FIGURE 53. Full-Level Glass Sectioning

An indication of the radiation distribution in the glass was obtained by measuring the dose rate of each wafer through a small hole in the cell wall. Each wafer was monitored at a distance of 54 in., with the detector viewing the full 1 1/2 in. diameter section of the glass. Then the dose rate per gram of glass in each wafer was calculated. The results for some representative glass runs are shown in Figure 54.

The main nonhomogeneity in the sectioned glasses was found at the top surface, and was due to a slagging action in which certain insoluble fine particles (e.g., CeO_2 , RuO_2 , Pd, etc.) were carried to the top of the melt by rising gas bubbles. In these laboratory-scale, full-level melts the nonhomogeneous layer was no more than 1/2-in. deep. In full-scale, nonradioactive canisters, the layer is sometimes deeper. In nonradioactive laboratory tests, slow rates of temperature rise have been shown to minimize the slagging action. The same trend has been apparent in the fully radioactive runs (see Table 24).

FIGURE 54. High-Level Waste Glass Dose Rate as a Function of Depth

A tendency for CeO_2 to settle toward the bottom has been observed in full-scale canisters of nonradioactive glass. There are indications that a similar settling may occur in the fully radioactive melts (see Figure 54). The hot cell where these melts are prepared is being equipped with a gamma spectroscopy system, which will enable positive identification of the radioactive isotopes causing the nonhomogeneous distribution of radioactivity. It is important to note, however, that the nonhomogeneities in the full-level glasses do not appear to affect the quality of the glass, as demonstrated by the leach test results discussed later in this chapter.

MICROSTRUCTURE OF FULL-LEVEL GLASS

Representative full-level waste glass samples were examined by staff members at the Hanford Engineering Development Laboratory (HEDL) hot-cell metallography facilities and by D. R. Farmelo of Battelle Memorial Institute, Columbus Laboratories (BCL), at BCL's metallographic hot lab. Although analyses were not comprehensive, major features of as-prepared and devitrified glasses were delineated. These analyses established that the full-level glasses, as prepared, have compositions considerably different from the target reference glass composition. The laboratory-prepared HLW calcine had a higher uranium concentration than desired, and lower cesium and molybdenum concentrations than expected. The calcine was not analyzed before the glasses were prepared; a detailed analysis is now being done.

The shielded microprobe available gave poor backscatter images and x-ray fluorescence maps, which made examination of individual crystals difficult. Elemental analyses of selected areas (usually 200x magnification) were used to examine homogeneity. Counting statistics, ranging from $\pm 2\%$ to 9% (depending on the element), were established for nine elements in the glass. The analyses given in Table 26 can therefore be assumed accurate to $\pm 10\%$ of the concentration indicated. For elements in low concentrations, an error factor of about ± 0.2 wt% is a realistic estimate.

Comparing the concentrations to the standard sample, the most notable features include high uranium and iron contents, and low concentrations of the volatile elements, molybdenum, ruthenium and cesium. The ruthenium was volatilized during batch calcination. It is conjectured that some of the cesium and molybdenum may have separated as a precipitate in the liquid waste, and, thus, not have been calcined homogeneously. Table 26 shows that iron, ruthenium and cerium concentrate in the top of the melt (CW 6-7). Cerium, as well, probably contributes to high dose rates in the bottom section, as presented earlier in Figure 54. Other elements, most notably cesium and strontium, are uniformly distributed. This means that the total volumetric concentrations of the second phases (e.g., CeO_2 , RuO_2) are not high, since other elements should be correspondingly lower in concentration where such segregation occurs.

TABLE 26. Microprobe Elemental Analyses of HLW Glass, wt%

Sample	Location	Si	Zn	K	Fe	Sr	Mo	Ru(a)	Pd	Cs	Ce(a)	U
72-68(b)	random	12.7	17.1	3.4	0.7	1.8	2.7	1.4 wt% 22-9835(c)	0.8	1.7	1.7 wt%	1.3
CW 3-3 middle	center	12.0	16.5	3.3	2.9	1.5	0.8	---	---	0.7	~1	8.4
CW 6-7 top	random	15.0	16.5	3.4	4.4	1.1	0.8	2291	---	0.7	2200	---
CW 6-4 middle	edge	16.9	19.8	3.2	2.0	1.5	0.2	110	---	0.6	541	---
CW 6-4 middle	center	16.4	22.0	3.6	1.6	1.4	0.2	350	---	0.6	1275	7.3
CW 6-4 middle	Devitri- fied, 800°C, 1 wk center	16.3	16.1	3.4	1.7	1.1	0.4	278	---	0.5	822	---
CW 6-2 bottom	random	15.7	20.8	3.6	1.9	1.4	0.2	282	---	0.6	1362	---

(a) Total counts rather than wt%

(b) Non-radioactive standard reference glass (72-68)

(c) Range in counts due to dispersion of ruthenium as discrete crystallites in the glass

Some of the prepared glasses were devitrified by annealing at 800°C for one week. Based on the results presented in the chapter on phase behavior, such annealing should yield equilibrium concentrations of major products. Figure 55 shows micrographs of three of the full-level glass preparations, CW-3, CW-5 and CW-11. In all three preparations, there are regions with high concentrations of insolubles, primarily CeO_2 , RuO_2 , Fe_3O_4 and Pd. Because of the low concentrations of molybdenum in the PW-Zorita waste (see Table 26), few dendritic SrMoO_4 crystals were observed. Zinc orthosilicate (Zn_2SiO_4) was the major phase present, as with simulated glasses. By comparing the micrographs in Figure 55 with those in Figures 36 and 37, and with the data in Table 20, it can be concluded in a qualitative fashion that there are no major differences in the crystallization behavior of simulated and actual devitrified HLW glass. A more quantitative comparison will develop from continued studies.

LEACH RATES OF FULL-LEVEL GLASS

The first of the eight full-level radioactive glass runs, CW-2, was used for a dynamic leach test, following the IAEA procedure (except for sample preparation). This test was started in February 1976 and will be continued for at least 3 years. Four wafers of the glass, identified as top, upper middle, lower middle and bottom (see Figure 24), were selected for leaching. These sections were immersed in acetone to remove loose particles. They were then placed in quart polyethylene jars containing 500 ml of deionized water at 25°C. The glass sections were suspended off the bottom of the jar using a stainless steel wire holder, and will remain so for the duration of the test.

Table 27 shows the leach solution change schedule. The leachate sample volume for analysis, 10 ml, was immediately acidified with 100 λ concentrated HNO_3 , and placed in glass vials. The analysis performed on the leachate solutions includes the following steps:

- gross gamma spectroscopy
- alpha energy analysis
- beta analysis
- cesium removal and recount of remaining solution by gamma spectroscopy
- plutonium separation to eliminate alpha peak interferences and recount by alpha energy analysis.

FIGURE 55. Micrographs of Fully-Radioactive Devitrified Waste Glass

TABLE 27. High-Level Waste Glass Leach
Solution Sampling Schedule

Leach solutions containing glass wafers #2 through #7 were sampled and changed at 1:00 PM on the following days:

<u>Series No.</u>	<u>Leaching Date (Start)</u>	<u>Leaching Time</u>	<u>Cummulative Leaching Time, Days</u>
1	February 9, 1976	24 hours	1
2	February 10, 1976	24 hours	2
3	February 11, 1976	24 hours	3
4	February 13, 1976	24 hours	4
5	February 17, 1976	4 days	8
6	February 23, 1976	6 days	14
7	March 1, 1976	7 days	21
8	March 8, 1976	7 days	28
9	March 15, 1976	7 days	35
10	March 22, 1976	7 days	42
11	March 29, 1976	7 days	49
12	April 5, 1976	7 days	56
13	May 5, 1976	30 days	86
14	June 4, 1976	30 days	116
15	July 8, 1976	34 days	150
16	August 9, 1976	32 days	182

The first three of these steps have been completed to date to enable leach rates to be calculated for:

- ^{137}Cs
- ^{134}Cs
- ^{90}Sr
- $^{239+240}\text{Pu}$
- $^{244+243}\text{Cm}$
- ^{242}Cm

The remainder of the analysis should yield data on:

- ^{144}Ce
- ^{110}Ag
- ^{54}Mn
- ^{60}Co
- ^{155}Eu
- ^{154}Eu
- Limited data on ^{151}Sm , ^{241}Am , ^{237}Np .

The glass sections are quite homogeneous in isotope distribution as shown by a constancy of leach rate as a function of location in the samples. Figures 56 through 59 graphically present these findings. Plutonium seems to deviate the most, having a consistently higher leach rate for the middle glass sections.

Figure 60 compares the leaching behavior of cesium, strontium, plutonium, and curium for the top sections. In summary, leach rates based on cesium and strontium are in the lower 10^{-5} g/cm²/day region. The leach rate based on plutonium behavior is an order of magnitude lower; the rate based on curium is an order of magnitude below that of plutonium.

Research is now being directed toward an understanding of the varying leach rates (as indicated by a comparison of Figures 31, 32, 52 and 59) for different preparations of the reference zinc-borosilicate glass. We are confident that the work in progress will lead us to a resolution of this question.

a. Top and Bottom of Melt Specimen

b. Middle of Melt Specimen

FIGURE 56. Leach Rate of Full-Level Waste Glass at 25°C in Demineralized Water, Based on Cesium Behavior

a. Top and Bottom of Melt Specimen

b. Middle of Melt Specimen

FIGURE 57. Leach Rate of Full-Level Waste Glass at 25°C in Demineralized Water, Based on Plutonium Behavior

a. Top and Bottom of Melt Specimen

b. Middle of Melt Specimen

FIGURE 58. Leach Rate of Full-Level Waste Glass at 25°C in Demineralized Water, Based on Curium Behavior

a. Top and Bottom of Melt Specimen

b. Middle of Melt Specimen

FIGURE 59. Leach Rate of Full-Level Waste Glass at 25°C in Demineralized Water, Based on Strontium Behavior

FIGURE 60. Comparison of Isotopic Leach Rates from Full-Level Waste Glass at 25°C in Demineralized Water

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