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West Valley Glass Product Qualification Durability Studies, FY 1987-1988: Effects of Composition, Redox State, Thermal History, and Groundwater

M. A. H. Reimus   G. B. Mellinger
G. F. Piepel   L. R. Bunnell

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ABSTRACT

The product qualification subtask of the West Valley Support Task (WVST) at Pacific Northwest Laboratory (PNL) provides support for the waste form qualification efforts at West Valley Nuclear Services Co. Testing is being conducted to determine waste form chemical durability in support of these efforts. The effects of composition, ferrous/ferric ratio (redox state), thermal history, and groundwater are being investigated. Glasses were tested using modified Materials Characterization Center (MCC) -3 and MCC-1 test methods. Results obtained in fiscal years (FY) 1987 and 1988 are presented here.

SUMMARY

The product qualification subtask of the West Valley Support Task (WVST) at Pacific Northwest Laboratory (PNL) provides support for the waste form qualification efforts at West Valley Nuclear Services Co. Testing is being conducted to determine waste form chemical durability in support of these efforts. The effects of composition, ferrous/ferric ratio (redox state), thermal history, and groundwater are being investigated. Results obtained in fiscal years (FY) 1987 and 1988 are presented here.

Glasses were tested using modified Materials Characterization Center (MCC) -3 and MCC-1 test methods. Replicates were run for each glass composition. These 7- and 28-day tests are useful for initial studies, and applicable to waste form qualification; however, tests of longer duration are needed to determine the long-term durability of these glasses.

During FY 1987, two sets of compositional variation glasses were fabricated and leach tested with the 7-day MCC-3 test to determine the effect of composition on waste glass chemical durability. The first set of glasses consisted of eight variations of West Valley Ceramic Melter reference glass WVCM-47, while the second set consisted of 16 variations of reference glass WVCM-50. The set of eight glasses was selected to investigate the effects of specific single-component and other variations (from WVCM-47) of interest. The set of 16 glasses was selected using statistical experimental design techniques so as to provide the most information about the effect of varying composition within the specified compositional variation region. Boron releases of the glasses ranged from 34% above to 29% below the WVCM-50 value. A linear mixture model fit the data very well, and demonstrated that varying composition has a statistically significant effect on chemical durability (as quantified by boron release in the 7-day MCC-3 leach test). The fitted linear mixture model can be used to predict the effects on durability of varying the composition within the region investigated.

During FY 1988, sixteen glasses were fabricated based on statistically selected compositional variations of the WV-B801 composition. The glasses were examined for the presence of secondary (crystalline) phases, and the

glass compositions were analyzed. The glasses' chemical durabilities were characterized using 28-day MCC-1, and 7- and 28-day MCC-3 leach tests.

All of the glasses tested had observed normalized release rates below the Waste Acceptance Preliminary Specifications (WAPS). The applicable specification states that the normalized release rates of Na, Si, B, U, and Cs must be below 1 g/m^2-day or 28 g/m^2 in a 28-day MCC-1 test in deionized water at 90°C. However, the 95% upper confidence limit of the release over the compositional region investigated is 29.3 g/m^2, which accounts for short- and long-term within-laboratory variability in the leach testing and chemical analysis procedures. The 95% upper confidence limit increases to 41.1 g/m^2 when including a 20% lab-to-lab variability. Both of these latter values are above the proposed limit. Rather than concluding that the compositional region is too large, it may be that the limit needs to be reassessed. It is not clear whether the limit was suggested with statistical characterization of chemical durability in mind. Several options including a smaller composition region, need for statistical variability consideration, reduction in analytical variability, investigation of an additional composition region, or reassessment of the proposed limit should be further investigated. It is clear that lab-to-lab and within-lab uncertainties should not be ignored, either in characterizing the chemical durability of a region of glass compositions, or in the specification of an acceptance criterion.

The results of the microstructural characterization of the sixteen WV-8801 glass variations indicate that the composition changes within the region being characterized by PNL do not produce marked changes in the non-glass phases to be found in these glasses. Though some glass-to-glass variations occur, differences are subtle and the total amount of crystalline material is quite small. The formation of these crystalline phases during melter processing could cause sludge formation in the melter. Further study of the formation of these crystals should be undertaken.

Four glasses with identical composition (WVCM-50) but with different redox states were tested to determine the effect of redox state on the chemical durability of the reference glass. Analyses of the normalized elemental

releases from the glasses indicate that redox state does not have a statistically significant effect on the chemical durability.

West Valley reference glass (WVCM-50) was subjected to two types of heat treatment, then leach tested to determine the effects of thermal history on glass chemical durability. Two types of heat treatment were used: slow cooling--simulating glass canister cooling, and isothermal. Cubic spinel-type crystals [$(Fe,Ni)(Cr,Fe)_2O_4$] and ThO_2 crystals were observed in all treated specimens. Hematite-type crystals [$(Cr,Fe)_2O_3$] and Ru inclusions were observed in most of the specimens. Rapidly cooled glass specimens were more chemically durable than the more slowly cooled specimens. Based on B release, the slow-cool heat treatments caused a maximum decrease in durability of 40%. The isothermal heat treatments caused a maximum decrease of 100%. Isothermal treatments at 725°C for $\geq$ 12 h caused the most consistent decrease in durability, at 44%.

West Valley reference glass (WVCM-50) was tested in four groundwaters to determine the effect of groundwater on chemical durability. The four groundwaters tested were PBB1 and PBB3 (bedded salt site groundwaters), J-13 well water (a tuff groundwater), and GR-4 (a basalt groundwater). Groundwater type was found to have a definite effect on chemical durability, causing up to a factor of 5 increase in durability, based on B release, as compared to durability in DIW. The 7-day B releases from the glass were 0.045 g/m^2 in PBB1, 0.060 g/m^2 in PBB3, 0.076 g/m^2 in J-13 water, 0.092 g/m^2 in GR-4, and 0.209 g/m^2 in deionized water.

ACKNOWLEDGMENTS

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1.0 INTRODUCTION

The Product Qualification Subtask of the West Valley Support Task (WVST) at Pacific Northwest Laboratory (PNL) provides support for the waste form qualification efforts for the West Valley Demonstration Project (WVDP) at West Valley, New York. West Valley was the site of the Nuclear Fuel Services commercial nuclear fuel reprocessing facility until operations terminated in 1972. The State of New York then assumed responsibility for the high-level waste (HLW) stored in underground tanks at the site. The Department of Energy (DOE) is assisting, through the WVDP, in retrieving and solidifying these wastes. The site contractor for the WVDP is West Valley Nuclear Services Co., Inc. (WVNS).

The overall objective of PNL's WVST is to provide the technical support required by the WVDP, including the transfer of DOE-developed HLW treatment technology. Specific objectives include 1) providing characterization data that support the West Valley glass waste form acceptability and 2) assisting WVNS with the technology and equipment required to successfully vitrify the high-level waste.

Testing is being conducted by PNL's Product Qualification subtask to determine waste form chemical durability in support of West Valley's waste form qualification efforts. The effects of composition, ferrous/ferric ratio (redox state), heat treatment, and groundwater are being investigated. The results of these studies will help determine the limits under which WVNS can operate their melter system to produce glass that is durable enough to meet repository acceptance specifications and provide data needed for demonstrating compliance with these specifications. The chemical durability of the glass within specified composition variation regions was studied with the aid of statistical techniques during FY 1987 and 1988. Studies to determine the effects of redox state, thermal history, and groundwater were conducted during FY 1987. Results obtained from studies conducted during FY 1987 and 1988 are presented here.

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2.0 CONCLUSIONS

Based on the results of the studies conducted during FY 1987 and 1988, the following conclusions were reached:

- The linear mixture models developed in FY 1987 may be used to predict how varying composition affects the durability of the reference glasses (WVCM-47 and -50) within the defined composition region.

- Leach test results indicate that the addition of 0.1 wt% total noble metal oxides does not significantly affect the reference glass durability (FY 1987).

- The linear mixture models developed during FY 1988 may be used to predict how varying composition affects the durability of reference glass WV-8801 within the defined composition region studied.

- The chemical durability of the target composition (WVCM-50 with 1 wt% less B_2O_3 and 1 wt% more K_2O) was not strongly affected by the variation of glass redox state over the Fe^{2+}/Fe^{3+} range of 0.07 to 0.42. The pH of the leachate increased with increasing Fe^{2+}/Fe^{3+} ratio; however, this rise is probably due to Fe^{2+} oxidation in the leachate (FY 1987).

- Certain isothermal heat treatments can cause up to a twofold decrease in the chemical durability of the target composition. However, heat treatments that simulate anticipated canister cooling conditions have no substantial effects on the chemical durability of this glass (FY 1987).

- The target composition is more durable in groundwater than in deionized water by up to a factor of 5 based on B release (FY 1987).

- All glasses tested during FY 1988 had observed normalized B release rates below 1 $g/m^2 \cdot day$ or 28 g/m^2 based on the 28-day MCC-1 tests. However, the 95% upper confidence limit on maximum B release over the composition region tested in FY 1988 is 29.3 g/m^2 (28-day

2.1

MCC-1, 90°C, deaerated DIW) which accounts for short- and long-term within-laboratory variability and 41.1 g/m^2 when including 20% lab-to-lab variability.

- The normalized release limit of 1 g/m^2·day (28-day MCC-1 90°C, DIW, leach test conditions) suggested by the Nevada Nuclear Waste Storage Investigations Project needs to be assessed with the statistical characterization of chemical durability in mind (FY 1988).

- Lab-to-lab and within-lab statistical uncertainties should not be ignored, either in characterizing the chemical durability of a glass composition region, or in selecting an acceptance criterion (FY 1988).

- Crystalline phases were noted in some of the glasses and are a processing concern because of the potential for sludge buildup in the melter. Further study of the formation of these crystalline phases should be undertaken.

3.0 EXPERIMENTAL METHODS AND APPROACH

3.1 GLASS FABRICATION

All glasses tested were prepared according to specific target oxide compositions with source chemicals consisting mainly of carbonates and oxides. The source chemicals used are listed in Table 3.1. The sources of the "waste mix" oxides indicated in Table 3.1, were blended together to form a waste mix component. The individual glasses were batched with this waste mix and other oxide sources as appropriate for their target compositions. The U and Th oxide sources were added to the batches at a later time. All batches were blended prior to melting to insure homogeneity. When oxidation state control was required, a small amount of graphite was added to the batch during the melting process.

Each batch was melted at its approximate T100P (temperature at which the glass viscosity is 100 poise) for 1 hour in a Pt crucible with one melt stir at 30-min elapsed time. The glass was air quenched, cooled to room temperature, then ground to approximate -100 + 200 mesh size in a disk mill. The U and Th oxide sources were added to this powdered glass, the mixture was briefly agitated, and then was added to a ceramic crucible. When fabricating a redox-adjusted glass, a small amount of graphite was added to the mixture at this point. The mixture was then melted at its approximate T100P for 2 h. The glass was stirred at 30-min intervals.

3.2 LEACH TESTING

All glasses were tested with a modified MCC-3 (MCC 1986) leach test method. A number of glasses were tested with the MCC-1 leach test method (MCC 1986). Brief descriptions of these methods follow.

3.2.1 Modified MCC-3 Leach Test Method

Glass specimens were ground in an automatic mortar and pestle and then sieved to obtain -100 +200 mesh powders. These specimens were placed in

3.1

<u>TABLE 3.1</u>. Glass Oxide Sources

	Glass Oxide	Oxide Source
	Al_2O_3	Al_2O_3
	B_2O_3	H_3BO_3
	Fe_2O_3	Fe_2O_3
	MnO_2*	MnO_2
	P_2O_5	$(NH_4)_2HPO_4$
	PdO_2	PdO
	RhO_2	Rh_2O_3
	RuO_2	RuO_2
	SiO_2	SiO_2
Actinides	ThO_2	ThO_2
	UO_2	UO_2
Alkaline Earths	$BaO*$	$CaCO_3$
	CaO	$CaCO_3$
	$MgO*$	$MgO + MgSO_4$
Alkali	K_2O*	K_2CO_3
	Li_2O*	Li_2CO_3
	Na_2O	Na_2CO_3
Waste Mix[(a)]	CeO_2*	CeO_2
	Cr_2O_3	Cr_2O_3
	Cs_2O*	Cs_2CO_3
	CuO	CuO
	La_2O_3*	La_2O_3
	MoO_3*	MoO_3
	Nd_2O_3*	Nd_2O_3
	$NiO*$	NiO
	$Pr_6O_{11}*$	Pr_6O_{11}
	Sm_2O_3*	Sm_2O_3
	SnO_2**	SnO_2
	SO_3*	$MgSO_4$
	$SrO*$	$SrCO_3$
	TeO_2**	TeO_2
	TiO_2*	TiO_2
	Y_2O_3*	Y_2O_3
	ZnO	ZnO
	ZrO_2*	ZrO_2

(a) Oxides listed here form the waste mix of the
     West Valley reference glasses WVCM-50 and WV-8801.
*   Oxides form the waste mix of WVCM-47 reference
     glass.
**   Additional oxides included in WV-8801 reference
     glass waste mix.

Teflon[a] leach containers along with deaerated, deionized water (DIW). The sealed containers were placed in an air-tight enclosure which contained 250 g of fresh, unused Ascarite[b] (a CO_2 sorbent). This enclosure was then placed in a 90°C oven for the specified test period (7 or 28 days). The containers were briefly removed from the enclosure and gently agitated once a day.

The modifications of the standard MCC-3 leach test method used in these tests included use of deaerated, DIW instead of aerated DIW, and once-daily test container agitation instead of continuous agitation. The solubility of CO_2 increases with pH and CO_2 acts as a buffer in solution to prevent pH rise. As one does not expect a source of CO_2 inside waste glass canisters, CO_2 is not expected to act as a pH buffer. Deaerated DIW also does not contain CO_2 and its use as a reactant prevents against pH buffering effects.

At the conclusion of the leach test period, an aliquot of the leachate was filtered through a 0.45-μm membrane. An aliquot of the filtered leachate was then filtered through an 18-Å filter. The leached glass was removed from the leach containers and the containers were then rinsed with deionized water and filled with 40 mL of 1% nitric acid solution (acid strip) and placed in a 90°C oven overnight. The filtered aliquots (0.45 μm and 18 Å) and the acid-strip solutions were submitted for analysis. Analysis of the 18-Å filtered solution, when compared to that of the 0.45-μm filtered solution, provides information on dissolution product colloid formation. Analysis of the acid-strip solution is used to determine if dissolution products are plating out on the test container walls.

Normalized elemental mass releases were calculated using the following equation:

$$NR_i = C_i / (F_i \times (SA \times W)/V) \tag{3.1}$$

(a) Trademark of E. I. du Pont de Nemours & Co., Inc.
(b) Trademark of Arthur H. Thomas.

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where NR_i = normalized mass release of element i (g/m^2)
$\quad\quad\quad C_i$ = concentration of element i in leachate (g/m^3)
$\quad\quad\quad F_i$ = fraction of element i in glass (dimensionless)
$\quad\quad\quad SA$ = surface area of glass/g of glass $(m^2/g)^{(a)}$
$\quad\quad\quad W$ = mass of glass sample leached (g)
$\quad\quad\quad V$ = volume of leachant (m^3).

3.2.2 MCC-1 Leach Test Method

Monolithic specimens of the glasses were cut on a low-speed diamond-blade wafering saw with deionized water used for lubrication. These samples were placed in Teflon jars along with deaerated deionized water. The sealed jars were placed in an air-tight enclosure which contained 250 g of fresh, unused Ascarite. This enclosure was then placed in a 90°C oven for a period of 28 days.

At the conclusion of the leach test period, the pH of the leachate was determined from an aliquot of the leachate. The test specimens were removed from the test container and sufficient nitric acid was added to the leachate in the container such that a 1% nitric acid solution resulted. The container was then placed in a 90°C oven overnight. An aliquot of the solution was decanted and submitted for analysis.

Normalized elemental mass releases were calculated using the following equation:

$$NR_i = C_i / [F_i \times (SA/V)] \quad\quad\quad\quad\quad\quad (3.2)$$

where $\quad NR_i$ = normalized mass release of element i (g/m^2)
$\quad\quad\quad C_i$ = concentration of element i in leachate (g/m^3)
$\quad\quad\quad F_i$ = fraction of element i in glass (dimensionless)
$\quad\quad SA/V$ = surface area of glass/volume of leach solution (m^{-1}).[b]

(a) Value of 0.02 m^2/g used, SA/V used = 2000 m^{-1}.
(b) Value of 10 m^{-1} used.

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3.3 GLASS AND SOLUTION ANALYSES

All glass specimens were analyzed using inductively coupled plasma
(ICP), laser fluorescence, and atomic absorption spectrophotometry techni-
ques. Redox states were determined, when appropriate, with spectrophoto-
metric techniques. Samples were prepared for optical examination by standard
metallographic cutting and polishing techniques. Polished specimens were
examined optically at various magnifications to obtain both a general view
and details of any crystalline phases which might be present. The specimens
were then prepared and submitted for scanning electron microscopy (SEM)
analysis. Each specimen was first examined generally and with reference to
the optical micrographs provided to the operator. Any non-glass phases seen
were examined, usually at higher magnifications, and energy dispersive x-ray
analysis (EDX) was used to provide an elemental analysis of these phases.

Solution analyses were performed with ICP, laser fluorescence, and
atomic absorption (AA) techniques. All normalized releases obtained from
MCC-3 methods were calculated from the elemental concentrations of the
0.45-μm filtered solutions. Analyses of the 18-Å and acid-strip solutions
are not presented here. Analyses of the 18-Å filtered solutions indicated
that very few, if any, colloidal dissolution products were formed during the
test periods. Analyses of the acid-strip solutions indicated that the disso-
lution products did not plate out on the test container walls.

3.4 COMPOSITION REGIONS--FY 1987

Two sets of glasses were tested at PNL during FY 1987 to investigate the
effects of compositional variability. The first set, consisting of glasses
designated DG-WV1 through DG-WV8, was fabricated and tested from November
1986 to January 1987. The second set, consisting of glasses designated
DG-WV15 through DG-WV30, was fabricated and tested from April to June 1987.
The first set of eight glasses consisted of WVCM-47 and several, mainly one-
component, variations of this composition. The second set of 16 glasses
consisted of the WVCM-50 reference glass and 15 vertices of a polyhedronal
composition region centered around WVCM-50. The compositions of the WVCM-47

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TABLE 3.2. Composition of West Valley Reference Glasses WVCM-47 and WVCM-50

Oxides	Weight Percent	
	DG-WV1; WVCM-47	DG-WV30; WVCM-50
Al_2O_3	8.05	9.86
B_2O_3	12.08	12.27
BaO	0.05	0.19
CaO	0.60	0.82
CeO_2	0.07	0.72
Cr_2O_3	0.20	0.14
Cs_2O	0.08	0.07
CuO	0.00	0.04
Fe_2O_3	12.20	11.93
K_2O	1.29	1.61
La_2O_3	0.03	0.04
Li_2O	2.03	2.22
MgO	1.33	0.79
MnO_2	1.31	1.21
MoO_3	0.01	0.04
Na_2O	9.27	9.79
Nd_2O	0.12	0.14
NiO	0.28	0.31
P_2O_5	2.52	2.47
PdO_2	0.00	0.00
Pr_6O_{11}	0.03	0.04
RhO_2	0.00	0.00
RuO_2	0.00	0.00
SiO_2	42.59	39.60
Sm_2O_3	0.03	0.02
SO_3	0.30	0.23
SrO	0.03	0.02
ThO_2	3.61	3.52
TiO_2	0.99	0.84
UO_2	0.56	0.61
Y_2O_3	0.02	0.02
ZnO_2	0.00	0.03
ZrO_2	0.29	0.40
TOTAL	99.97	99.99

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and WVCM-50 reference glasses are given in Table 3.2. Both glass composi-
tions were developed by Catholic University of America (CUA).

3.4.1 First Set of Glasses

The first set of compositional variability glasses were based on varia-
tions about the WVCM-47 reference glass composition. The eight glasses
fabricated and tested have the following descriptions:

Glass Code	Description
DG-WV1	CUA reference glass - WVCM-47
DG-WV2	WVCM-47 glass with Ru, Rh, Pd oxides
DG-WV3	Alternate glass (designated ATM-10)
DG-WV4	WVCM-47 with higher Na_2O (12.20 vs. 9.27 wt%)
DG-WV5	WVCM-47 with lower Al_2O_3 (6.00 vs. 8.05 wt%)
DG-WV6	WVCM-47 with higher P_2O_5 (3.50 vs. 2.52 wt%)
DG-WV7	WVCM-47 with higher ThO_2 (5.40 vs. 3.61 wt%)
DG-WV8	WVCM-47 with lower B_2O_3 (7.30 vs. 12.08 wt%)

Glasses DG-WV2 and DG-WV4 through DG-WV8 are variations from DG-WV1 which
were obtained by choosing higher or lower values of the oxides indicated, and
proportionally adjusting the remaining components of DG-WV1 to offset the
change(s). The target and as-analyzed compositions of these glasses are
given in Table 3.3. The as-analyzed compositions are each from a single
analysis and are normalized to 100 weight percent (wt%).

3.4.2 Second Set of Glasses

The second set of 16 glasses tested in FY 1987 consisted of the WVCM-50
reference glass and 15 vertices of a polyhedronal composition variation
region around WVCM-50. The compositional variation region is given in
Table 3.4. The 15 vertex compositions were chosen using computer-aided
experimental design techniques (Piepel 1988; Snee 1985) to provide optimum
information for fitting linear mixture models (Cornell 1981). The target and
as-analyzed compositions of the 16 glasses are given in Table 3.5.

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TABLE 3.3. Compositions of First Set of FY 1987 Compositional Variability Glasses, wt%

Oxide	DG-WV1 Target	Analyzed[a]	DG-WV2 Target	Analyzed	DG-WV3 Target	Analyzed	DG-WV4 Target	Analyzed	DG-WV5 Target	Analyzed	DG-WV6 Target	Analyzed	DG-WV7 Target	Analyzed	DG-WV8 Target	Analyzed
Al_2O_3	8.05	8.74	8.04	8.61	6.50	7.16	7.79	8.38	6.00	6.90	7.97	8.55	7.90	8.84	8.49	9.01
B_2O_3	12.08	12.15	12.07	12.17	9.25	9.33	11.69	11.77	12.35	12.41	11.96	12.15	11.86	12.15	7.30	7.51
BaO	0.05	0.05	0.05	0.05	0.05	0.07	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
CaO	0.60	0.68	0.60	0.83	0.56	0.63	0.58	0.68	0.61	0.68	0.59	0.69	0.59	0.65	0.63	0.67
CeO_2	0.07	0.07	0.07	0.07	0.07	0.10	0.07	0.07	0.07	0.09	0.07	0.05	0.07	0.07	0.07	0.10
Cr_2O_3	0.20	0.19	0.20	0.20	0.29	0.29	0.19	0.20	0.20	0.21	0.20	0.19	0.20	0.20	0.21	0.19
Cs_2O	0.08	0.05	0.08	0.05	0.07	0.06	0.08	0.05	0.08	0.05	0.08	0.05	0.08	0.04	0.08	0.14
Fe_2O_3	12.20	11.74	12.19	11.72	11.30	10.81	11.81	11.06	12.41	11.91	12.08	11.55	11.98	11.55	12.87	12.29
K_2O	1.29	1.16	1.29	0.91	3.33	1.92	1.25	1.71	1.32	1.50	1.28	0.70	1.27	1.27	1.36	1.71
La_2O_3	0.03	0.04	0.03	0.04	0.03	0.05	0.03	0.04	0.03	0.04	0.03	0.04	0.03	0.04	0.03	0.03
Li_2O	2.03	1.74	2.03	1.76	2.82	2.34	1.97	1.71	2.08	1.76	2.01	1.71	1.99	1.71	2.14	1.84
MgO	1.33	1.32	1.33	1.30	1.21	1.70	1.29	1.29	1.36	1.35	1.32	1.29	1.31	1.28	1.40	1.39
MnO_2	1.31	1.30	1.31	1.32	1.22	1.76	1.27	1.30	1.34	1.36	1.30	1.30	1.29	1.29	1.38	1.37
MoO_3	0.01	0.01	0.01	0.01	0.00	0.00	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Na_2O	9.27	9.13	9.26	9.04	10.16	9.82	12.20	11.47	9.48	9.10	9.18	9.13	9.10	8.68	9.78	9.38
Nd_2O_3	0.12	0.12	0.12	0.11	0.17	0.16	0.12	0.14	0.12	0.12	0.12	0.11	0.12	0.09	0.13	0.13
NiO	0.28	0.31	0.28	0.27	0.32	0.36	0.27	0.27	0.29	0.30	0.28	0.28	0.28	0.28	0.30	0.30
P_2O_5	2.52	2.58	2.52	2.60	2.33	2.41	2.44	2.54	2.58	2.63	3.50	3.56	2.48	2.51	2.66	2.68
PdO_2	0.00	0.00	0.01	0.01	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Pr_6O_{11}	0.03	0.03	0.03	0.03	0.00	0.00	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03
RhO_2	0.00	0.00	0.01	0.01	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
RuO_2	0.00	0.00	0.08	0.08	0.07	0.07	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
SiO_2	42.59	43.25	42.55	43.60	44.87	45.46	41.22	41.94	43.54	44.43	42.16	43.42	41.80	43.03	44.91	45.83
Sm_2O_3	0.03	0.03	0.03	0.03	0.00	0.00	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03
SO_3	0.30	0.30	0.30	0.30	0.27	0.27	0.29	0.29	0.31	0.31	0.30	0.30	0.29	0.29	0.32	0.32
SrO	0.03	0.03	0.03	0.03	0.03	0.04	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03
ThO_2	3.61	2.86	3.61	2.80	3.34	2.73	3.50	2.94	3.69	3.11	3.58	2.75	5.40	3.83	3.81	2.75
TiO_2	0.99	0.96	0.99	0.96	0.91	1.22	0.96	0.90	1.01	0.97	0.98	0.93	0.97	0.96	1.05	1.01
UO_2	0.58	0.54	0.56	0.53	0.52	0.54	0.54	0.54	0.57	0.00	0.56	0.53	0.55	0.46	0.59	0.58
Y_2O_3	0.02	0.02	0.02	0.02	0.02	0.03	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02
ZrO_2	0.29	0.59	0.29	0.56	0.27	0.64	0.28	0.54	0.30	0.60	0.29	0.56	0.28	0.62	0.31	0.57
Total	99.97	100	99.99	100	100	100	100.01	100	99.91	100	100.01	100	100.01	100	99.99	100

(a) All glasses analyzed with ICP, AA, and laser fluorescence analysis techniques, compositions normalized to 100%.

3.8

TABLE 3.4. Definition of Compositional Variation Region Based on WVCM-50

	Single Component Constraints, wt%	
$9.0 \leq$	Al_2O_3	≤ 12.0
$10.0 \leq$	B_2O_3	≤ 14.0
$1.0 \leq$	$BaO+CaO+MgO$ [a]	≤ 3.0
$9.0 \leq$	Fe_2O_3	≤ 15.0
$11.6 \leq$	$K_2O+Li_2O+Na_2O$ [a]	≤ 15.6
$0.5 \leq$	MnO_2	≤ 2.5
$1.5 \leq$	P_2O_5	≤ 3.5
$36.0 \leq$	SiO_2	≤ 44.0
$2.0 \leq$	ThO_2	≤ 5.25
$0.1 \leq$	UO_2	≤ 1.0
$1.0 \leq$	Others	≤ 8.0

	Multiple Component Constraints, wt%	
$48 \leq$	$SiO_2+Al_2O_3$	≤ 54
$23.6 \leq$	Alkalis $+ B_2O_3$	≤ 27.6
$3.3 \leq$	$(SiO_2+Al_2O_3)/Alkalis$	≤ 4.1
$3.7 \leq$	$(SiO_2+Al_2O_3)/B_2O_3$	≤ 4.7

(a) The $BaO:CaO:MgO$ and $K_2O:Li_2O:Na_2O$ wt% ratios were held constant at their levels in the WVCM-50 glass.

3.5 COMPOSITION REGION--FY 1988

The composition region studied during FY 1988 is described in Table 3.6. The region is based on composition variations of the West Valley reference glass composition WV-8801 (composition listed in Table 3.7). A computer-aided experimental design approach was used to generate the 16-glass test matrix that was used to characterize the chemical durability of the composition region. The target and as-analyzed compositions of the 16 glasses are given in Tables 3.7a and b. Note that the glass labeled DG-WV33 has the WV-8801 composition.

TABLE 3.5. Compositions of Second Set of FY 1987 Compositional Variability Glasses: DG-WV15 - DG-WV30, wt%

Oxide	DG-WV15		DG-WV16		DG-WV17		DG-WV18		DG-WV19		DG-WV20		DG-WV21		DG-WV22	
	Target	Analyzed[a]	Target	Analyzed	Target	Analyzed	Target	Analyzed	Target	Analyzed	Target	Analyzed	Target	Analyzed	Target	Analyzed
Al_2O_3	9.00	9.60	9.00	9.43	9.00	9.43	9.00	9.47	12.00	12.23	12.00	12.24	12.00	12.51	12.00	12.50
B_2O_3	12.97	12.58	12.97	12.61	10.21	9.78	10.95	10.62	10.35	10.08	11.06	10.62	10.32	10.05	11.82	11.57
BaO	0.32	0.33	0.32	0.32	0.32	0.32	0.11	0.11	0.32	0.32	0.32	0.31	0.11	0.11	1.11	0.11
CaO	1.37	1.36	1.37	1.37	1.37	1.43	0.46	0.54	1.37	1.31	1.37	1.34	0.46	0.50	0.46	0.50
MgO	1.32	1.27	1.32	1.22	1.32	1.29	0.44	0.44	1.32	1.28	1.32	1.42	0.44	0.53	0.44	0.48
Fe_2O_3	9.00	8.80	15.00	14.42	9.00	8.87	15.00	14.44	15.00	14.20	9.00	8.75	15.00	14.67	15.00	14.03
K_2O	1.72	1.64	1.38	1.31	1.72	2.07	1.84	1.75	1.56	1.97	1.48	2.23	1.73	1.23	1.39	1.84
Li_2O	2.37	2.73	1.91	1.91	2.37	2.34	2.54	2.44	2.16	2.07	2.04	2.04	2.39	2.31	1.92	1.82
Na_2O	10.46	10.17	8.42	8.64	10.46	10.57	11.22	11.14	9.53	9.88	9.02	8.63	10.56	10.46	8.47	8.31
MnO_2	2.50	2.51	2.22	2.23	2.50	2.49	0.50	0.54	0.50	0.50	0.50	0.52	2.50	2.50	2.50	2.46
P_2O_5	1.50	1.33	3.50	3.23	1.50	1.24	1.50	1.55	1.50	1.35	3.50	3.34	3.50	3.38	1.50	1.43
SiO_2	39.00	39.79	39.00	39.95	39.00	39.57	42.48	43.20	36.65	36.01	39.40	39.95	36.49	37.54	36.30	37.38
ThO_2	2.00	1.66	2.00	1.60	5.14	4.69	2.37	1.96	5.25	5.24	2.00	1.87	2.00	1.59	2.00	1.75
UO_2	1.00	0.92	0.10	0.13	0.10	0.08	0.10	0.09	1.00	0.93	1.00	0.95	1.00	0.92	0.10	0.11
Others	5.47	5.33	1.49	1.63	5.99	5.84	1.49	1.70	1.49	1.64	5.99	5.81	1.50	1.68	5.99	5.69
Total	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100

TABLE 3.5. (contd)

Oxide	DG-WV23 Target	DG-WV23 Analyzed[a]	DG-WV24 Target	DG-WV24 Analyzed	DG-WV25 Target	DG-WV25 Analyzed	DG-WV26 Target	DG-WV26 Analyzed	DG-WV27 Target	DG-WV27 Analyzed	DG-WV28 Target	DG-WV28 Analyzed	DG-WV29 Target	DG-WV29 Analyzed	DG-WV30 Target	DG-WV30 Analyzed
Al_2O_3	9.00	9.42	12.00	12.32	9.00	9.30	12.00	12.27	12.00	12.17	9.00	9.68	9.00	9.28	9.86	10.07
B_2O_3	12.97	12.48	14.00	13.22	11.28	10.90	14.00	13.38	13.01	12.58	11.00	10.66	12.00	11.45	12.27	11.88
BaO	0.11	0.11	0.11	0.11	0.11	0.10	0.32	0.30	0.11	0.11	0.11	0.11	0.32	0.32	0.19	0.20
CaO	0.46	0.50	0.46	0.48	0.46	0.50	1.37	1.34	0.46	0.49	0.46	0.48	1.37	1.33	0.82	0.84
MgO	0.44	0.54	0.44	0.56	0.44	0.53	1.32	1.35	0.44	0.62	0.44	0.62	1.32	1.36	0.79	1.01
Fe_2O_3	14.57	14.24	9.00	8.67	9.00	8.67	9.00	8.67	9.00	8.68	12.72	12.11	9.00	8.74	11.93	11.48
K_2O	1.38	1.86	1.60	2.52	1.53	2.02	1.51	2.64	1.72	2.45	1.49	1.35	1.84	1.84	1.61	1.81
Li_2O	1.91	1.80	2.22	2.05	2.11	2.03	2.08	2.00	2.38	2.28	2.05	2.05	2.54	2.57	2.22	2.10
Na_2O	8.42	8.23	9.78	9.56	9.30	9.09	9.18	9.09	10.49	10.14	9.06	8.86	11.22	10.74	9.79	9.63
MnO_2	0.50	0.51	2.50	2.44	2.45	2.40	0.50	0.55	0.50	0.51	0.50	0.52	0.50	0.50	1.21	1.20
P_2O_5	3.50	3.30	1.50	1.41	3.50	3.13	1.50	1.62	3.50	3.48	1.50	1.53	3.30	3.27	2.47	2.42
SiO_2	39.00	39.31	42.00	42.10	44.00	45.00	40.38	40.95	36.14	36.72	42.68	43.38	44.00	44.68	39.60	40.06
ThO_2	5.25	4.95	2.00	1.88	5.25	4.36	5.25	3.80	4.16	3.46	2.00	1.72	2.00	1.93	3.52	3.26
UO_2	1.00	0.93	0.90	0.93	0.10	0.10	0.10	0.10	0.10	0.11	1.00	0.96	0.10	0.10	0.61	0.59
Others	1.49	1.83	1.49	1.74	1.47	1.88	1.49	1.95	5.99	6.19	5.99	5.94	1.49	1.88	3.11	3.46
Total	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100

(a) All glasses analyzed with ICP, AA, and laser fluorescence techniques, compositions normalized to 100%.
(b) "Others" include the following oxide mix: CeO_2 (23.23), Cr_2O_3 (4.52), Cs_2O (2.26), CuO (1.29), La_2O_3 (1.29), MoO_3 (1.29), Nd_2O_3 (4.52), NiO (10.00), Pr_6O_{11} (1.29), Sm_2O_3 (0.65), SO_3 (7.42), SrO (0.65), TiO_2 (27.10), Y_2O_3 (0.65), ZnO_2 (0.97), ZrO_2 (12.90). Numbers in parentheses give relative wt% of the oxides in the mix.

3.11

TABLE 3.6. Definition of Compositional Variation Region Based on WV-8801, wt%

Component	WV-8801	Single Component Constraints Lower Bound	Single Component Constraints Upper Bound
Al_2O_3	7.75	4.5[d]	10.0
B_2O_3	9.26	6.0[e]	13.0
$BaO+CaO+MgO$[a]	1.77	0.5	2.5
Fe_2O_3	12.04	10.0	16.0
$K_2O+Li_2O+Na_2O$[a]	16.32	12.0	21.0[f]
MnO_2	1.30	0.1	2.0
P_2O_5	2.48	0.5	4.0
SiO_2	42.50	38.0	45.0
ThO_2	3.55	2.0	5.0
UO_2	0.54	0.1	2.0
Others[b]	2.49[c]	1.0	8.0

		Multiple Component Constraints Lower Bound	Multiple Component Constraints Upper Bound
$SiO_2+Al_2O_3$	50.25	45.0	52.0
$Alkalis+B_2O_3$	25.58	23.0	29.0
$(SiO_2+Al_2O_3)/Alkalis$	3.08	2.6	4.3
$(SiO_2+Al_2O_3)/B_2O_3$	5.43	4.0	6.5
SiO_2/Al_2O_3	5.48	3.8	8.0

(a) The BaO:CaO:MgO and $K_2O:LiO_2:Na_2O$ ratios are held constant at their levels in the WV-8801 glass.

(b) Others include the following oxide mix: CeO_2 (6.35), Cr_2O_3 (5.56), Cs_2O (3.57), CuO (2.38), La_2O_3 (1.59), MoO_3 (1.98), Nd_2O_3 (5.56), NiO (9.92), PdO_2 (1.19), Pr_6O_{11} (1.59), RhO_2 (0.79), RuO_2 (3.17), Sm_2O_3 (0.79), SnO_2 (1.19), SO_3 (8.73), SrO (0.79), TeO_2 (0.40), TiO_2 (35.32), Y_2O_3 (0.79), ZuO_2 (0.79), ZrO_2 (7.54). Number in parentheses give relative wt% of the oxides in this mix.

(c) This level for "Others" was obtained by subtracting from 100 the total weight percent levels of the preceding ten components.

(d) Due to the multiple component constraints, the attainable lower limit for Al_2O_3 is 5.0 wt%.

(e) Due to the multiple component constraints, the attainable lower limit for B_2O_3 is 6.92 wt%.

(f) Due to the multiple component constraints, the attainable upper limit for alkalis is 20.0 wt%.

TABLE 3.7. Target and "As Analyzed" Compositions (by weight percent) for the 16 WV-8801 Compositional Variation Glasses[a]

Target

Glass	Al_2O_3	B_2O_3	BaO +CaO +MgO	Fe_2O_3	K_2O +Li_2O +Na_2O	MnO_2	P_2O_5	SiO_2	ThO_2	UO_2	Others
DG-WV33	7.75	9.26	1.77	12.04	16.32	1.30	2.48	42.50	3.55	0.54	2.49
DG-WV34	5.00	11.25	0.50	10.00	17.31	2.00	1.94	40.00	2.00	2.00	8.00
DG-WV35	10.00	7.39	2.50	16.00	18.46	2.00	0.50	38.00	2.15	2.00	1.00
DG-WV36	5.14	11.56	0.50	16.00	12.00	0.10	0.50	41.10	5.00	0.10	8.00
DG-WV37	10.00	8.00	0.50	10.00	18.80	0.10	0.50	42.00	2.00	0.10	8.00
DG-WV38	10.00	7.83	0.50	10.00	15.17	2.00	0.50	40.90	5.00	0.10	8.00
DG-WV39	10.00	12.00	2.50	10.00	17.00	0.10	4.00	38.00	5.00	0.10	1.30
DG-WV40	5.54	7.68	2.50	16.00	15.32	0.10	0.50	44.36	5.00	2.00	1.00
DG-WV41	5.62	7.79	0.50	10.00	19.47	0.10	4.00	45.00	4.52	2.00	1.00
OG-WV42	5.00	6.92	2.50	10.00	16.48	2.00	4.00	40.00	5.00	0.10	8.00
DG-WV43	10.00	13.00	0.50	10.00	12.09	2.00	2.41	42.00	5.00	2.00	1.00
DG-WV44	7.90	11.48	0.50	16.00	17.52	0.10	0.50	38.00	5.00	2.00	1.00
DG-WV45	10.00	7.39	0.50	16.00	18.46	2.00	4.00	38.00	2.00	0.10	1.55
DG-WV46	7.00	13.00	2.50	10.90	16.00	2.00	0.50	45.00	2.00	0.10	1.00
DG-WV47	5.63	11.77	0.50	16.00	12.00	2.00	4.00	45.00	2.00	0.10	1.00
DG-WV48	10.00	11.40	2.50	10.00	12.00	0.10	4.00	38.00	2.00	2.00	8.00

As-Analyzed[b]

Glass	Al_2O_3	B_2O_3	BaO +CaO +MgO	Fe_2O_3	K_2O +Li_2O +Na_2O	MnO_2	P_2O_5	SiO_2	ThO_2	UO_2	Others
DG-WV33	8.22	9.03	1.43	11.45	16.86	1.28	2.47	42.50	3.37	0.50	2.89
DG-WV34	5.17	10.81	0.66	9.77	17.76	1.98	1.87	40.00	1.92	1.83	8.23
DG-WV35	10.02	7.15	2.54	14.98	18.19	1.95	0.60	38.00	2.78	2.40	1.39
DG-WV36	5.69	10.80	0.58	14.66	12.43	0.12	0.59	41.10	5.81	0.13	8.09
DG-WV37	9.98	7.78	0.52	9.77	19.11	0.13	0.50	42.00	2.09	0.14	7.99
DG-WV38	10.24	7.58	0.57	9.67	15.96	1.97	0.60	40.90	4.13	0.09	8.29
DG-WV39	10.05	11.22	2.40	9.28	17.72	0.11	3.81	38.00	5.11	0.10	2.20
DG-WV40	6.09	7.53	2.60	15.35	15.54	0.12	0.60	44.36	4.19	1.82	1.80
OG-WV41	5.92	7.26	0.74	9.48	18.36	0.12	3.80	45.00	5.27	1.99	2.06
DG-WV42	5.55	6.75	2.44	9.53	17.01	1.95	3.68	40.00	5.00	0.12	7.97
DG-WV43	10.04	12.43	0.72	9.53	13.11	1.94	2.39	42.00	4.14	1.92	1.78
DG-WV44	8.32	11.50	0.70	15.81	17.32	0.13	0.62	38.00	3.71	2.15	1.74
DG-WV45	10.21	7.31	0.59	15.51	18.82	2.01	3.90	38.00	1.79	0.10	1.76
DG-WV46	7.00	12.23	2.44	10.39	16.53	1.96	0.59	45.00	2.16	0.11	1.59
DG-WV47	5.69	11.21	0.58	14.94	13.09	1.94	3.93	45.00	1.95	0.12	1.55
DG-WV48	9.43	10.56	2.45	9.24	13.12	0.12	4.28	38.00	2.06	1.90	8.84

(a) DGWV-33 is the WV-8801 reference glass, while glasses DG-WV34 to DG-WV48 are extreme vertices of the compositional region defined in Table 1.
(b) The SiO_2 values of the "as analyzed" glass compositions were set to the target values due to a relatively large bias in the ICP analyses of SiO_2.

3.13

3.6 GLASS REDOX ADJUSTMENT

Four redox-adjusted glasses, DG-WV11R through DG-WV14R, were fabricated for this study. The target composition of the glass varies slightly from the WVCM-50 composition, with approximately 1 wt% less B_2O_3 and 1 wt% more K_2O. The redox state of the glass, as measured by the Fe^{2+}/Fe^{3+} ratio, was varied over a range of 0.07 to 0.42. This range represents the estimated Fe^{2+}/Fe^{3+} variability of glass to be produced by West Valley. The target oxide and as-analyzed compositions of these glasses are given in Table 3.8; Fe^{2+}/Fe^{3+} ratios are given in Table 3.9.

3.7 GLASS HEAT TREATMENTS

Nuclear waste glasses can devitrify at temperatures below the melter processing temperature. Devitrification is the formation of crystals in the glass. Crystal formation may lead to inhomogeneity of the glass product and, in some cases, a decrease in chemical durability as was observed when an excessive amount of acmite crystals formed in SRL-165 glass (Jantzen, Bickford, and Karraker 1984). To determine the type and extent of devitrification, the glass may be subjected to temperature conditions representing expected thermal history, e.g., slow cooling conditions simulating the cooling of a glass-filled canister. Devitrification kinetics may also be examined with a method involving heat treating specimens under isothermal conditions so that any thermally activated transformations that occur in the material can be identified and characterized.

To study the effects of thermal history on devitrification and chemical durability, the target composition used in the redox experiments was heat treated, then subjected to leach testing in FY 1987. The determination of these effects provides information regarding the processing conditions, e.g., canister cooling rates and melter idling conditions, necessary for producing a durable product. The data collected support glass qualification efforts. The glass was submitted to two types of heat treatment--slow cooling and isothermal. The slow cooling treatment simulates the thermal history of cooling glass in a recently filled waste canister intended for repository

3.14

TABLE 3.8. Compositions of Redox Adjusted Glasses (in wt%)

		As-Analyzed[a]			
Oxide	Target	OG-WV11R	DG-WV12R	DG-WV13R	OG-WV14R
Al_2O_3	9.99	10.46	10.52	10.58	10.58
B_2O_3	10.69	10.97	10.82	10.78	10.98
BaO	0.05	0.05	0.05	0.05	0.05
CaO	0.60	0.62	0.63	0.61	0.61
CeO_2	0.07	0.07	0.07	0.07	0.07
Cr_2O_3	0.18	0.17	0.17	0.17	0.17
Cs_2O	0.08	0.09	0.10	0.12	0.13
Fe_2O_3	12.19	11.90	11.82	11.90	11.99
K_2O	2.44	2.67	2.85	2.87	2.19
La_2O_3	0.03	0.03	0.03	0.03	0.03
Li_2O	2.63	2.63	2.57	2.59	2.61
MgO	1.33	1.25	1.25	1.26	1.25
MnO_2	1.31	1.32	1.31	1.31	1.31
MoO_3	0.01	0.01	0.01	0.01	0.01
Na_2O	9.58	9.52	9.58	9.38	9.51
Nd_2O_3	0.12	0.07	0.08	0.09	0.08
NiO	0.28	0.31	0.29	0.31	0.29
P_2O_5	2.52	2.48	2.52	2.50	2.50
PdO_2	0.01	0.01	0.01	0.01	0.01
Pr_6O_{11}	0.03	0.03	0.03	0.03	0.03
RhO_2	0.01	0.01	0.01	0.01	0.01
RuO_2	0.08	0.08	0.08	0.08	0.08
SiO_2	39.96	40.61	40.16	40.18	40.20
Sm_2O_3	0.03	0.03	0.03	0.03	0.03
SO_3	0.30	0.31	0.30	0.31	0.30
SrO	0.03	0.03	0.03	0.03	0.03
ThO_2	3.61	2.20	2.53	2.48	2.59
TiO_2	0.99	0.95	0.94	0.96	0.96
UO_2	0.56	0.63	0.65	0.69	0.64
Y_2O_3	0.02	0.02	0.01	0.02	0.02
ZrO_2	0.29	0.46	0.54	0.52	0.73
TOTAL	100.02	100.00	100.00	100.00	100.00
Fe^{2+}/Fe^{3+}[b]		0.068	0.126	0.236	0.424

(a) ICP, AA, and laser fluorescence analyses, normalized to 100%.

(b) Analyzed with spectrophotometric technique.

TABLE 3.9. Fe^{2+}/Fe^{3+} Ratios of Glasses Tested

	DG-WV11R	DG-WV12R	DG-WV13R	DG-WV14R
	0.068	0.131	0.237	0.409
	0.068	0.124	0.237	0.427
	0.068	0.123	0.233	0.429
	0.069	0.126	0.238	0.429
Average	0.068	0.126	0.236	0.424
Standard Deviation	5.00E-04	3.56E-03	2.22E-03	9.71E-03

disposal. The isothermal treatments are constant-temperature heat treatments, conducted at different temperatures for varying lengths of time.

3.7.1 Simulated Canister Cooling

Glasses were heat treated using programmed furnaces. The furnace controller was "programmed" with a series of linear cooling/heating rates which closely approximate cooling curves. Plots representing the actual cooling history of the glass samples are given in Figures 3.1 through 3.6. The furnace was programmed to shut off and cool down once a temperature of 400°C was reached. It took approximately 5 h for the furnace to reach room temperature (25°C) from this temperature. The glass structure is essentially frozen at 400°C and the subsequent 5-h cooling to 25°C does not affect the microstructure of the glass.

The cooling curves used were simulated versions of actual glass cooling curves obtained from two instrumented full-size glass canisters produced by West Valley (designated TC-18 and TC-23). The thermocouple positions in the canisters are illustrated in Figures 3.7 and 3.8. Samples HT-S-1 and 2 were cooled with cooling curves simulating temperatures observed with thermocouples placed approximately 30 in. from the bottom of canister TC-18. These thermocouples happened to be placed near pour batch boundaries; the glass was poured into the canister in batches, not continuously. This is why the glass is seen to cool, then suddenly heat up, then cool again. The cooling scheme used to treat HT-S-1 is the slowest cooling of the six schemes used.

3.16
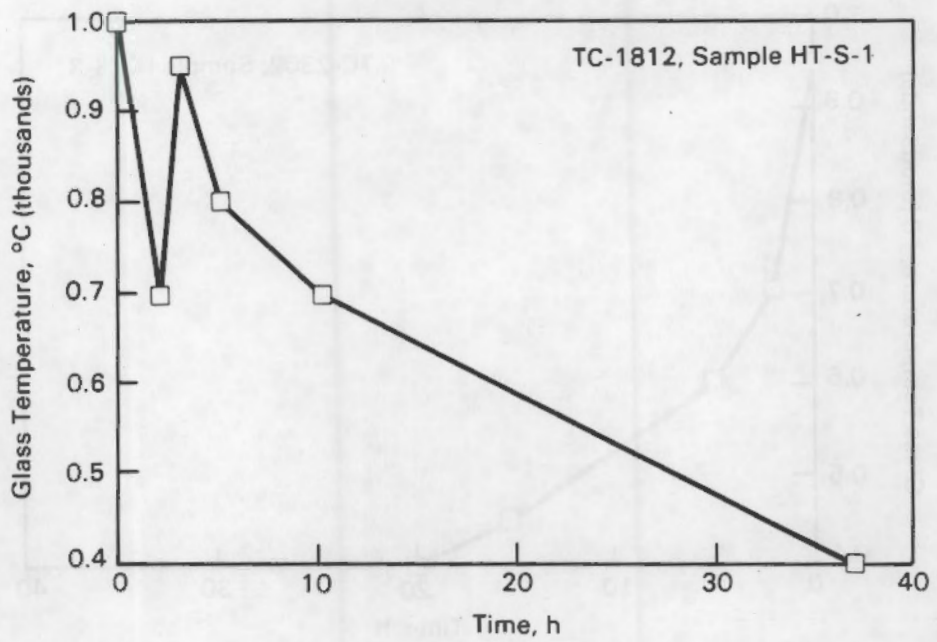
FIGURE 3.1. Sample HT-S-1 Cooling History
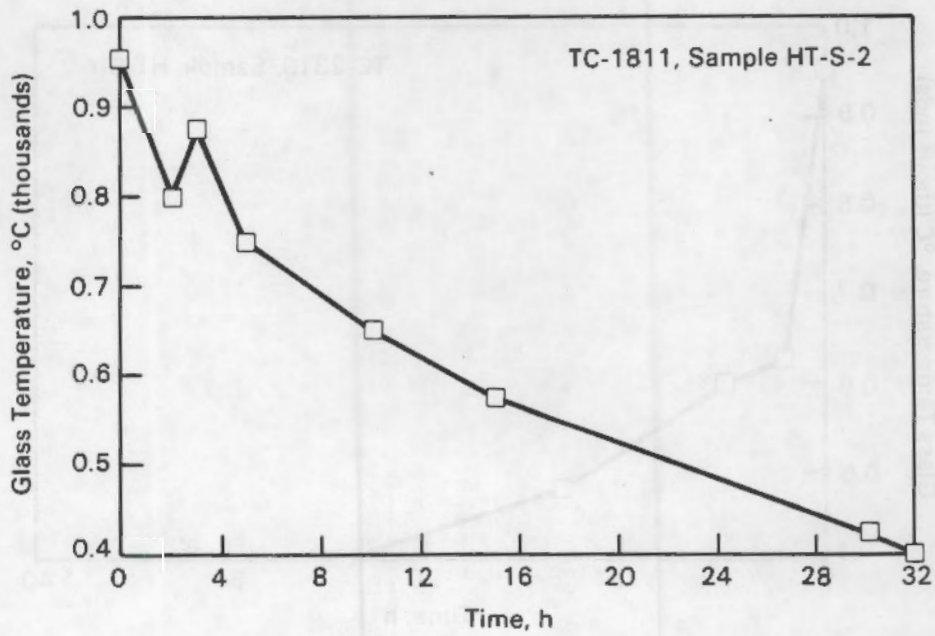
FIGURE 3.2. Sample HT-S-2 Cooling History

3.17
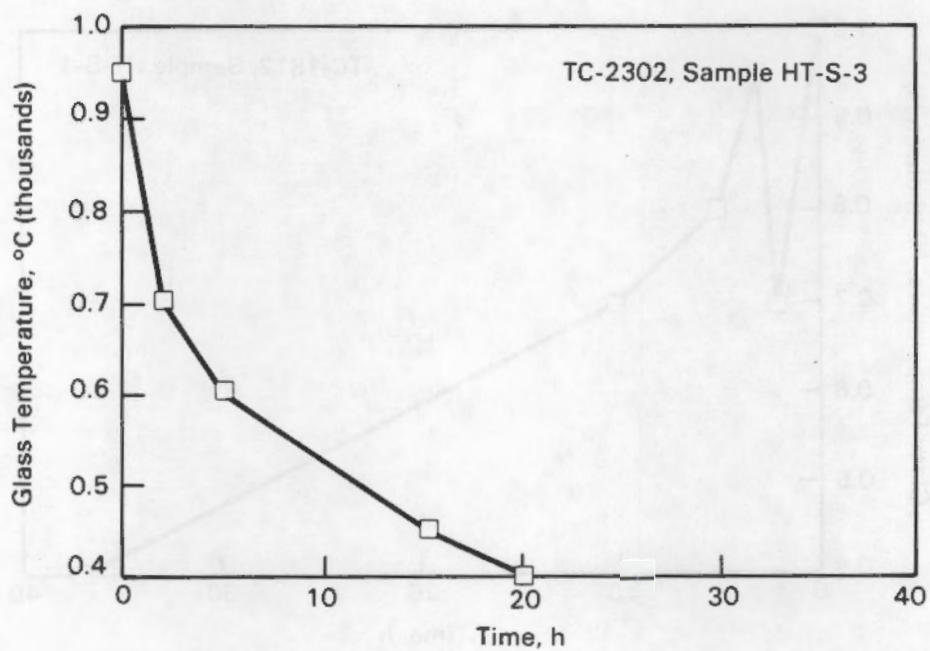
FIGURE 3.3. Sample HT-S-3 Cooling History
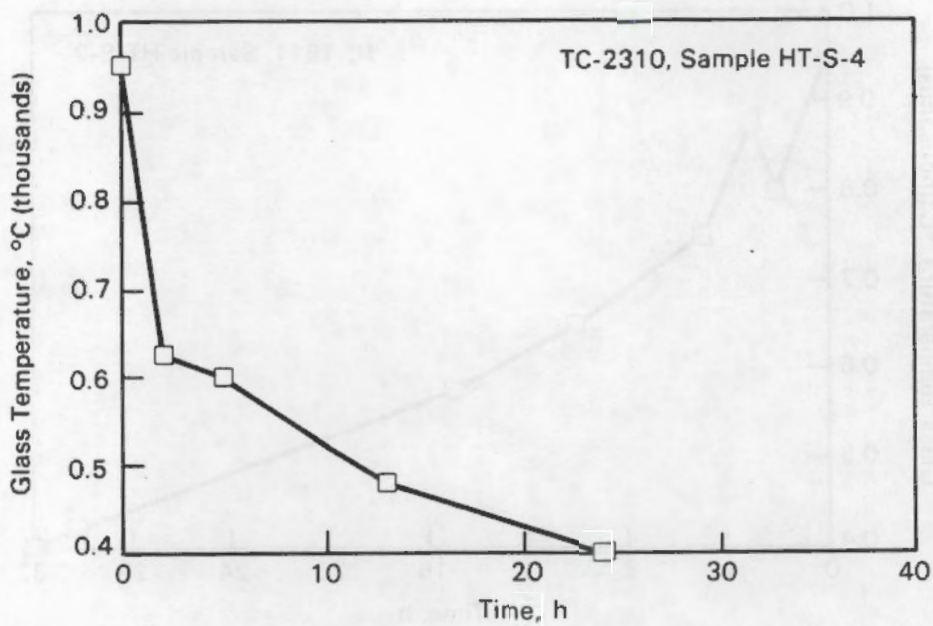
FIGURE 3.4. Sample HT-S-4 Cooling History
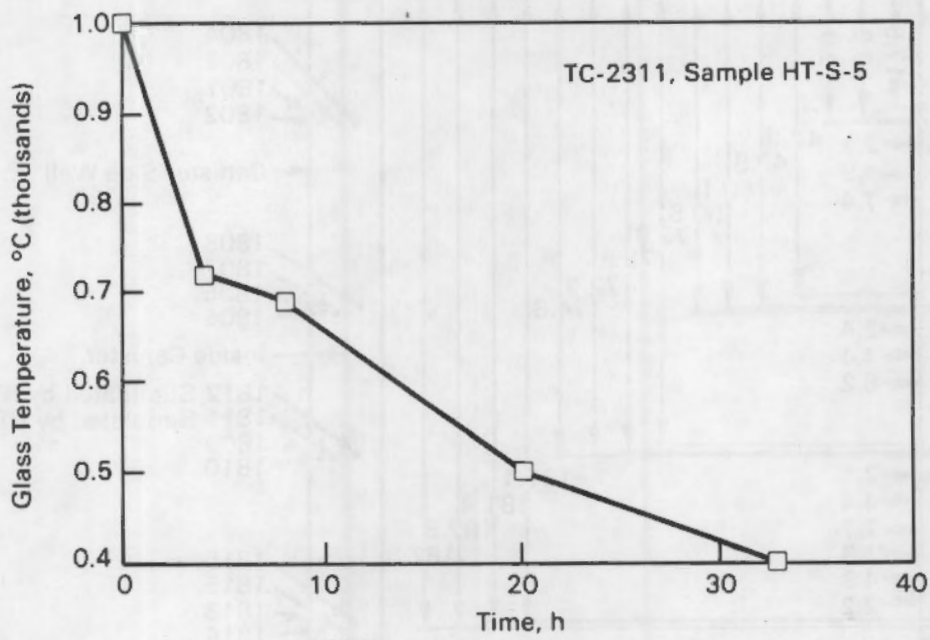
FIGURE 3.5. Sample HT-S-5 Cooling History
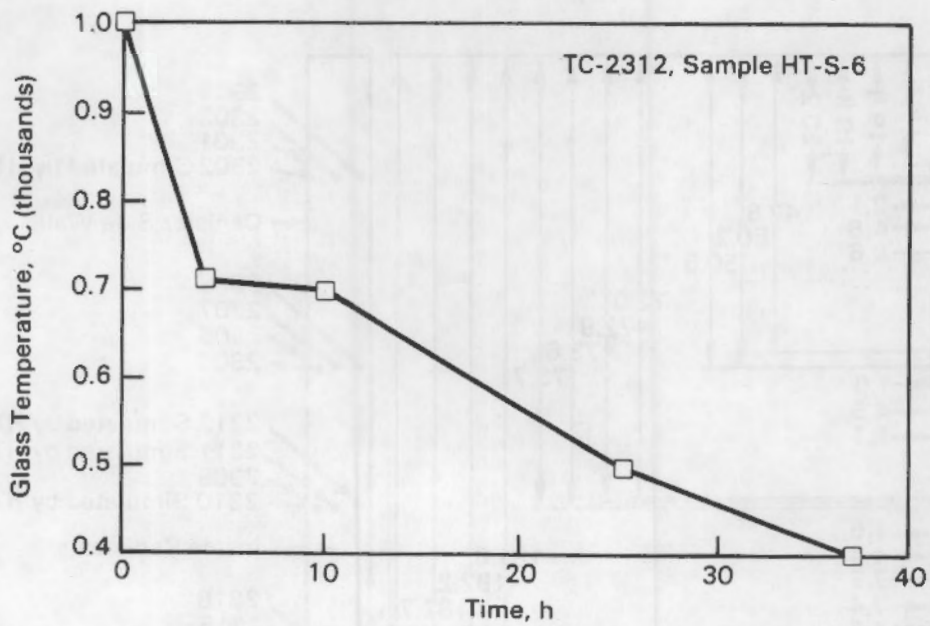
FIGURE 3.6. Sample HT-S-6 Cooling History
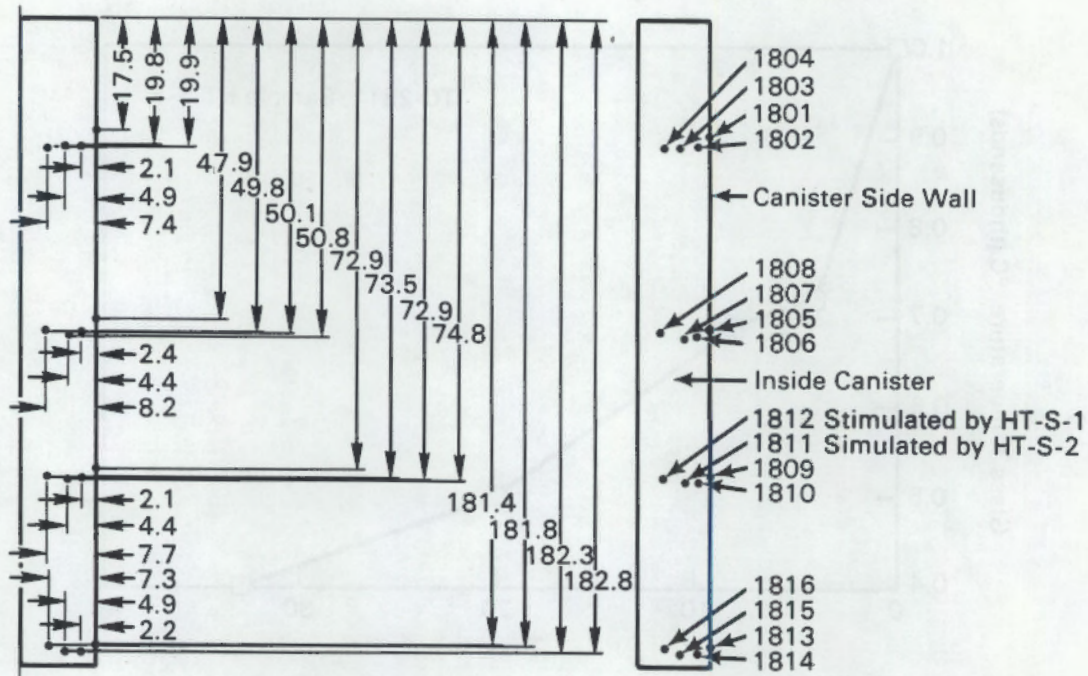
FIGURE 3.7. Thermocouple Locations in Canister TC-18. Simulated by heat-treatment samples HT-S-1 and 2.
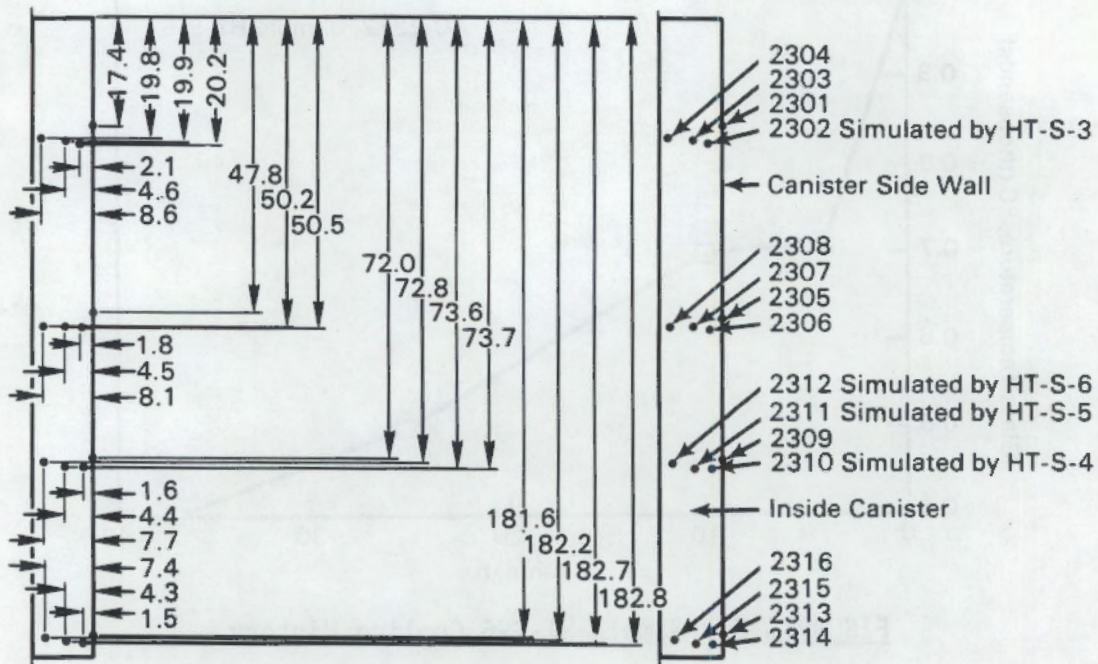
FIGURE 3.8. Thermocouple Locations in Canister TC-23. Simulated by heat-treatment samples HT-S-3, 4, 5, and 6.

3.20

The cooling scheme used to treat sample HT-S-3 simulates the temperature readings observed approximately 20 in. from the top of canister TC-23. This cooling scheme gives the fastest cooling of the six used. Cooling schemes used for samples HT-S-4, 5, and 6 were simulated temperatures observed approximately 30 in. from the bottom of canister TC-23.

Six samples of a 1.5 kg batch of West Valley reference waste glass were heat treated. The composition of the glass is the same as that used in the redox adjustment study. The target oxide and as-analyzed compositions of these glass samples are given in Table 3.10. The glass was treated in the following manner. A specified amount of crushed glass was placed in a fused silica crucible and put in the furnace at 1200°C. When the glass was in a molten state (after about 20 min), the furnace controller program was activated. The temperature of the furnace was monitored over time with a thermocouple with continuous strip chart read-out. The crucible was removed from the furnace at a temperature of roughly 100°C, allowed to cool to room temperature, then sectioned and a vertical slice removed and polished. The slice was then examined and analyses taken with SEM/EDX and x-ray diffraction (XRD). A portion of the remaining glass, not including glass comprising the glass/crucible interface, was crushed and sieved in preparation for leach testing.

3.7.2 Isothermal Heat Treatments

West Valley Nuclear Services (WVNS) specified the specific annealing heat treatments to be used in this work. The specified heat treatment test matrix is given in Table 3.11. The matrix consists of five different treatment temperatures and holding times varying from 6 to 240 h. The selection of this matrix was based on work performed at Alfred University.

A total of 15 samples from three 1.25 kg batches of West Valley reference glass (labeled DG-WV31A, B, and C) were heat treated. The composition of the glass is the same as that used in the simulated canister cooling treatments. Random samples of half of the treated specimens (8 samples) were submitted for chemical analysis to determine their compositions. These analyses were used to determine the average compositions of the three glass

TABLE 3.10. Compositions of Slow Cool Heat Treated Glasses, wt%

Oxide	Target	As-Analyzed[a]					
		HT-S-1	HT-S-2	HT-S-3	HT-S-4	HT-S-5	HT-S-6
Al_2O_3	9.99	10.60	10.32	10.41	10.37	10.33	10.35
B_2O_3	10.69	10.81	10.93	10.82	10.87	10.96	10.90
BaO	0.05	0.04	0.05	0.04	0.05	0.05	0.05
CaO	0.60	0.64	0.64	0.66	0.62	0.64	0.63
CeO_2	0.07	0.07	0.07	0.07	0.07	0.07	0.07
Cr_2O_3	0.18	0.19	0.18	0.19	0.19	0.17	0.19
Cs_2O	0.08	0.08	0.07	0.07	0.06	0.07	0.07
Fe_2O_3	12.19	11.85	11.67	11.76	11.81	11.58	11.74
K_2O	2.44	2.30	2.33	2.42	2.20	2.43	2.21
La_2O_3	0.03	0.04	0.04	0.03	0.03	0.04	0.04
Li_2O	2.63	2.57	2.56	2.55	2.53	2.59	2.55
MgO	1.33	1.29	1.29	1.30	1.30	1.28	1.30
MnO_2	1.31	1.34	1.33	1.36	1.35	1.33	1.36
MoO_3	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Na_2O	9.58	9.06	9.23	9.15	9.26	9.19	9.13
Nd_2O_3	0.12	0.11	0.13	0.11	0.13	0.11	0.13
NiO	0.28	0.29	0.27	0.29	0.28	0.29	0.28
P_2O_5	2.52	2.54	2.54	2.51	2.53	2.52	2.56
PdO_2	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Pr_6O_{11}	0.03	0.03	0.03	0.03	0.03	0.03	0.03
RhO_2	0.01	0.01	0.01	0.01	0.01	0.01	0.01
RuO_2	0.08	0.12	0.13	0.12	0.13	0.11	0.13
SiO_2	39.96	41.15	41.41	41.31	41.39	41.22	41.40
Sm_2O_3	0.03	0.03	0.03	0.03	0.03	0.03	0.03
SO_3	0.30	0.31	0.32	0.31	0.31	0.31	0.31
SrO	0.03	0.02	0.02	0.02	0.02	0.02	0.02
ThO_2	3.61	2.51	2.48	2.49	2.52	2.62	2.56
TiO_2	0.99	0.94	0.91	0.93	0.94	0.92	0.91
UO_2	0.56	0.49	0.49	0.49	0.49	0.51	0.50
Y_2O_3	0.02	0.02	0.02	0.02	0.02	0.02	0.02
ZrO_2	0.29	0.52	0.46	0.47	0.43	0.50	0.49
TOTAL	100.02	100.00	100.00	100.00	100.00	100.00	100.00

(a) ICP, AA, and laser fluorescence analyses, normalized to 100%.

TABLE 3.11. Isothermal Heat Treatment Test Matrix

Specimen #	Temperature, °C	Holding Time, h
HT-S-7 - 8	500	120, 240
HT-S-9 - 11	600	12, 48, 240
HT-S-12 - 16	725	6, 12, 48, 120, 240
HT-S-17 - 19	800	12, 48, 240
HT-S-20 - 21	900	120, 240
HT-S-22 (Test Standard)	500	2

batches. No volatility losses of the specimen glasses or other compositional changes due to the heat treatments were observed. The target oxide and as-analyzed compositions of these glass batches are given in Table 3.12.

The glass was treated in the following manner. A portion of crushed glass was placed in a covered fused silica crucible and put in the furnace at 1200°C. When the glass was in a molten state (after about 20 minutes), the crucible was removed and placed in a heat-treatment oven heated to the specified temperature. The oven temperature was monitored daily. The crucible remained in the oven for a specified holding time, then was removed and annealed for 2 h at 500°C in an annealing oven. After 2 h had passed, the oven was turned off and allowed to cool over night. The crucible was removed from the oven, then sectioned and a vertical slice was removed and polished. The slice was analyzed with XRD and SEM/EDX. A test standard, HT-S-22, was prepared in the manner described above except that it was not heat treated prior to the 500°C anneal.

A portion of each heat-treated glass, not including glass comprising the glass/crucible interface, was crushed and sieved in preparation for 7-day, MCC-3 leach testing.

3.8 GROUNDWATER LEACH TESTING

One West Valley reference glass was leach tested in four different groundwaters. The groundwaters used represent repository groundwaters.

TABLE 3.12. Compositions of DG-WV31 Batches, wt%

Oxide	Target	As-Analyzed[a]		
		Batch A[b]	Batch B[c]	Batch C
Al_2O_3	9.99	11.10	10.99	11.14
B_2O_3	10.69	10.53	10.71	10.32
BaO	0.05	0.05	0.05	0.05
CaO	0.60	0.77	0.63	0.61
CeO_2	0.07	0.00	0.03	0.06
Cr_2O_3	0.18	0.18	0.18	0.17
Cs_2O	0.08	0.06	0.06	0.06
CuO	0.00	0.01	0.01	0.00
Fe_2O_3	12.19	11.74	11.93	11.65
K_2O	2.44	2.76	2.74	3.04
La_2O_3	0.03	0.03	0.03	0.04
Li_2O	2.63	2.55	2.56	2.50
MgO	1.33	1.25	1.25	1.29
MnO_2	1.31	1.2B	1.31	1.28
MoO_3	0.01	0.00	0.00	0.00
Na_2O	9.58	9.55	9.47	9.24
Nd_2O_3	0.12	0.12	0.12	0.14
NiO	0.28	0.31	0.34	0.32
P_2O_5	2.52	2.52	2.54	2.56
PdO_2	0.01	0.01	0.01	0.01
Pr_6O_{11}	0.03	0.03	0.03	0.03
RhO_2	0.01	0.01	0.01	0.01
RuO_2	0.08	0.08	0.08	0.08
SiO_2	39.96	39.89	40.39	39.77
Sm_2O_3	0.03	0.03	0.03	0.03
SO_3	0.30	0.30	0.30	0.31
SrO	0.03	0.03	0.03	0.03
ThO_2	3.61	2.68	2.33	3.28
TiO_2	0.99	0.93	0.92	0.92
UO_2	0.56	0.51	0.45	0.51
Y_2O_3	0.02	0.02	0.02	0.02
ZrO_2	0.29	0.66	0.47	0.51
TOTAL	100.02	100.00	100.00	100.00

(a) ICP, AA, and laser fluorescence analyses, normalized to 100%.
(b) Average of 3 analyses
(c) Average of 4 analyses

3.24

Leach testing was done to determine the effect of different types of repository groundwaters on the reference glass durability.

3.8.1 Groundwater Descriptions

Four leachants representing repository groundwaters were used in this study. Their compositions are given in Tables 3.13 through 3.16. One of these, J-13, is actual groundwater recovered from a well at the Yucca Mountain repository site selected by DOE for site characterization. The

TABLE 3.13. Composition of J-13 Well Water--Tuff Groundwater Used in Groundwater Study

	Concentration, ppm		
Species	As Analyzed[a]	As Analyzed[b]	Blank[c]
B	0.20	0.132	0.16*
Na	48.20	44.70	44.90*
K	6.64	5.11	4.80*
Ca	13.30	12.70	12.60
Si	32.60	27.10	27.60*
Mg	2.17	1.92	1.33
F	2.30	2.20	2.50
Cl	7.09	0.21	7.10
SO_4	17.20	18.70	17.00
NO_3	7.64	9.60	8.50
IC[d]	24.20	NA[e]	NA
pH	8.12	8.20[f]	8.26[g]

(a) ICP, IC and organic C analyses reported by material custodian.
(b) Averages, reported by Oversby, 1985.
(c) ICP and IC analyses of test blank sample. Concentrations marked with an asterisk were used for correction of test results.
(d) Inorganic carbon.
(e) Not available.
(f) pH measured immediately preceding test.
(g) pH measured at test termination.

TABLE 3.14. Composition of PBB1 Brine Used in Groundwater Study

	Concentration, ppm	
Species	Target	As Analyzed[a]
Na	124000.0	124000.0
Ca	1600.0	1300.0
Mg	134.0	104.0
K	39.0	87.9
Sr	35.0	13.7
Cl	192000.0	185000.0
SO_4	3840.0	3500.0
Br	32.0	42.0
HCO_3	30.5	16.2

(a) ICP and ion chromatograph (IC) analyses.

TABLE 15. Composition of PBB3 Brine Used in Groundwater Study

	Concentration, ppm	
Species	Target	As Analyzed[a]
Na	25000 ± 5000	22900
Ca	18700 ± 2000	18500
Mg	62500 ± 6000	56600
K	11000 ± 2000	12100
Cl	240000 ± 20000	243000
SO_4	250 ± 150	209
Br	3400 ± 700	3550

(a) ICP and IC analyses.

other three are synthetic groundwaters, prepared with specific compositions, used in testing the effects of these repository groundwaters on the nuclear waste package. Two of the synthetic groundwaters, PBB1 and PBB3, represent groundwater generated by a bedded salt site. The other, GR-4, represents basalt groundwater.

TABLE 3.16. Composition of GR-4 - Basalt Groundwater Used in Groundwater Study

	Concentration, ppm		
Species	Target	As Analyzed[a]	Blank[b]
Na	334.0	364.5	349.5*
K	13.8	14.15	13.8 *
Ca	2.2	2.22	2.2
Si	45.0	43.45	36.3 *
F	19.9	19.9	20.0
Cl	405.0	409.85	420.0
SO_4	4.0	4.2	3.8
IC[c]	18.1	19.25	NA[d]
pH	9.70	10.18[e]	9.66[f]

(a) ICP and IC analyses - information supplied by material custodian.
(b) ICP and IC analyses of test blank sample. Concentrations marked with an asterisk were used for correction of test results.
(c) Inorganic carbon.
(d) Information not available.
(e) pH measured immediately preceding test.
(f) pH measured at test termination at 25°C.

The J-13 water is obtained from the J-13 well located on the Yucca Mountain site in Nevada. The reference repository horizon is a welded, devitrified portion of the Topopah Spring Member of the Paintbrush Tuff. The water from well J-13 has been adopted as a reference water chemistry for experimental work (Oversby 1985). The composition of J-13 water used in this study is given in Table 3.13.

PBB1 and PBB3 are synthetic brines developed to support PNL laboratory work performed to determine the general corrosion resistance of waste package components in contact with Permian Basin salt and brine derived therefrom. PBB1 represents the brine resulting from dissolution of salt core samples from a Permian Basin salt horizon considered representative of a bedded-salt-site repository. The specific salt core samples were obtained from G. Friemel Hole No. 1 near Amarillo, Texas, and are representative of the Cycle 4 salt horizon in that region. PBB3 represents an inclusion brine

chemistry, i.e., a brine that exists in inclusions in a bedded salt as opposed to brines resulting from a hypothetical water intrusion, such as PBB1. The chemical composition of PBB3 was supplied to PNL by the Salt Repository Project (SRP) in December 1983. The compositions of the PB81 and PBB3 brines used in this study are given in Tables 3.14 and 3.15, respectively.

GR-4 water is chemically representative of groundwater found in the reference repository location (RRL) area of the Grande Ronde basalt formation underlying the Hanford Site near Richland, Washington (Dill et al. 1985). This reference synthetic groundwater was developed to be used in tests including the interaction of groundwater with basalt rock, waste forms, and engineered barriers. To evaluate the results of these tests, it is imperative that the experiments be carried out using a common groundwater of known stable constituents. Because of the instability of the water system and logistical problems associated with collecting and shipping large volumes of groundwater over long distances, it was deemed necessary to develop a synthetic groundwater "recipe." The composition of this water is given in Table 3.16.

3.8.2 Leach Testing and Blank Correction

Four samples of a batch of West Valley reference waste glass were leach tested in the groundwaters. The composition of the glass is the same as that used in the redox adjustment and heat treatment studies. The target oxide and as-analyzed compositions of the glass are given in Table 3.17.

The concentrations of the leachates were corrected with test blanks. This was done with the brine solutions (PBB1 and PBB3) by the analytical laboratory with matrix matching. A sample of the clean brine was run with a sample of the leachate brine for the solution matrix matching. The results reported by the laboratory reflected only those elements which were higher in concentration in the leachate than the clean brine. The concentrations of the tuff and basalt groundwater leachates were corrected by subtracting the concentration of elements found in the blank from the leachate concentrations. This could not be done for Ca concentration in basalt groundwater nor

TABLE 3.17. Composition of West Valley Reference Glass Used in Groundwater Effects Study, wt%

Oxides	Target	As Analyzed[a]
Al_2O_3	9.99	11.32
B_2O_3	10.69	10.72
BaO	0.05	0.05
CaO	0.60	0.58
CeO_2	0.07	0.07
Cr_2O_3	0.18	0.00
Cs_2O	0.08	0.05
CuO	0.00	0.03
Fe_2O_3	12.19	11.52
K_2O	2.44	2.79
La_2O_3	0.03	0.03
Li_2O	2.63	2.61
MgO	1.33	1.26
MnO_2	1.31	1.21
MoO_3	0.01	0.01
Na_2O	9.58	8.99
Nd_2O_3	0.12	0.12
NiO	0.28	0.00
P_2O_5	2.52	2.55
PdO_2	0.01	0.01
Pr_6O_{11}	0.03	0.03
RhO_2	0.01	0.01
RuO_2	0.08	0.06
SiO_2	39.96	40.62
Sm_2O_3	0.03	0.03
SO_3	0.30	0.30
SrO	0.03	0.03
ThO_2	3.61	3.04
TiO_2	0.99	0.96
UO_2	0.56	0.52
Y_2O_3	0.02	0.02
ZrO_2	0.29	0.47
TOTAL	100.02	100.00

(a) ICP, AA, and laser fluorescence analyses, normalized to 100%.

Ca and Mg concentrations in tuff groundwater as these concentrations were higher in the blanks than in the leachates. Both of these must have formed compounds during the leaching process which precipitated from the leaching solution. Tuff and basalt groundwater test blank compositions are given in Tables 3.13 and 3.16, respectively.

4.0 RESULTS AND DISCUSSION

4.1 COMPOSITION EFFECTS - FY 1987

The results from the FY 1987 MCC-3 and MCC-1 leach tests of glasses DG-WV1 through DG-WV8 and DG-WV15 through DG-WV30 show how variations in glass composition relate to variations in glass durability. The test results are described in the following sections.

4.1.1 First Set of FY 1987 Glasses--DG-WV1 Through DG-WV8

MCC-3, 7-day Leach Testing Results

Table 4.1 lists the normalized elemental mass releases of B, Cs, Na, Si, Th, U, and those elements whose oxide contributed at least 1 wt% of the glass composition. Each value given represents the average obtained from three replicate tests. The three replicate tests were performed at the same time under the same conditions, and the resulting leachates were chemically analyzed at the same time under the same conditions. Hence the replicates only include short-term variations in the leach testing and leachate analysis processes.

The analysis of these releases shows that the chemical durabilities of the reference glass DG-WV1, and the glass containing noble metal (Rh, Ru, Pd) oxides, DG-WV2, are essentially identical. The least chemically durable glass appears to be the "high Na_2O" glass (DG-WV4), as was expected (increasing amounts of alkali decreases chemical durability). The glasses containing relatively low amounts of Al_2O_3 (DG-WV3 and DG-WV5) are less chemically durable than the reference glass, as was also expected (increasing amounts of Al_2O_3 increases chemical durability). The "high" P_2O_5 and ThO_2 (DG-WV6 and DG-WV7) and "low" B_2O_3 glasses (DG-WV8) appear to be as chemically durable as the reference glass. This indicates that these variations in P_2O_5, ThO_2, and B_2O_3 have little, if any, real effect on the product chemical durability.

Graphical representations of B and Si releases are given in Figure 4.1. The error bars represent short-term experimental error of ± two standard deviations (sds). The sds are based on replicate tests performed at the same time and do not include the time-related component of variability.

TABLE 4.1. Average Normalized Mass Releases of Glasses DG-WV1 Through DG-WV8 (7-day MCC-3, Deaerated DIW, 90°C), g/m^2

	Average Normalized Mass Release (g/m^2)							
Element	DG-WV1	DG-WV2	DG-WV3	DG-WV4	DG-WV5	DG-WV6	DG-WV7	DG-WV8
Al	0.106	0.109	0.098	0.110	0.097	0.115	0.109	0.113
B	0.186	0.191	0.237	0.239	0.229	0.188	0.188	0.187
Cs	0.104	0.092	0.137	0.092	0.082	0.093	0.120	0.040
Fe	0.002	0.003	0.004	0.003	0.003	0.003	0.003	0.003
K	0.021	0.022	0.043	0.014	0.022	0.006	0.033	0.026
Li	0.301	0.305	0.300	0.294	0.328	0.301	0.323	0.319
Mg	0.000	0.000	0.008	0.000	0.000	0.000	0.000	0.005
Mn	0.001	0.003	0.003	0.002	0.002	0.002	0.002	0.003
Na	0.158	0.163	0.218	0.239	0.204	0.155	0.170	0.176
P	0.105	0.107	0.196	0.182	0.147	0.097	0.108	0.133
Si	0.116	0.117	0.129	0.123	0.127	0.123	0.119	0.118
Th	0.001	0.002	0.001	0.001	0.001	0.002	0.001	0.002
Ti	0.001	0.002	0.002	0.001	0.001	0.002	0.001	0.002
U	0.026	0.031	0.031	0.029	0.030	0.033	0.038	0.037
pH[a]	9.15	9.27	9.41	9.22	9.37	9.02	8.78	9.33

(a) pH measured at test termination at 25°C.
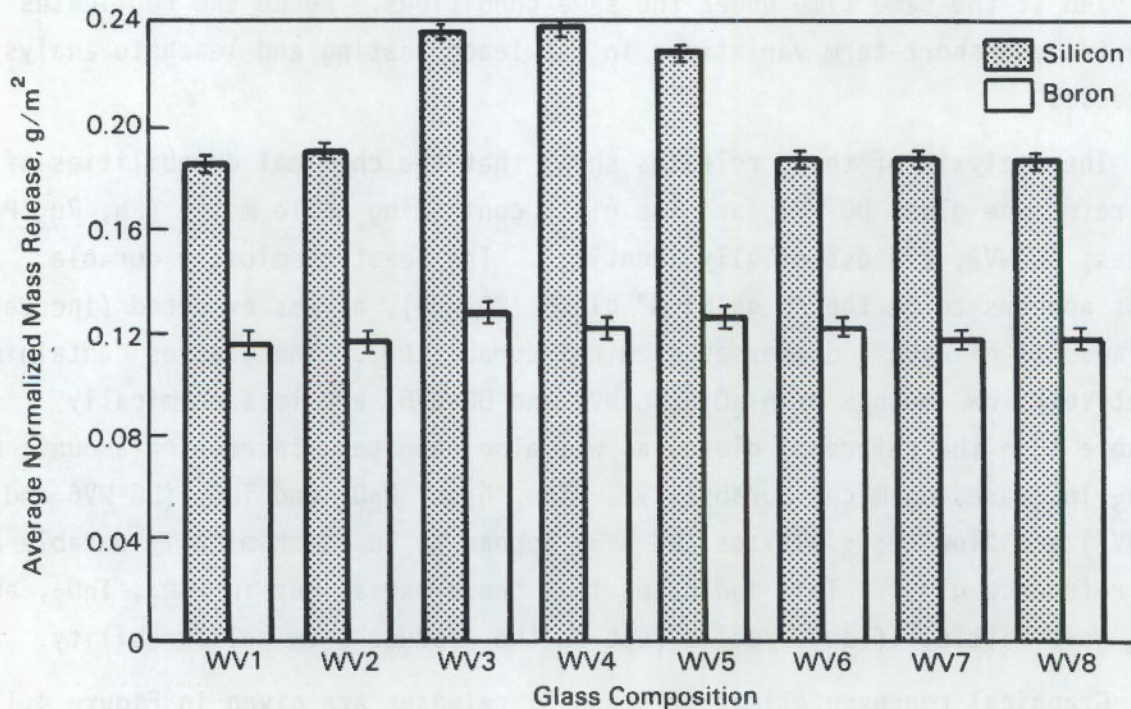
FIGURE 4.1. Comparison of Boron and Silicon Normalized Mass Releases from DG-WV1 Through DG-WV8. Modified MCC-3 test, 90°C, deaerated deionized water, 7-day.

4.2

Figure 4.1 shows that Si release is relatively consistent among each glass tested, indicating that its solubility limit was reached during the test period. The B release data show that DG-WV3, DG-WV4, and DG-WV5 are the least chemically durable, with the other five compositions exhibiting greater chemical durability.

MCC-1, 28-day Leach Testing Results

Glasses DG-WV1 through DG-WV8 were also subjected to 28-day MCC-1 leach testing. Table 4.2 lists the normalized elemental mass releases of B, Cs, Na, Si, Th, U, and those elements whose oxide contributed at least 1 wt% of the glass composition. Each value given represents the average obtained from three replicate tests. Graphical representations of Si and B releases are given in Figure 4.2. The error bars represent ± two sds. The sds are based on replicate tests performed at the same time and do not include the time-related component of variability. The results are similar to those observed from MCC-3 leach testing of the glass. A major difference is that no Th release was observed with MCC-1 testing whereas a small amount of Th release

TABLE 4.2. Average Normalized Mass Releases of Glasses DG-WV1 Through DG-WV8 (28-day MCC-1, Deaerated DIW, 90°C), g/m^2

Element	Average Normalized Mass Release							
	DG-WV1	DG-WV2	DG-WV3	DG-WV4	DG-WV5	DG-WV6	DG-WV7	DG-WV8
Al	7.956	8.071	8.969	9.931	7.953	8.011	7.913	7.497
B	9.499	9.940	14.066	14.011	10.908	9.330	9.530	8.672
Cs	20.193	20.167	34.396	28.813	26.279	22.499	27.229	6.792
Fe	0.043	0.046	0.095	0.049	0.080	0.109	0.063	0.047
K	1.385	7.540	6.066	3.758	1.345	5.760	3.491	3.049
Li	9.230	9.952	13.839	13.935	11.169	9.171	9.604	8.605
Mg	5.672	5.367	1.303	1.417	4.196	5.507	5.635	5.209
Mn	0.085	0.088	0.105	0.065	0.097	0.137	0.102	0.085
Na	9.008	9.536	13.479	13.795	10.630	8.886	9.545	8.736
P	5.623	5.592	10.122	9.906	6.129	4.941	4.564	5.417
Si	8.443	8.586	11.027	10.950	9.232	8.344	8.518	7.765
Th	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Ti	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
U	1.508	1.411	1.441	1.518	1.265	1.168	1.725	1.334
pH[a]	8.95	8.70	9.10	9.08	8.82	8.48	8.58	8.79

(a) pH measured at test termination at 25°C.

4.3
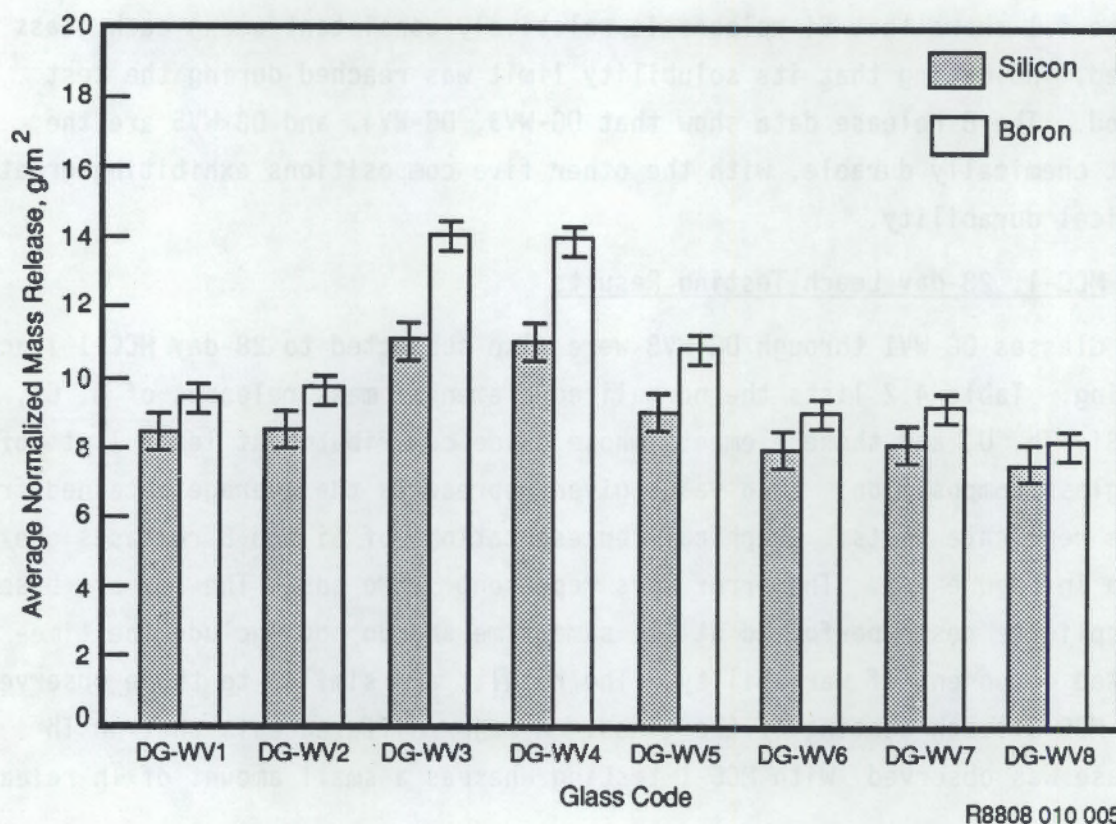
FIGURE 4.2. Comparison of Si and B Normalized Mass Releases from DG-WV1 Through DG-WV8 (MCC-1 test, 90°C, deaerated DIW, 28-day)

was observed with MCC-3 testing. Analysis of these releases shows that the chemical durability of the reference glass, DG-WV1, and reference glass containing noble metal (Rh, Ru, Pd) oxides, DG-WV2, are essentially identical, and that the variations in P_2O_5, ThO_2 and B_2O_3 have little, if any, real effect on the product chemical durability.

4.1.2 Second Set of FY 1987 Glasses--DG-WV15 Through DG-WV30

MCC-3, 7-day Leach Test Results

Table 4.3 lists the normalized elemental mass releases, obtained through 7-day MCC-3 tests of B, Cs, Na, Si, Th, U, and those elements whose oxide contributed at least 1 wt% of the glass composition. Each value given represents the average obtained from three replicate tests.

4.4

Element	DG-WV15	DG-WV16	DG-WV17	DG-WV18	DG-WV19	DG-WV20	DG-WV21	DG-WV22
Al	0.103	0.108	0.110	0.127	0.126	0.113	0.150	0.136
B	0.264	0.181	0.273	0.210	0.207	0.148	0.205	0.185
Ca	0.001	0.003	0.000	0.000	0.000	0.000	0.012	0.008
Ce	0.000	0.000	0.000	0.000	0.000	0.000	0.005	0.004
Cs	0.097	0.089	0.097	0.061	0.085	0.112	0.099	0.091
Fe	0.002	0.002	0.002	0.005	0.002	0.002	0.006	0.003
K	0.103	0.113	0.106	0.141	0.102	0.000	0.202	0.076
Li	0.287	0.243	0.296	0.266	0.286	0.241	0.252	0.294
Mg	0.006	0.005	0.000	0.000	0.006	0.000	0.011	0.000
Mn	0.002	0.002	0.002	0.004	0.002	0.001	0.005	0.003
Na	0.243	0.155	0.248	0.207	0.190	0.125	0.205	0.160
P	0.215	0.084	0.237	0.170	0.170	0.051	0.131	0.091
Si	0.115	0.111	0.117	0.126	0.112	0.105	0.136	0.128
Th	0.000	0.000	0.000	0.004	0.001	0.000	0.010	0.007
Ti	0.000	0.001	0.000	0.004	0.000	0.001	0.006	0.003
U	0.023	0.022	0.019	0.042	0.036	0.006	0.044	0.036
pH[a]	7.88	8.56	9.26	9.18	9.03	8.57	8.86	8.44

Element	DG-WV23	DG-WV24	DG-WV25	DG-WV26	DG-WV27	DG-WV28	DG-WV29	DG-WV30
Al	0.136	0.123	0.125	0.101	0.149	0.130	0.101	0.126
B	0.232	0.193	0.179	0.172	0.250	0.188	0.207	0.205
Ca	0.000	0.000	0.000	0.000	0.004	0.007	0.004	0.006
Ce	0.019	0.000	0.000	0.000	0.004	0.006	0.000	0.000
Cs	0.031	0.071	0.082	0.108	0.071	0.073	0.103	0.099
Fe	0.020	0.004	0.005	0.002	0.008	0.009	0.005	0.002
K	0.054	0.058	0.032	0.064	0.064	0.061	0.097	0.113
Li	0.294	0.284	0.264	0.265	0.300	0.301	0.260	0.281
Mg	0.012	0.000	0.000	0.000	0.000	0.000	0.012	0.003
Mn	0.015	0.003	0.002	0.002	0.004	0.008	0.005	0.001
Na	0.172	0.156	0.153	0.144	0.208	0.156	0.194	0.206
P	0.078	0.141	0.085	0.094	0.105	0.103	0.201	0.123
Si	0.132	0.117	0.119	0.098	0.133	0.128	0.113	0.122
Th	0.023	0.003	0.002	0.000	0.007	0.011	0.000	0.001
Ti	0.021	0.003	0.002	0.001	0.007	0.008	0.001	0.001
U	0.052	0.030	0.031	0.028	0.022	0.034	0.033	0.029
pH[a]	9.29	9.39	9.50	9.43	9.48	9.49	9.80	9.66

(a) pH measured at test termination at 25°C.

Graphical representation of Si and B releases are given in Figures 4.3 and 4.4. Based on B release, the glasses were ordered from least to most chemically durable in these figures. The error bars represent ± two sds. The sds are based on replicate tests performed at the same time and do not
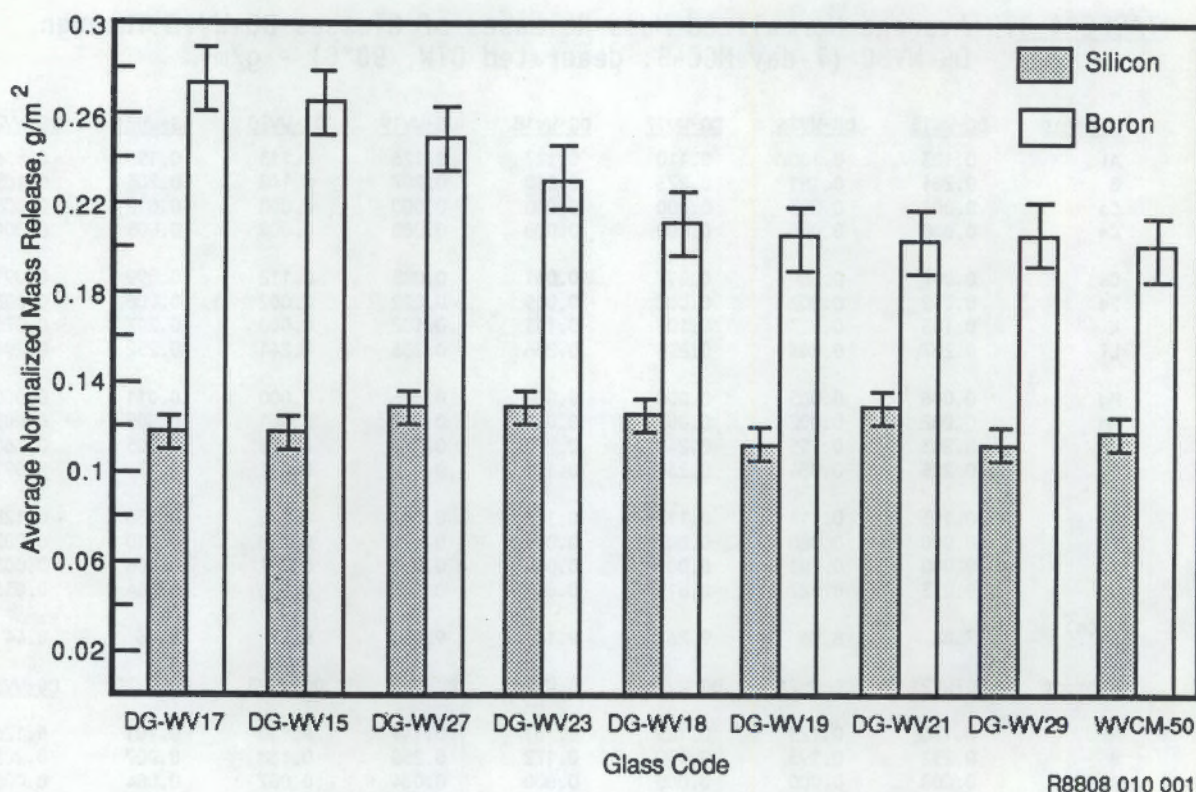
FIGURE 4.3. Comparison of Si and B Normalized Mass Releases of Least Durable of Second Set of Compositional Variability Glasses (Ordered from least to greatest durability based on boron release. Modified MCC-3 test, 90°C, deareated DIW, 7-day.)

include the time-related component of variability. The releases of the reference glass, WVCM-50 (DG-WV30), are included in each figure for direct comparison.

Roughly half of the glasses tested had greater chemical durability than the nominal WVCM-50 composition. The compositional variation caused maximum B releases of 34% higher and 29% lower than WVCM-50. The two least chemically durable glasses, DG-WV17 and DG-WV15, contain low amounts of (Al_2O_3 + SiO_2) and high amounts of Alkaline earths, MnO_2, and "other" oxides relative to the nominal WVCM-50 composition.[a] This combination apparently is disrupting the Si-O-Si glass network, making H_2O attack easier and allowing

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(a) See footnote on Table 3.5 for complete listing of other oxides.

4.6
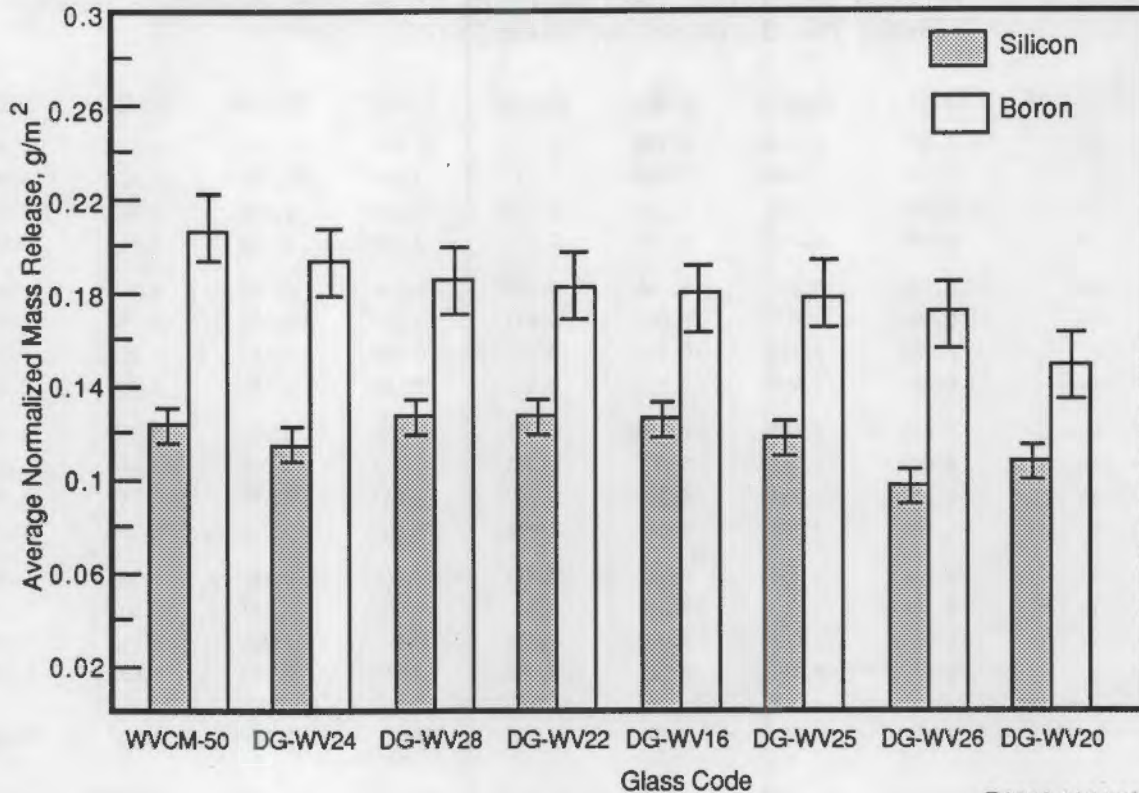
FIGURE 4.4. Comparison of Si and B Normalized Mass Releases of Most Durable of Second Set of Compositional Variability Glasses (Ordered from least to greatest durability based on boron release. Modified MCC-3 test, 90°C, deareated DIW, 7-day.)

the solution pH to increase with increased glass dissolution. The most chemically durable glass, DG-WV20, contains high amounts of ($Al_2O_3 + SiO_2$) and was observed to have the highest T100P (temperature at which the viscosity of the glass is 100 poise). The structure of this glass is more chemically resistant to H_2O attack, possibly due to having more bridging oxygens within its random structure.

MCC-3, 28-Day Leach Test Results

Table 4.4 lists the normalized elemental mass releases of B, Cs, Na, Si, Th, U, and those elements whose oxide contributed at least 1 wt% of the glass composition. Each value given represents the average obtained from three replicate tests.

TABLE 4.4. Average Normalized Mass Releases of Glasses DG-WV15 - DG-WV30 (28-day MCC-3, Deaerated Water, 90°C), g/m^2

Element	DG-WV15	DG-WV16	DG-WV17	DG-WV18	DG-WV19	DG-WV20	DG-WV21	DG-WV22
Al	0.121	0.126	0.118	0.151	0.155	0.141	0.176	0.161
B	0.412	0.268	0.350	0.291	0.309	0.199	0.270	0.267
Ca	0.003	0.004	0.003	0.009	0.005	0.004	0.011	0.013
Ce	0.000	0.000	0.000	0.000	0.000	0.002	0.007	0.011
Cs	0.114	0.054	0.146	0.105	0.144	0.100	0.111	0.073
Fe	0.009	0.008	0.007	0.013	0.011	0.008	0.014	0.007
K	0.122	0.138	0.180	0.110	0.136	0.122	0.096	0.101
Li	0.436	0.401	0.381	0.385	0.422	0.381	0.360	0.443
Mg	0.018	0.025	0.010	0.038	0.035	0.015	0.017	0.000
Mn	0.009	0.011	0.007	0.015	0.012	0.005	0.016	0.011
Na	0.302	0.211	0.330	0.260	0.261	0.152	0.247	0.194
P	0.261	0.148	0.238	0.216	0.253	0.059	0.161	0.087
Si	0.144	0.138	0.137	0.151	0.147	0.135	0.161	0.157
Th	0.001	0.002	0.000	0.004	0.002	0.001	0.003	0.003
Ti	0.002	0.003	0.002	0.006	0.002	0.005	0.013	0.007
U	0.029	0.035	0.021	0.050	0.065	0.013	0.053	0.048
pH[a]	9.45	8.88	9.69	9.66	9.47	9.40	9.03	8.86

Element	DG-WV23	DG-WV24	DG-WV25	DG-WV26	DG-WV27	DG-WV28	DG-WV29	DG-WV30
Al	0.173	0.144	0.137	0.122	0.168	0.156	0.124	0.139
B	0.423	0.282	0.213	0.255	0.449	0.229	0.297	0.271
Ca	0.017	0.002	0.002	0.002	0.001	0.008	0.006	0.003
Ce	0.036	0.000	0.000	0.000	0.010	0.013	0.000	0.000
Cs	0.062	0.113	0.150	0.116	0.085	0.122	0.110	0.127
Fe	0.038	0.010	0.011	0.008	0.014	0.015	0.015	0.008
K	0.071	0.134	0.245	0.105	0.088	0.118	0.156	0.166
Li	0.614	0.405	0.353	0.372	0.473	0.406	0.357	0.380
Mg	0.019	0.026	0.008	0.022	0.000	0.017	0.033	0.022
Mn	0.027	0.014	0.008	0.008	0.008	0.017	0.015	0.008
Na	0.227	0.202	0.173	0.188	0.284	0.170	0.270	0.226
P	0.051	0.079	0.038	0.054	0.059	0.050	0.212	0.081
Si	0.167	0.140	0.138	0.129	0.151	0.151	0.143	0.140
Th	0.029	0.003	0.004	0.001	0.008	0.009	0.004	0.002
Ti	0.035	0.006	0.007	0.003	0.012	0.013	0.008	0.003
U	0.066	0.046	0.031	0.034	0.034	0.032	0.061	0.034
pH[a]	8.82	8.88	9.07	8.82	9.06	9.07	9.38	9.24

(a) pH measured at test termination at 25°C.

4.8

Graphical representation of B and Si are given in Figures 4.5 and 4.6. Based on B release, the glasses were ordered from least to most chemically durable in these figures. The error bars represent ± two sds. The sds are based on replicate tests performed at the same time and do not include the time-related component of variability. Error bars are not given for Si due to their small range. The releases of the reference glass, WVCM-50 (DG-WV30) are included in each figure for direct comparison.

The results of the 28-day testing correspond with what was observed with 7-day testing. The normalized releases are higher than in the 7-day testing (from 10 to 300%) as are the test termination leachant pH values (0.3 to 0.5 pH units); however, the relative order of durabilities of the glasses, based on B release, corresponds to the 7-day test results. Roughly half of

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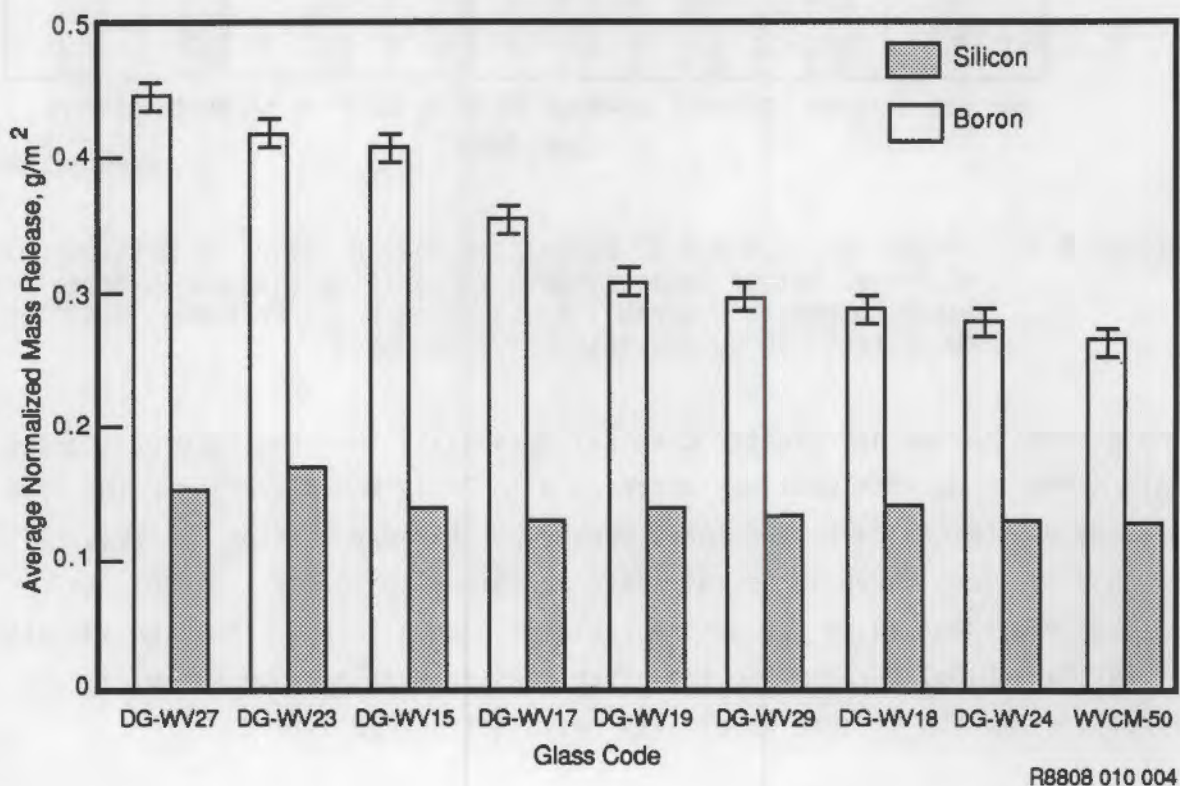
FIGURE 4.5. Comparison of B and Si Normalized Mass Releases of Least Durable of Second Set of Compositional Variability Glasses (Ordered from least to greatest durability based on boron release. Modified MCC-3 test, 90°C, deareated DIW, 28-day.)

4.9
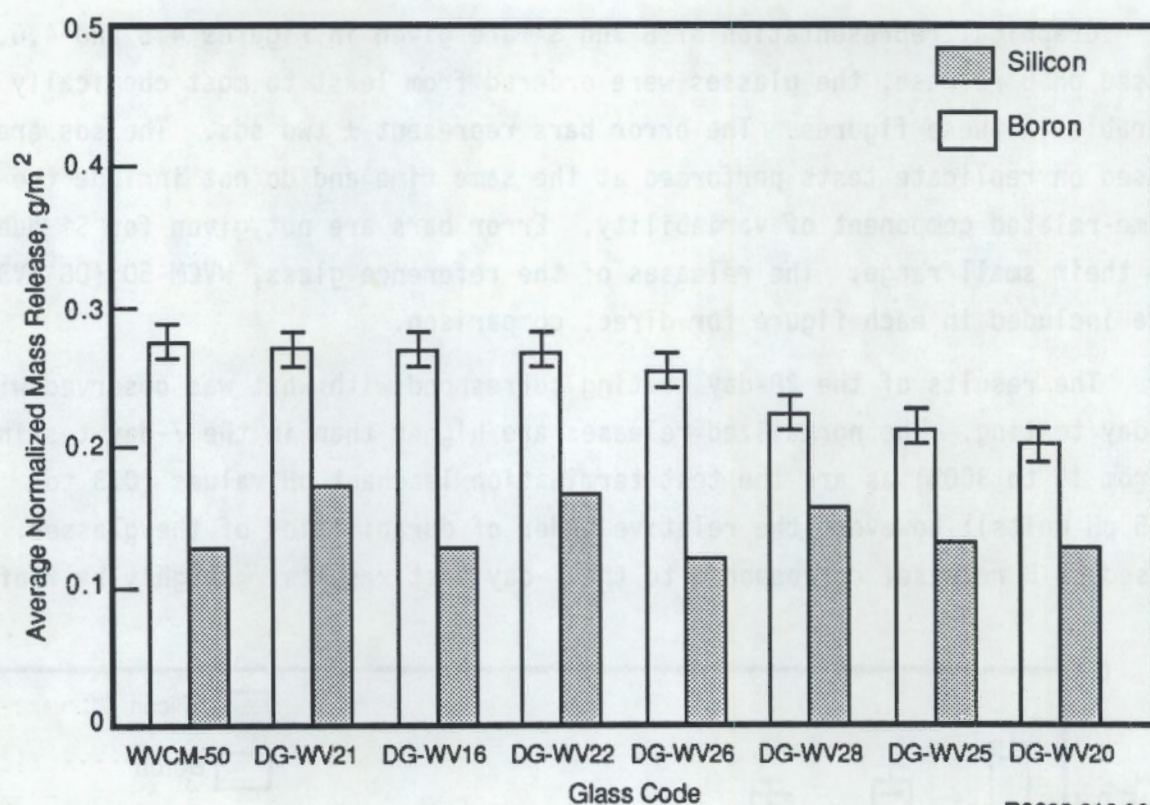
FIGURE 4.6. Comparison of B and Si Normalized Mass Releases of Most Durable of Second Set of Compositional Variability Glasses (Ordered from least to greatest durability based on boron release. Modified MCC-3 test, 90°C, deareated DIW, 28-day.)

the glasses tested had greater chemical durability than the reference glass. This corresponds with what was observed with 7-day MCC-3 testing. The four glasses determined to be the least durable with 7-day testing, DG-WV15, 17, 23, and 27, were shown to be the least durable with 28-day testing also. DG-WV20 was shown to be the most durable with both tests. The high amounts of $(Al_2O_3 + SiO_2)$ relative to the other glasses must enhance the glass structure, making it more chemically resistant to H_2O attack.

4.10

4.2 EMPIRICAL MODELING AND STATISTICAL ANALYSIS OF FY 1987 NORMALIZED BORON RELEASE DATA

4.2.1 Empirical Models for Normalized Boron Release

To determine whether or not varying composition within the composition region studied (defined in Table 3.4) has a statistically significant effect on normalized release, i.e., chemical durability, empirical mixture models were fit to the normalized B release data obtained from the 7-day MCC-3 tests. These mixture models account for the fact that the component weight fractions sum to unity. A linear mixture model of the form

$$\text{Normalized Boron Release (NBR)} = \sum_{i=1}^{11} b_i x_i \qquad (4.1)$$

was fit, where $x_1, \ldots, x_{11}$ are the weight fractions of the 11 oxide components listed under Single Component Constraints in Table 4 and $b_1, \ldots, b_{11}$ are the model parameters estimated via least squares regression. Models of this form are useful in assessing the importance of the components, provided the linear blending effects of the components are large relative to the nonlinear blending effects. Models of this form can indicate whether or not varying composition affects chemical durability, even if they have a moderate lack of fit.

Models were fit to the total 24 compositional variability glasses and also to the second set of 16. Least squares regression was used to estimate the parameters of the model. The fitted models for the 16- and 24-glass data sets are given respectively in Equation (4) and Equation (5):

$$\begin{aligned}
\text{NBR} = {}&-1.4572\ Al_2O_3 + 1.0393\ B_2O_3 - 0.3764\ (BaO+CaO+MgO) + \qquad (4.2)\\
&0.4039\ Fe_2O_3 + 2.3528\ (K_2O+Li_2O+Na_2O) + 0.9566\ MnO_2 + \\
&0.1607\ P_2O_5 - 0.4841\ SiO_2 + 0.9420\ ThO_2 + 1.8447\ UO_2 + \\
&0.7892\ \text{Others}
\end{aligned}$$

and

$$NBR = -1.3200\ Al_2O_3 + 0.6571\ B_2O_3 - 0.2333\ (BaO+CaO+MgO) + \quad (4.3)$$
$$0.3999\ Fe_2O_3 + 2.0574\ (K_2O+Li_2O+Na_2O) + 1.0203\ MnO_2 +$$
$$0.2260\ P_2O_5 - 0.3245\ SiO_2 + 0.9641\ ThO_2 + 1.7413\ UO_2 +$$
$$0.8085\ Others$$

where NBR is normalized boron release from the 7-day MCC-3 leach test, g/m^2. These two models fit their respective data sets well, with respective R^2 values (proportion of total variation in NBR explained) of 0.94 and 0.90. The models do not have a statistically significant lack of fit. Varying composition within the defined composition region (Table 3.4) does appear to have a statistically significant effect on chemical durability.

Linear mixture models similar to (4.2) and (4.3) were also fit to normalized Si release, but are not presented here. However, the model fit to the Si release data from all 24 FY 1987 glasses was applied to produce an effects plot to be discussed shortly.

Equation (4.2) was used to predict NBR for the eight glasses of the first set. The results were used to check the usefulness of the models as predictive tools, i.e., to validate the models. Table 4.5 lists the measured and predicted values for each glass. The individual and simultaneous 95% prediction intervals for each glass are also given in Table 4.5. The individual prediction intervals provide 95% confidence that the interval will contain a single observed value of NBR for the corresponding glass. The eight simultaneous prediction intervals (Miller 1981) provide 95% confidence that all eight intervals will contain individual measured NBR values.

As shown by Table 4.5, the predicted NBR values compare well with the observed values, and the observed values all fall within both the individual and simultaneous prediction intervals. This is very good evidence that the models can be reasonably used for prediction purposes within the composition region studied.

Effects plots (Piepel 1982) that demonstrate the effects of varying individual oxide components are presented in Figures 4.7 and 4.8 for B and Si releases. In a given effects plot, there is one effect curve for each

4.12

TABLE 4.5. Comparison of Observed Normalized Boron Release Values to Predicted Values and Prediction Intervals (7-day MCC-3), g/m^2

| | | | 95% Prediction Intervals | | | |
| | | | Individual | | Simultaneous | |
Glass	Observed Values (g/m^2)	Predicted Value	Lower Limit	Upper Limit	Lower Limit	Upper Limit
DG-WV1	0.1842,0.1855,0.1868	0.1875	0.1194	0.2557	0.0399	0.3352
DG-WV2	0.1892,0.1918,0.1905	0.1793	0.1133	0.2453	0.0363	0.3224
DG-WV3	0.2364,0.2364,0.2364	0.2210	0.1362	0.3059	0.0372	0.4048
DG-WV4	0.2339,0.2407,0.2407	0.2594	0.1642	0.3546	0.0531	0.4658
DG-WV5	0.2296,0.2270,0.2296	0.2219	0.1372	0.3066	0.0384	0.4054
DG-WV6	0.1868,0.1882,0.1882	0.1765	0.1107	0.2423	0.0340	0.3191
DG-WV7	0.1855,0.1895,0.1895	0.1849	0.1168	0.2530	0.0373	0.3326
DG-WV8	0.1869,0.1847,0.1865	0.1480	0.0871	0.2089	0.0160	0.2801
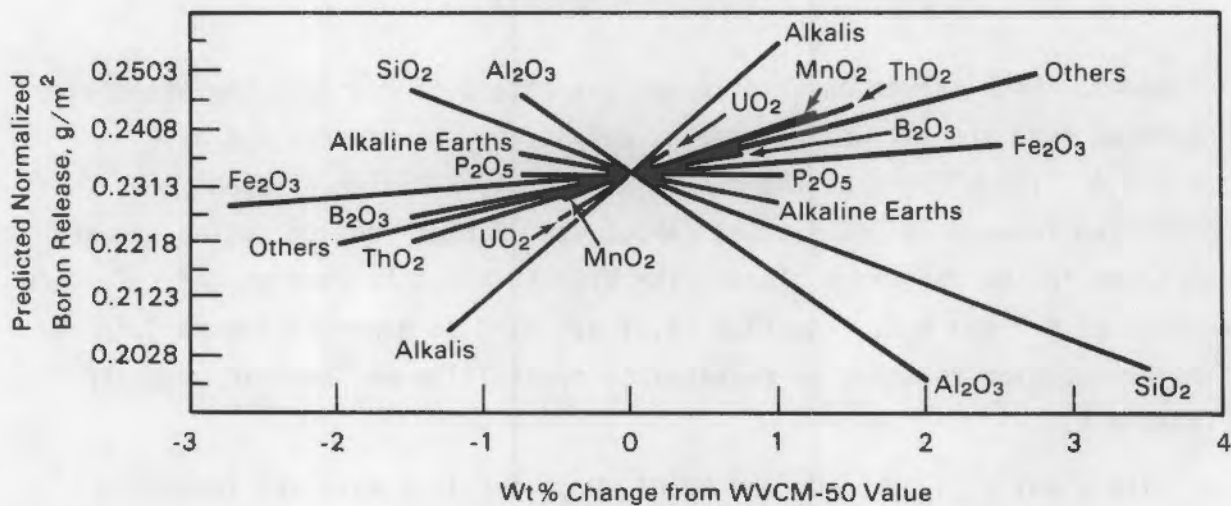
FIGURE 4.7. Component Effects Plot for Normalized Boron Release from Glasses in the WVCM-50-Based Compositional Region Tested with the 7-day Modified MCC-3 Test. (Deaerated DIW, 90°C, 24-glass linear mixture model.)
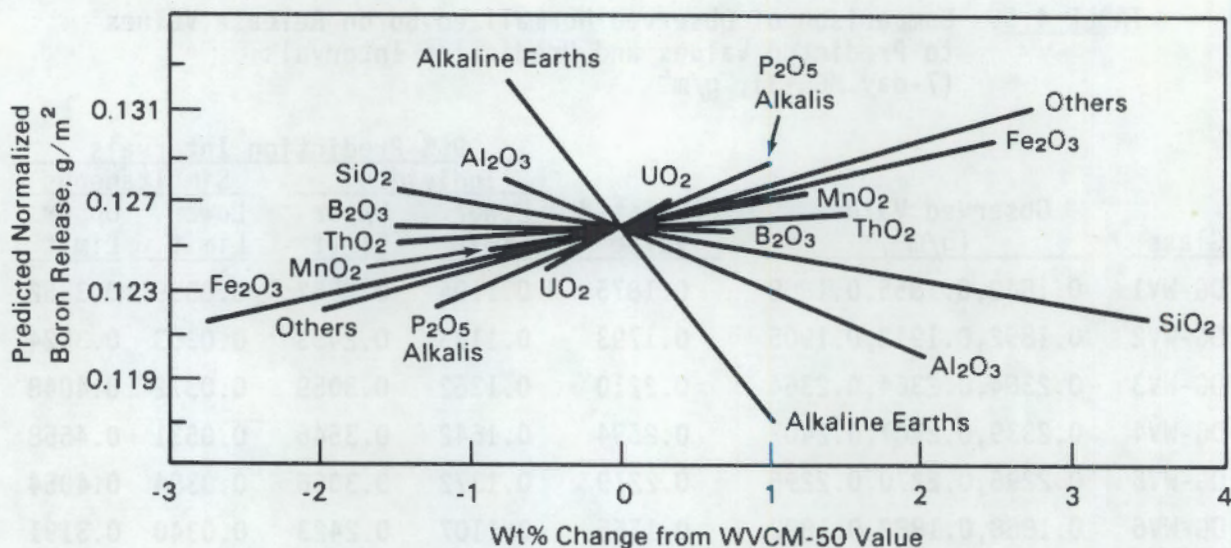
FIGURE 4.8.   Component Effects Plot for Normalized Silicon Release from
                Glasses in the WVCM-50-Based Compositional Region Tested
                with the 7-day Modified MCC-3 Test. (Deaerated DIW, 90°C,
                24-glass linear-mixture model.)

component. Each effect curve displays the effect of changing the associated
component over its allowable range as defined by the constraints of
Table 3.4. The effects of the curves are merely a series of predicted
normalized release values plotted versus wt% changes from the value of each
component in the reference glass. The WVCM-50 glass is used as the reference
in Figures 4.7 and 4.8. Equation (4.3) was used to generate Figure 4.7. A
similar equation relating Si releases to composition was used to generate
Figure 4.8.

The alkalis (K_2O, Li_2O, and Na_2O), UO_2, and ThO_2 have the largest
positive effects on B release per-unit wt% change. Increasing their levels
tends to decrease the glass chemical durability. Conversely, the oxides
Al_2O_3 and SiO_2 have the largest per-unit negative effects on B release. From
a practical standpoint, it may only be the total effects of the components
that are of interest. Although the per-unit effect of UO_2 is relatively
large, its total effect is not as large as those of MnO_2, ThO_2, and "other"
oxides which have larger ranges. Components such as P_2O_5, Fe_2O_3, B_2O_3, and

4.14

the alkaline earths (BaO, CaO, and MgO) that have nearly horizontal effects curves in Figure 4.7 do not appear to have much effect on B release within the region studied.

4.2.2 Boron Release Data Uncertainty

The statistical analysis of elemental release data requires an estimation of the uncertainties in the experimentally obtained release values. To estimate these uncertainties, DG-WV1 glass was leached in triplicate four separate times over a 6-month period, which provides for estimating both short- and long-term within-laboratory uncertainties in elemental release results. The normalized releases of DG-WV1 glass and estimates of the test normalized release standard deviations are given in Appendix A. Both the size of the estimate of uncertainty and how well it is known are important factors in the statistical tests and confidence and tolerance bands results to be discussed shortly.

The estimate of normalized boron release uncertainty is 0.018 g/m^2 for the DG-WV1 glass, which translates into a 10.8% relative standard deviation (RSD). The estimate includes short- and long-term variations from 7-day MCC-3 sample preparation and leach test procedures, as well as uncertainties from ICP analyses of the leachates. Because all tests were performed by PNL and all leachates were analyzed by the same laboratory, the estimate of uncertainty does not include lab-to-lab variation. However, the 6-month time frame over which the four sets of tests were performed may partially simulate the variation from different labs.

An important point to recognize about the above estimate of B release uncertainty is that it is based on a small number of "degrees of freedom" (df), i.e., a small amount of data. Specifically, the estimate has 3 df, because the leach tests on DG-WV1 were repeated only four times. Because of the small df, it is not possible to have great confidence in the estimate, which is reflected in the statistical procedures. For example, the confidence and tolerance bands to be discussed below will be wider because of the small number of df. This "problem" can be resolved by carefully devoting a portion of future experimental efforts to properly executed replicate tests (and leachate analyses) so as to obtain an estimate of uncertainty with

higher df. Specific comments related to the consequences of small df for the estimate of uncertainty are given in the following sections as appropriate.

4.2.3 Confidence and Tolerance Bands

The 95% confidence bands and 95%/95% tolerance bands on the fitted mixture model are used as a means of characterizing the NBR and corresponding uncertainty over the region of interest. The formulas for these two types of bands are given in Appendix B. Explanations of their interpretations are given below.

> 95% Confidence Bands: Provide 95% confidence that every glass in the region has average NBR within the confidence bands.

> 95%/95% Tolerance Bands: Provide at least 95% confidence that 95% of the time every glass in the region will have NBR within the tolerance bands.

Confidence bands make a statement about _average_ NBR behavior for each glass, while tolerance bands make a statement about the _range_ of NBR behavior for each glass.

4.2.4 Application of Confidence and Tolerance Bands

Because the 95% confidence bands and 95%/95% tolerance bands for the model are 12-dimensional surfaces (for each lower and upper band), they cannot be easily displayed. However, the bands can be applied to identify the worst predicted NBR within the region of interest. The linearity of the model implies that the largest predicted value of NBR must occur at one of the extreme vertices of the region. The results of applying the model and the upper limit formulas of the corresponding 95% confidence and 95%/95% tolerance bands allow the following statements to be made. NBR values from the 7-day MCC-3 test have been divided by 7 in these statements to yield per-day release values.

- The largest predicted NBR over the region is 0.044 $g/m^2 \cdot day$. Many of the extreme vertices have predicted values that approach this level.

4.16

- There is a 97.5% confidence that every glass in the region has an average NBR less than 0.071 $g/m^2 \cdot day$.

- There is at least a 97.5% confidence that 97.5% of the time every glass in the region will have NBR less than 0.114 $g/m^2 \cdot day$.

The last two statements are one-sided (i.e., they only refer to the worst NBR) 97.5% confidence statements derived from the two-sided 95% confidence and 95%/95% tolerance bands, respectively. One-sided 95% confidence statements could be produced if desired, and would reduce the size of the 0.071 and 0.114 values in the last two statements.

4.3 COMPOSITION EFFECTS - FY 1988

Tables 4.6, 4.7, and 4.8 list the normalized elemental mass releases of B, Si, Th, U, and those elements whose oxides contributed at least 1 wt% of the glass composition. Each value given represents the average obtained from two replicate tests. The two replicate tests were performed at the same time under the same conditions and the resulting leachates were chemically analyzed at the same time under the same conditions. Hence, the replicates only include short-term variations in the leach testing and leachate analysis processes. Table 4.6 lists the 28-day MCC-1 normalized elemental mass releases. Tables 4.7 and 4.8 list the 7-day (Table 4.7) and 28-day (Table 4.8) MCC-3 normalized elemental mass releases.

Graphical representations of the 28-day MCC-1 normalized elemental release rates of B and Si from the glasses are given in Figures 4.9 and 4.10. The release rates were obtained by dividing the normalized releases by 28 days; the length of the test. The error bars represent ± two sds. The sds are based on replicate tests performed at the same time and do not include the time-related component of variability. The glasses are ordered from most to least durable. The reference glass (DG-WV33) durability is roughly in the middle of this ordering. These figures illustrate that all of the glasses tested have observed normalized release rates below the Tuff repository's requirement of 1 $g/m^2 \cdot day$ in a 28-day MCC-1 test.

TABLE 4.6. Average Normalized Releases of Glasses DG-WV33 Through DG-WV48 (28-day MCC-1, 90°C, Deaerated DIW), g/m^2

Element	DGWV33	DGWV34	DGWV35	DGWV36	DGWV37	DGWV38	DGWV39	DGWV40
Al	9.672	13.369	12.279	6.909	11.036	7.443	8.026	7.211
B	15.201	18.947	18.661	12.008	13.920	10.901	13.489	14.352
Fe	0.041	0.067	0.092	0.034	0.053	0.043	0.097	0.063
K	9.701	11.461	11.063	6.040	9.323	5.513	6.506	7.811
Li	13.170	18.499	15.123	9.331	13.010	8.265	10.564	11.194
Mg	0.000	0.000	0.000	0.000	0.000	0.000	0.627	0.448
Mn	0.000	0.000	0.131	0.000	0.000	0.020	0.000	0.000
Na	16.883	21.194	23.207	12.491	15.131	11.462	14.941	16.027
P	12.630	17.901	11.269	7.513	11.233	5.635	10.442	9.240
Si	12.703	16.515	15.707	11.285	12.721	10.340	11.672	11.938
Th	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
U	1.869	0.732	3.308	0.960	0.960	0.882	1.475	1.983
pH[(a)]	9.48	9.55	9.89	9.16	9.66	9.30	9.25	9.62

Element	DGWV41	DGWV42	DGWV43	DGWV44	DGWV45	DGWV46	DGWV47	DGWV48
Al	9.585	9.116	6.056	11.955	12.028	8.215	5.458	5.551
B	14.832	15.683	7.794	17.097	16.598	15.318	8.576	7.765
Fe^{3+}	0.101	0.031	0.045	0.057	0.110	0.078	0.044	0.036
K	8.604	10.666	4.395	11.728	10.311	7.697	3.285	2.790
Li	13.329	16.669	6.428	14.068	12.904	12.661	5.804	5.699
Mg	0.000	0.000	0.000	0.000	0.000	0.000	0.000	4.097
Mn	0.000	0.052	0.063	0.000	0.066	0.097	0.059	0.000
Na	17.809	16.968	7.845	20.626	19.470	16.850	9.018	7.944
P	14.070	12.124	4.175	11.087	16.408	11.087	6.723	3.853
Si	14.110	12.338	7.835	15.635	15.402	13.117	8.730	8.119
Th	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
U	2.564	0.615	0.745	3.031	3.347	2.579	1.135	0.152
pH[(a)]	9.66	9.59	8.69	9.61	9.53	9.43	8.80	8.59

(a) pH measured at test termination at 25°C.

4.18

TABLE 4.7. Average Normalized Releases of Glasses DG-WV33 Through DG-WV48 (7-day MCC-3, 90°C, Deaerated DIW), g/m^2

Element	DGWV33	DGWV34	DGWV35	DGWV36	DGWV37	DGWV38	DGWV39	DGWV40
Al	0.108	0.113	0.175	0.101	0.147	0.130	0.113	0.096
B	0.214	0.334	0.370	0.213	0.210	0.183	0.229	0.290
Fe	0.003	0.003	0.008	0.001	0.007	0.003	0.002	0.003
K	0.140	0.144	0.207	0.102	0.070	0.110	0.113	0.157
Li	0.323	0.451	0.483	0.360	0.335	0.334	0.328	0.401
Mg	0.006	0.000	0.015	0.000	0.000	0.000	0.003	0.007
Mn	0.003	0.002	0.005	0.000	0.006	0.002	0.001	0.002
Na	0.255	0.328	0.411	0.210	0.266	0.210	0.256	0.310
P	0.176	0.215	0.263	0.115	0.184	0.130	0.180	0.213
Si	0.123	0.147	0.174	0.123	0.141	0.125	0.119	0.149
Th	0.001	0.001	0.005	0.001	0.005	0.002	0.001	0.001
U	0.039	0.011	0.087	0.017	0.020	0.017	0.028	0.046
pH[a]	10.13	10.16	10.78	9.48	10.47	10.05	9.77	10.18

Element	DGWV41	DGWV42	DGWV43	DGWV44	DGWV45	DGWV46	DGWV47	DGWV48
Al	0.125	0.083	0.125	0.135	0.164	0.100	0.115	0.119
B	0.273	0.350	0.162	0.286	0.253	0.305	0.184	0.155
Fe	0.011	0.002	0.028	0.004	0.009	0.006	0.025	0.003
K	0.148	0.175	0.077	0.158	0.161	0.129	0.080	0.067
Li	0.382	0.480	0.306	0.418	0.365	0.392	0.307	0.316
Mg	0.010	0.000	0.017	0.005	0.000	0.013	0.012	0.002
Mn	0.008	0.002	0.016	0.003	0.007	0.006	0.019	0.002
Na	0.358	0.393	0.142	0.317	0.323	0.287	0.179	0.159
P	0.247	0.318	0.081	0.152	0.271	0.179	0.118	0.057
Si	0.157	0.162	0.126	0.129	0.153	0.133	0.130	0.120
Th	0.004	0.000	0.018	0.003	0.007	0.004	0.022	0.002
U	0.062	0.015	0.048	0.039	0.047	0.049	0.040	0.004
pH[a]	10.34	9.19	10.19	10.29	10.37	9.83	9.15	9.13

(a) pH measured at test termination at 25°C.

TABLE 4.8. Average Normalized Releases of Glasses DG-WV33 Through DG-WV48 (28-day MCC-3, 90°C, Deaerated DIW), g/m^2

Element	DGWV33	DGWV34	DGWV35	DGWV36	DGWV37	DGWV38	DGWV39	DGWV40
Al	0.122	0.116	0.191	0.118	0.175	0.154	0.124	0.094
B	0.317	0.689	0.538	0.313	0.287	0.229	0.420	0.411
Fe	0.012	0.012	0.024	0.003	0.017	0.007	0.012	0.013
K	0.125	0.153	0.206	0.098	0.141	0.099	0.108	0.167
Li	0.390	0.714	0.557	0.478	0.409	0.400	0.428	0.455
Mg	0.021	0.019	0.019	0.000	0.020	0.016	0.023	0.019
Mn	0.011	0.015	0.014	0.005	0.017	0.008	0.011	0.008
Na	0.342	0.578	0.591	0.263	0.369	0.263	0.379	0.419
P	0.262	0.319	0.423	0.153	0.259	0.166	0.270	0.342
Si	0.166	0.199	0.230	0.151	0.185	0.157	0.151	0.195
Th	0.006	0.008	0.021	0.003	0.015	0.006	0.004	0.006
U	0.058	0.016	0.053	0.039	0.032	0.026	0.037	0.086
pH[a]	10.27	10.35	11.06	9.69	10.82	10.40	10.01	10.39

Element	DGWV41	DGWV42	DGWV43	DGWV44	DGWV45	DGWV46	DGWV47	DGWV48
Al	0.134	0.080	0.157	0.154	0.181	0.097	0.136	0.150
B	0.385	0.483	0.282	0.509	0.343	0.850	0.312	0.225
Fe	0.024	0.007	0.056	0.011	0.021	0.018	0.041	0.009
K	0.146	0.186	0.059	0.142	0.162	0.151	0.070	0.063
Li	0.402	0.530	0.453	0.560	0.384	0.865	0.429	0.422
Mg	0.040	0.010	0.036	0.027	0.036	0.033	0.026	0.016
Mn	0.025	0.006	0.037	0.016	0.025	0.025	0.033	0.009
Na	0.515	0.526	0.187	0.460	0.439	0.659	0.245	0.134
P	0.314	0.443	0.114	0.213	0.343	0.305	0.162	0.081
Si	0.193	0.209	0.167	0.164	0.189	0.177	0.164	0.158
Th	0.010	0.001	0.039	0.008	0.019	0.026	0.038	0.009
U	0.079	0.025	0.079	0.055	0.068	0.080	0.062	0.010
pH[a]	10.63	10.52	9.36	10.50	10.64	10.08	9.40	9.43

(a) pH measured at test termination at 25°C.

4.20
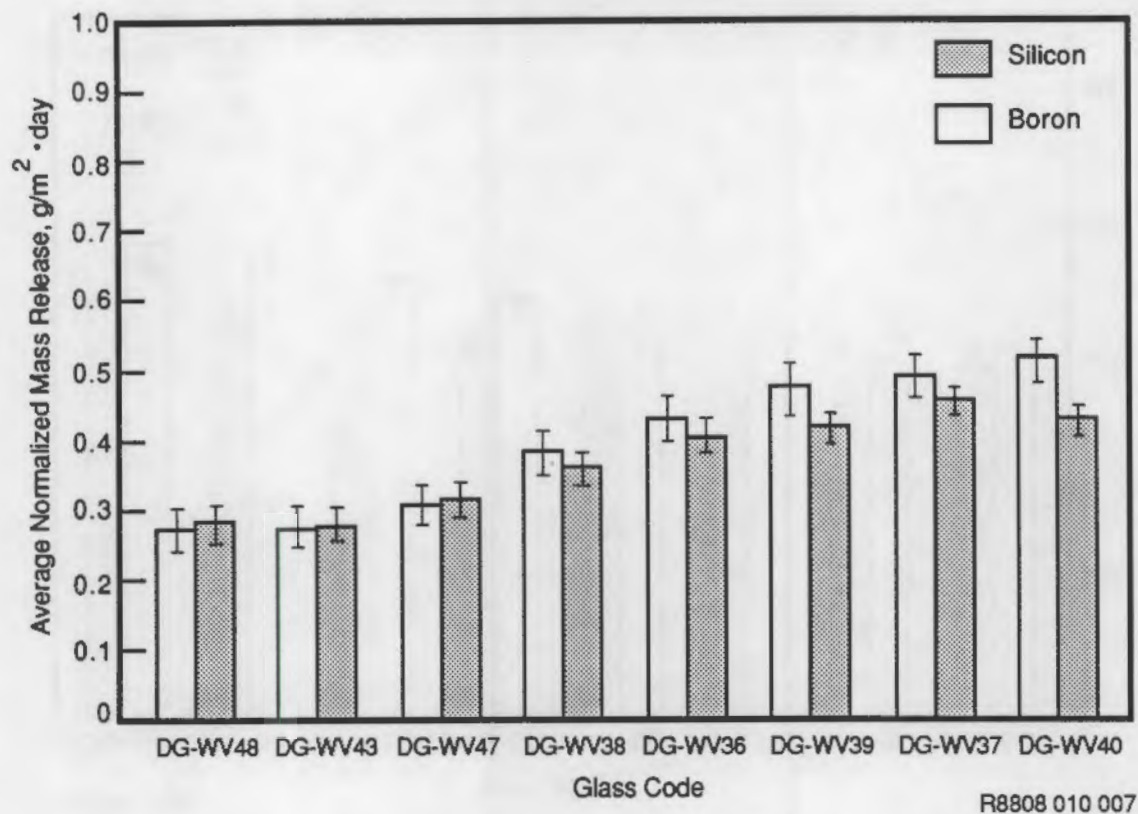
FIGURE 4.9. Comparison of B and Si Average Normalized Releases of Most Durable of FY 1988 Compositional Variability Glasses (Ordered from greatest to least durable based on B release; 28-day MCC-1 test, 90°C, deaerated DIW)

Some general statements may be made about the leach test results. A few more than half of the glass compositions tested are more durable than the reference composition based on B release. The Th release of the glasses is minimal. Uranium releases were up to 17 times greater than Th releases. The release of alkali follows the B and Si release trends of the glasses.

The 28-day MCC-3 releases are roughly 1.5 times as large as the 7-day results. If the release rates of the glasses were constant over time, the 28-day releases would be four times as large. This illustrates the fact that the release rates of the glasses slow considerably with time and leachant saturation with dissolution products.

The MCC-1 release rates are much higher than the MCC-3 release rates. Dissolution rates are a function of glass surface area to leachate volume

4.21
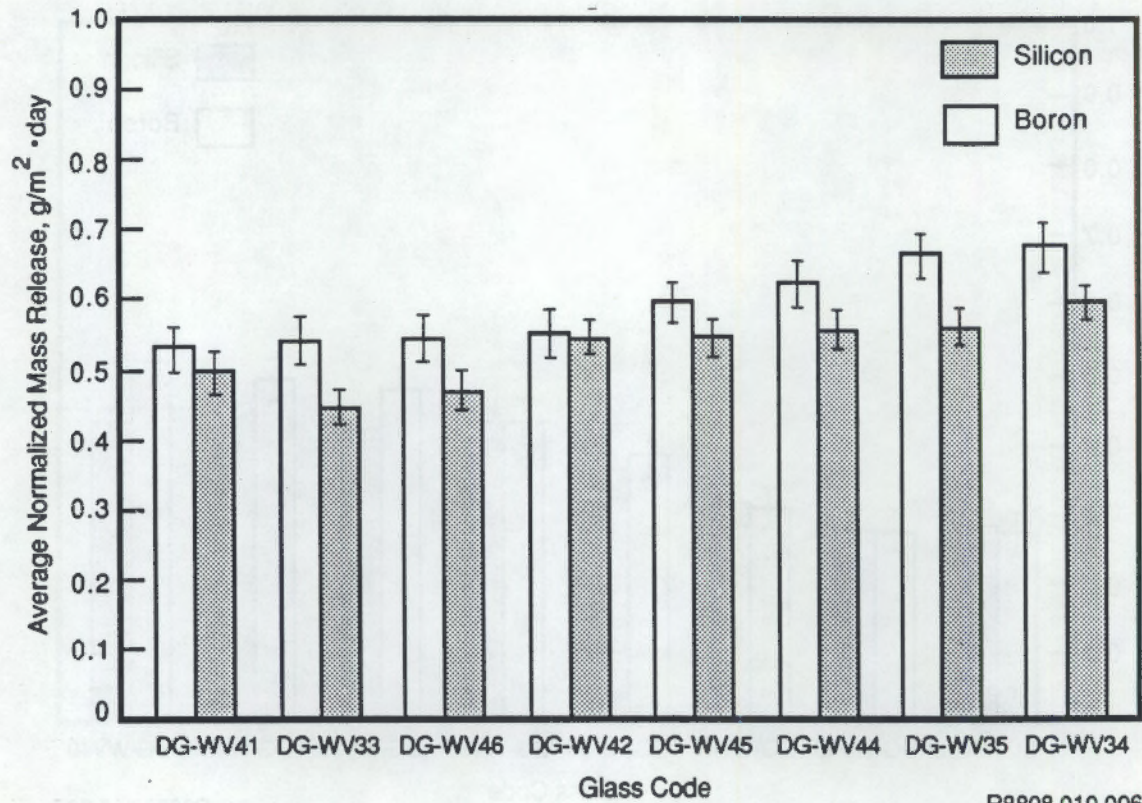
FIGURE 4.10. Comparison of B and Si Average Normalized Releases of Least Durable of FY 1988 Compositional Variability Glasses (Ordered from greatest to least durable based on B release; 28-day MCC-1 test, 90°C, deaerated DIW)

(SA/V) ratios as well as test duration (t). At lower values of (SA/V)·t, more rapid dissolution is expected to occur. This is reflected in these results.

4.4 STATISTICAL ANALYSIS AND EMPIRICAL MODELING OF FY 1988 NORMALIZED RELEASE DATA

A statistical approach for characterizing chemical durability of glasses within a specified compositional region was applied to the characterization of NBRs from the set of FY 1988 glasses. Briefly, the approach involved the following steps:

4.22

- defining the compositional region of glasses to be characterized

- selecting a test matrix of compositions via computer-aided statistical experimental design techniques

- leach testing the test matrix of compositions

- estimating short- and long-term within-lab and lab-to-lab uncertainties in the glass analysis, leach testing, and leachate analysis processes

- empirically modeling the leach test results via mixture models

- investigating glass component effects on durability

- constructing statistical confidence and tolerance statements to describe chemical durability over the compositional region.

The statistical confidence and tolerance statements describing durability are made with the fitted empirical models and appropriate estimates of within- and between-lab uncertainty. Although the glass analyses, leach testing, and leachate analyses were all performed by one lab (PNL) at essentially one time, the results are still subject to lab-to-lab variation and short- and long-term within-lab variation. Somewhat different results would have been obtained if the experimental work was performed by PNL or another laboratory at another time. Hence, lab-to-lab and short- and long-term within-lab variation must be taken into account in statistically characterizing chemical durability.

In order to construct statistical confidence and tolerance statements about NBR, within- and between-lab variations must be assessed. Specifically, it is necessary to obtain estimates of short-term within-lab, long-term within-lab, and lab-to-lab standard deviations for the leach testing (including test preparation), leachate analysis, and glass analysis processes.

A portion of the FY 1988 experimental effort was directed at replicating leach tests, leachate analyses, and glass analyses to provide estimates of the required short- and long-term within-lab standard deviations. A limited literature review was conducted in order to gather information about within-

and between-laboratory variations, and the results are summarized in Appendix C. The estimates of short- and long-term within-lab standard deviations that resulted from the FY 1988 efforts are summarized in Appendix D. However, these results were obtained too late to be used in developing the confidence and tolerance bands discussed later in this section. Still, they compare very well with the standard deviations obtained from the literature survey.

Table C.8 of Appendix C contains a summary of the percent relative standard deviation (%RSD) for the various types of uncertainty associated with determining NBR. Although some of the %RSDs are based on limited data, it is clear that short-term within-lab uncertainty is smaller than long-term within-lab uncertainty, which in turn is smaller than lab-to-lab uncertainty. Further, although the relative magnitudes of the various types of uncertainty are somewhat uncertain, it seems apparent that the combined uncertainty is probably at least 20%, and could be considerably higher depending on the actual lab-to-lab uncertainty.

For the purposes of constructing confidence and tolerance statements about the normalized releases, the %RSDs given in Table 4.9 were used. Because the magnitude of lab-to-lab uncertainty is not well-known at this time, three values were considered, 10%, 20%, and 50%, as shown in Table 4.9.

4.4.1 Linear Mixture Models Fit to Normalized Boron Release Data

A linear mixture model of the form given by Equation (4.1) was fitted to the NBR data from the 28-day MCC-1 and 7-day MCC-3 tests. The fitted linear mixture model for the 28-day MCC-1 test is

$$
\begin{aligned}
NBR = {} & -78.02\ Al_2O_3 + 26.84\ B_2O_3 + 56.06\ (BaO+CaO+MgO) + \qquad (4.4) \\
& 30.86\ Fe_2O_3 + 151.07\ (K_2O+Li_2O+Na_2O) + 72.97\ MnO_2 - \\
& 46.29\ P_2O_5 - 30.00\ SiO_2 + 23.06\ ThO_2 + 35.90\ UO_2 + \\
& 5.37\ Others,
\end{aligned}
$$

4.24

TABLE 4.9. Relative Standard Deviations and Degrees of Freedom Used as the Basis for the Confidence and Tolerance Statements (WV-8801-Based Compositional Variation Region)

Source of Uncertainty	MCC-1, 28-Day %RSD	MCC-1, 28-Day df	MCC-3, 7-Day %RSD	MCC-3, 7-Day df
Short-term Within-Lab				
• Leach Testing and Leachate Analysis	3%	7	3%	30
• Glass Analysis (B_2O_3)	2.5%	17	2.5%	17
Long-Term Within-Lab				
• Leach Testing and Leachate Analysis	6%	4	11%	3
• Glass Analysis (B_2O_3)	2%	17	2%	17
Total Within-Lab	7.5%	9	11.8%	4
Lab-to-Lab				
• Leach Testing and Leachate Analysis	10%	6	10%	6
	20%	12	20%	12
	50%	16	50%	16
• Glass Analysis (B_2O_3)	5%	2	5%	2
Total Within-Lab & Lab-to-Lab	13.5%	14	16.3%	10
	21.9%	16	23.8%	17
	50.8%	17	51.6%	18

Notes 1. The %RSD and Degrees of Freedom (df) values above were chosen based on the findings in Appendix B.
2. Three values for lab-to-lab leach testing and leachate analysis uncertainty were chosen because of the extreme range in %RSD values for the three applicable cases found during the literature review (see Table B.4). The 10%, 20%, and 50% values selected above are somewhat less than the 19%, 31%, and 64% values given in Table B.4, because the latter values also include long-term within-lab variation.
3. The df associated with the total %RSD of NBR were obtained as a weighted average of the df of each contributing source of variation according to Satterthwaite's formula (Montgomery 1976).

4.25

with an R^2 value of 0.95. The fitted linear mixture model for the 7-day MCC-3 test is

$$NBR = -1.86 \ Al_2O_3 + 0.34 \ B2O_3 + 3.02 \ (BaO+CaO+MgO) + \qquad (4.5)$$
$$0.54 \ Fe_2O_3 + 2.24 \ (K_2O+Li_2O+Na_2O) + 2.84 \ MnO_2 -$$
$$0.77 \ P_2O_5 - 0.40 \ SiO_2 + 0.88 \ ThO_2 + 1.59 \ UO_2 +$$
$$0.17 \ Others,$$

with an R^2 value of 0.97. R^2 measures the proportion of variation in NBR values explained by a fitted model, so it is clear that the linear mixture models (4.4) and (4.5) fit the data quite well. Statistical tests based on short-and long-term within-lab uncertainties indicate that the fitted models do not have a significant lack-of-fit.

4.4.2 Component Effects Plots

The effects of varying the 11 individual oxide components are displayed in the effects plots (Piepel 1982) of Figures 4.11 and 4.12, which correspond respectively to the fitted linear mixture models (4.4) and (4.5). Each effect curve displays the effect of changing the associated component over its allowable range (as defined by the constraints in Table 3.6).

From the practical standpoint of characterizing chemical durability over the compositional region, the total effects are probably of most interest. Figures 4.11 and 4.12 show for both the 28-day MCC-1 and 7-day MCC-3 tests that Al_2O_3, SiO_2, and P_2O_5 have the largest negative total effects on NBR increasing their levels lowers NBR), while alkalis have the largest positive total effect (i.e., increasing the alkali level raises NBR). The remaining components appear to have less significant or negligible effects within the compositional region of Table 3.6.

4.4.3 Confidence and Tolerance Statements About Normalized Boron Release Over the Composition Region

The final step in the statistical approach for characterizing NBR from the 2B-day MCC-1 and 7-day MCC-3 tests is to construct statistical confidence and tolerance statements from the fitted NBR models and the estimates of
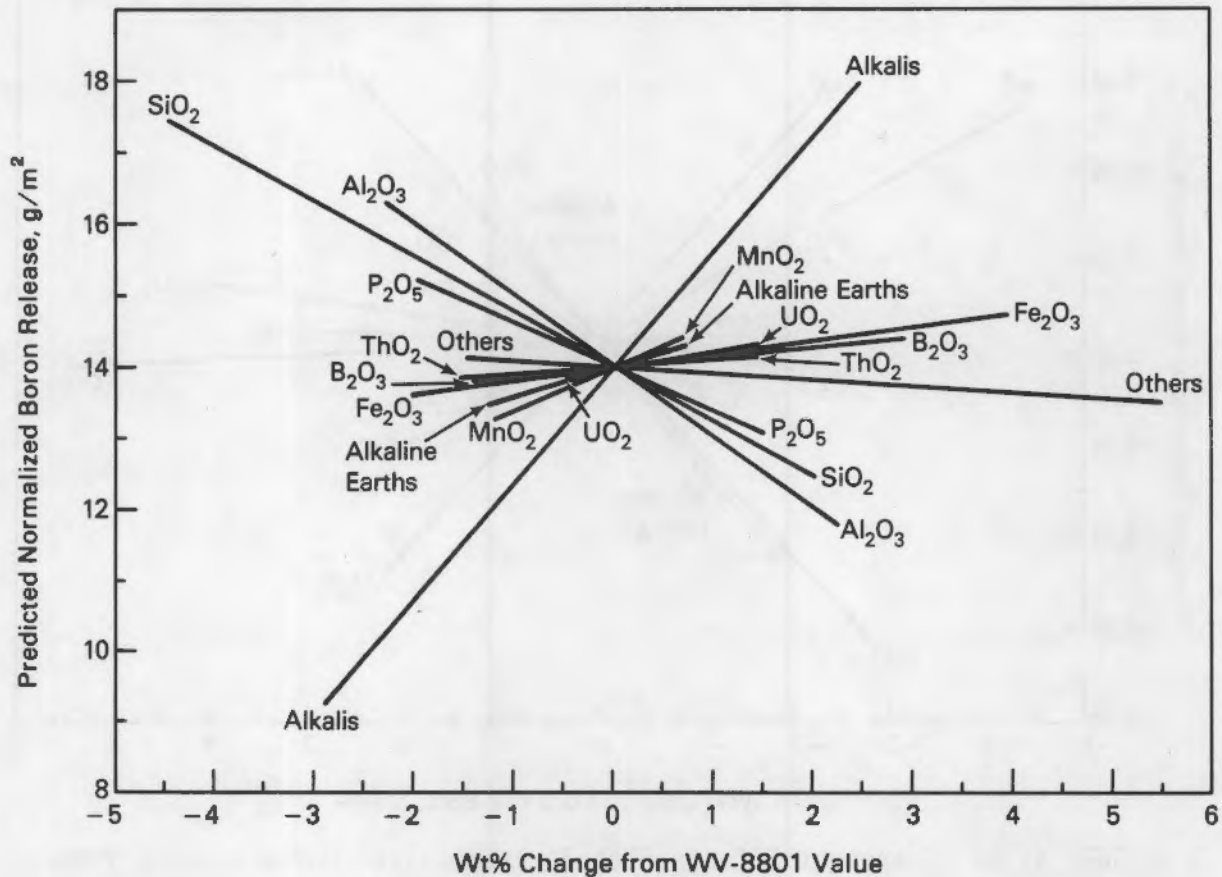
FIGURE 4.11. Component Effects Plot for Normalized Boron Release from Glasses in the WV-8801-Based Compositional Region Tested with the 28-Day MCC-1 Test

short-term within-lab, long-term within-lab, and lab-to-lab uncertainties. Specifically, one-sided upper 95% confidence and 95%/95% tolerance bands were constructed for the fitted linear mixture models given in Equations (4.4) and (4.5), using the uncertainties given in Table 4.9. The formulas for constructing the confidence and tolerance bands are given in Appendix A.

The interpretation of the one-sided confidence and tolerance bands is as follows:

95% One-Sided Upper Confidence Band: provides 95% confidence that all glasses in the compositional region have true (or average) NBR less than the band.

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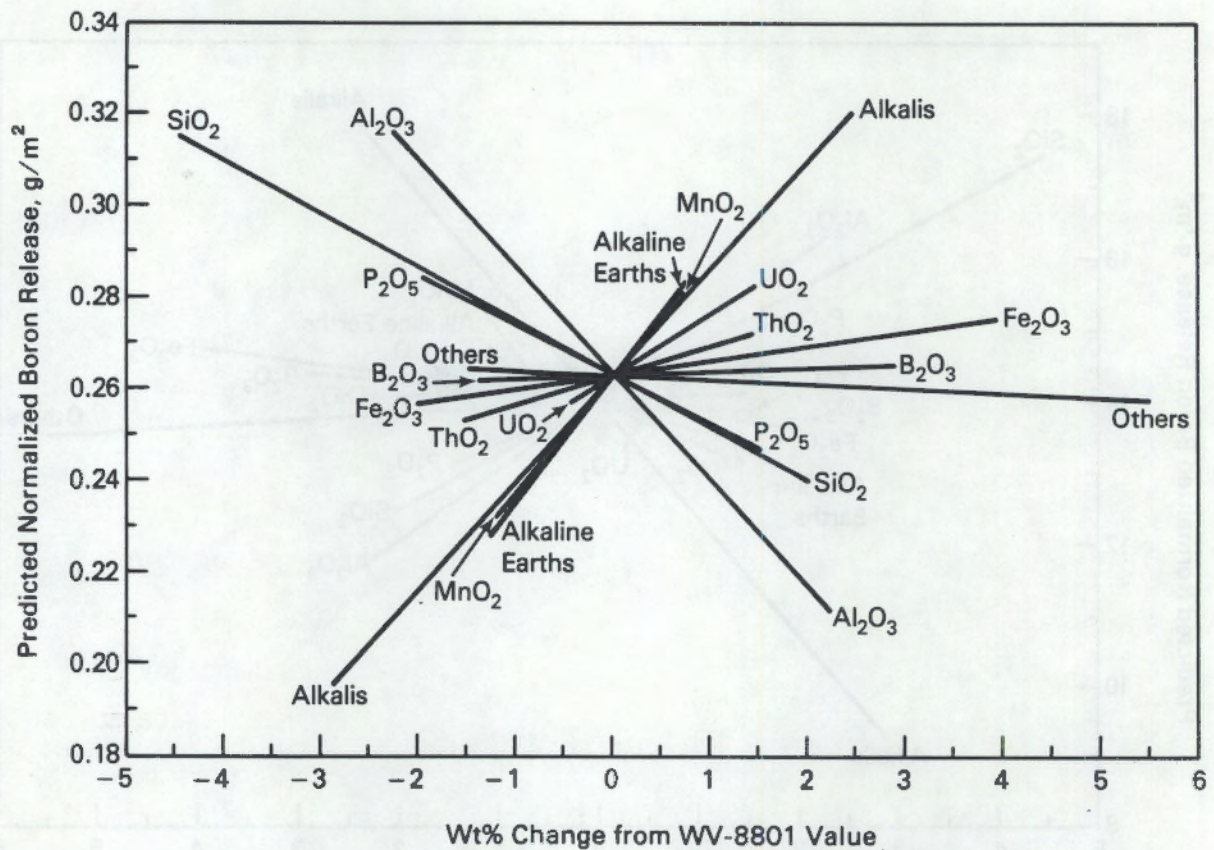
FIGURE 4.12. Component Effects Plot for Normalized Boron Release from Glasses in the WV-8801-Based Compositional Region Tested with the 7-Day MCC-3 Test

95%/95% One-Sided Upper Tolerance Band: provides at least 95% confidence that all glasses in the compositional region will have NBR less than the band 95% of the time.

A confidence band makes a statement about the mean of the NBR distribution for each glass in the region, while a tolerance band makes a statement about the 95th percentile of the NBR distribution for each glass in the region. One-sided upper confidence and tolerance bands are constructed because the concern is only about how large NBR may be, not how small it may be. The fitted models (4.4) and (4.5) can be used to predict the largest NBR over the region, and the confidence and tolerance bands can be applied to yield confidence and tolerance statements about the largest value of NBR over the region.

4.28

Because of the linearity of models (4.4) and (4.5), the maximum values on the fitted, 95% confidence and 95%/95% tolerance surfaces occur at one of the extreme vertices of the compositional region. The extreme vertices were generated as one step of selecting the test matrix. The fitted models (4.4) and (4.5) and the corresponding one-sided upper 95% confidence and 95%/95% tolerance band formulas were applied to the extreme vertices using the various combinations of uncertainties in Table 4.9.

The largest values of NBR obtained from the fitted models and the confidence and tolerance band formulas are given in Table 4.10. Although results are given for the case of within-lab uncertainty (i.e., without lab-to-lab uncertainty), those values are given for comparison purposes only. Lab-to-lab variation/uncertainty cannot be ignored. The results that include 10% lab-to-lab uncertainty may be viewed as an optimistic or "best case" possibility, and the results that include 50% lab-to-lab uncertainty may be viewed as a pessimistic or "worst case" possibility. The results based on 20% lab-to-lab uncertainty might be considered as a more realistic or "middle ground" possibility.

All of the confidence and tolerance values on NBR for the 28-day MCC-1 test are above 28 g/m^2, the level corresponding to the 1 g/m^2·day criterion suggested by the Nevada Nuclear Waste Storage Investigations Project. This criterion in listed in the Waste Acceptance Preliminary Specifications (WAPs). The applicable specification states that the normalized release rates of Na, Si, B, U, and Cs must be below 1 g/m^2-day or 28 g/m^2 in a 28-day MCC-1 test in DIW at 90°C. Thus, there are glasses in the WV-8801-based compositional region that may not meet this criterion. Rather than conclude from this that the compositional region around WV-8801 is too large, it may be that the 1 g/m^2·day criterion needs to be reassessed. It is not clear whether the 1 g/m^2·day criterion was suggested with statistical characterization of chemical durability in mind. Several options, including a smaller composition region, need for statistical variability consideration, reduction in analytical variability, investigation of an additional composition region, or reassessment of the proposed limit, should be further investigated. It is clear that lab-to-lab and within-lab uncertainties cannot be ignored, either

4.29

<u>TABLE 4.10</u>. Confidence and Tolerance Band Statements for Maximum Normalized Boron Releases (g/m^2) Over the WV-8801-Based Compositional Variation Region

	28-Day MCC-1	7-Day MCC-3
Predicted by Linear Mixture Models	22.2	0.46
95% Upper Confidence Band		
• Short- and Long-Term Within-Lab Uncertainty	29.3	0.76
• Short- and Long-Term Within-Lab + 10% Lab-to-Lab Uncertainty	34.0	0.75[a]
• Short- and Long-Term Within-Lab + 20% Lab-to-Lab Uncertainty	41.1	0.85
• Short- and Long-Term Within-Lab + 50% Lab-to-Lab Uncertainty	66.1	1.31
95%/95% Upper Tolerance Band		
• Short- and Long-Term Within-Lab Uncertainty	34.6	1.04
• Short- and Long-Term Within-Lab + 10% Lab-to-Lab Uncertainty	42.3	0.98[a]
• Short- and Long-Term Within-Lab + 20% Lab-to-Lab Uncertainty	54.1	1.13
• Short- and Long-Term Within-Lab + 50% Lab-to-Lab Uncertainty	95.7	1.91

(a) These values are smaller than the values that only account for within-lab variation because of differences in the degrees of freedom (see Table 4.9).

in characterizing the chemical durability of a region of glass compositions, or in the selection of an acceptance criterion.

Long-term within-lab and lab-to-lab variations were seen to be significant contributors to the uncertainty of the chemical durability of glasses within the region explored. Additional information on the magnitude of these

4.3D

uncertainties is needed to obtain more defensible confidence and tolerance statements. This is especially true of lab-to-lab variation.

4.5 MICROSTRUCTURE OF FY 1988 SET OF GLASSES

In this variability study, the compositions are not being varied on a one-at-a-time basis; therefore, there are many possible interactions which confound simple interpretations of the presence of various phases. Instead of intercomparing all of the 16 glasses with each other, it was judged more reasonable to use glass DG-WV33 (WV-8801) as the internal standard for comparison purposes; this is the "target" composition upon which the compositional variability study was based. After first closely examining this glass to ensure that it possessed a fairly typical concentration of phases which had been seen previously, the micrographs for each of the other glasses in the study were placed side-by-side with those for DG-WV33, and any deviations were noted. Table 4.11 summarizes these observations. Figures 4.13 through 4.15 are micrographs of DG-WV33, DG-WV44, and DG-WV47 showing typical crystalline formations.

In general, the glasses contained small amounts of relatively small and widely scattered crystalline phases. Thoria crystallites were present in essentially all of the glasses and it is likely that these crystallites are an artifact of the glass fabrication. Thoria is a very stable oxide and thus slow to dissolve; these inclusions most likely represent incompletely dissolved feed material rather than material precipitated from solution in the glass. Additional phases were provided by noble metals such as Pd and Rh, which have very low solubilities in glasses and are not incorporated in the glass during melting. The remaining crystalline phases, such as various spinels, are typically deposited from glass melts because they are more stable as crystals than when dissolved in the glass.

One exception to this general trend in microstructure was glass DG-WV41, which was free from non-glass phases of any type. It is not clear why this occurred. As shown in Table 3.7, DG-WV41 was relatively low in Al_2O_3, probably giving it good fluidity. It was also quite well-fluxed with alkali oxides, which probably also enhanced its fluidity. However, the method by

TABLE 4.11. Optical and SEM Microscopy Observations of Glasses
DG-WV33 Through DG-WV48

Glass #	Comments
DG-WV33 (WV-8801)	Widely scattered globular masses of small particles identified as undissolved $ThO2$, not in a cubic habit, plus a low concentration of globular metallics[a] identified as either Rh or Ru and phases containing Si, Ru, Al, Fe, and K.[b] This glass is shown in Figure 4.13.
DG-WV34	Has widely scattered metallics, less concentrated than DG-WV33. Hexagonal phase containing Si, Rh, Pd, Cr, Fe.[b] Also spinel containing Cr, Fe, and Ni.
DG-WV35	Small crystals visible optically at low magnification, mottled background appearance at high magnification. Very well-developed cubic ThO_2 crystals in globular zones, other scattered small spinel crystals. No composition difference corresponding to mottled appearance visible on SEM.
DG-WV36	About same as DG-WV33, but many more very small crystals, mostly acicular but some cubic. Some undissolved ThD_2, cubic crystals are Fe-Cr-Ni spinel, with some dissolved Rh. Few Ru-Si-Fe crystals,[b] aciculars mostly Si-Fe.
DG-WV37	Slightly more crystalline than DG-WV33, small and widely distributed. Phases are Ru-Pd metallic, Fe-Cr-Ni spinel, Rh metallic, Ru metallic, Ru-Pd metallic, and acicular Fe-Si[b] crystals like DG-WV36.
DG-WV38	Crystals smaller and more widely dispersed than DG-WV33. Some mottled appearance at 500X optical. Few large undissolved ThD_2 particles, Fe-Ni-Cr spinel, Si-Pd metallic, Ru-Si metallics, spinel containing Ru.
DG-WV39	Very few crystalline phases. Widely scattered crystals are mostly Ru or a mixture of Ru crystals and Ru-Rh ones.
DG-WV40	Very similar to DG-WV33. Few large undissolved particles of ThO_2, with obvious cubic crystals. Si-Ru-Fe[b] metallic, Ru metallic.
DG-WV41	Specimen is absolutely clean--no crystalline phases.
DG-WV42	Less metallics than DG-WV33, mottled background phase, very small. Pd metallics, Cr-Fe-Ni spinel, Rh metallics, small number of undissolved ThO_2 particles, not well-crystallized.
DG-WV43	Appearance and frequency of crystals much like DG-WV33, additional Si-Ru-Fe phase,[b] some undissolved ThO_2.

4.32

TABLE 4.11. (contd)

Glass #	Comments
DG-WV44	Crystals are very small, fairly prominent mottled appearance. Si-Ru-Fe metallics, with Si-Fe acicular crystals attached. Some undissolved ThO_2. Glass contains tiny spheroids, possible liquid-liquid separation where spheroids are fainter gray features in background. These features are shown in Figure 4.14.
DG-WV45	Crystals appear similar to DG-WV33, but at lower frequency. Some Ru metallics, with attached acicular Fe-Si crystals, some Fe spinels. A few areas of undissolved ThO_2, not well-crystallized.
DG-WV46	Very few crystals visible. Rh-Pd metallics, Fe-Rh crystals, Si-Ru crystals.
DG-WV47	Very few metallics, less than DG-WV33. Main feature is small Si-Ru-Fe metallics,[b] surrounded by radial acicular crystals of Si-Fe. This feature is shown in Figure 4.15. Glass contains small spheroids. Some undissolved ThO_2, well crystallized.
DG-WV48	Similar to DG-WV33. Scattered metallics, mottled background. Ru-Rh metallics, Fe-Cr-Ni spinels, Pt-Rh metallics. Some undissolved ThO_2, not crystalline. Some small spheroids, like DG-WV44.

(a) In this table, the term "metallic" is used in a common manner which may not be precise, i.e., metallics refer to phases which appear as bright against the glass background in optical microscopy. The high concentration of heavy metals usually makes these phases bright in the electron microscope although, as in the case of the spinels, they may not be actual metals.

(b) Si in these phases may be caused by electron shine of material in contact with the phase. The electron beam penetrates to a depth of approximately 5 μm and therefore the analysis can reflect the composition of material touching the phase in addition to the phase or area being investigated with the electron probe.

which these glasses were made would lessen these fluidity effects, since melting was started at 1150°C and temperatures were raised until experienced personnel judged the viscosity to be in the 50 to 100 poise range. Since all the glasses were melted at a comparable viscosity, it is not obvious that these types of compositional differences should have resulted in a glass that

4.33

5 mm
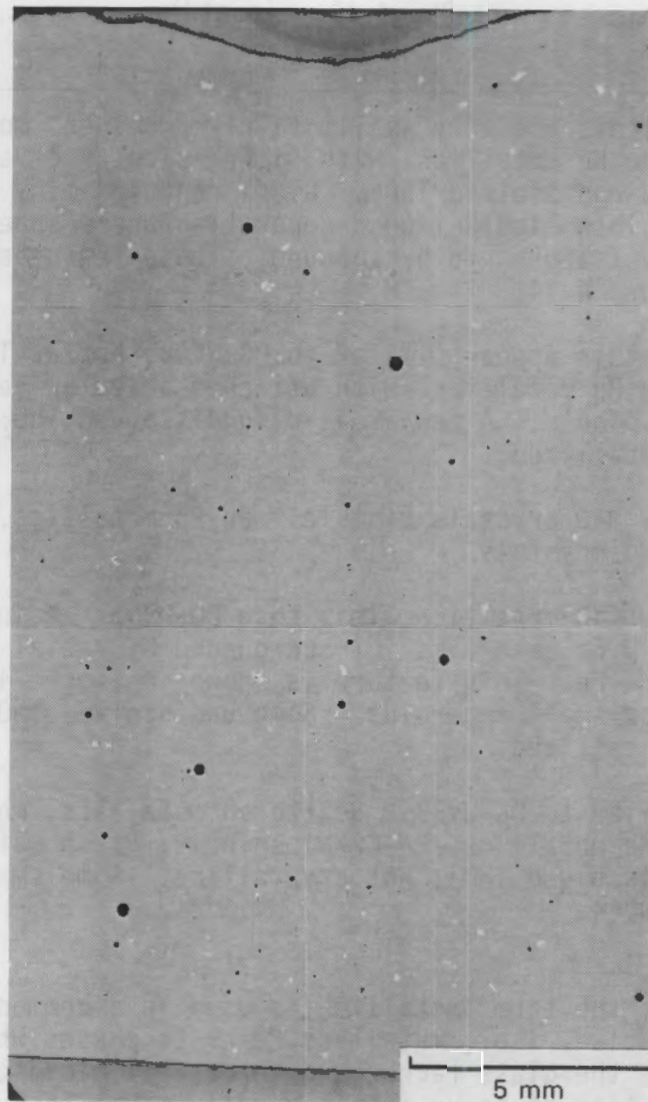
FIGURE 4.13. Optical Micrograph (6.5 X) of DG-WV33 (WV-8801).
Black dots are bubbles, white areas are "metallics"
mentioned in Table 4.11.

was free from crystals. Also, excessively fluid glasses can be prone to
crystallization because of the high diffusion rates thus provided. However,
the decrease in Al_2O_3 increases the solubility of elements by increasing the
number of open sites in the glass matrix.

The lack of crystallinity in glass DG-WV41 may have been due to a
greater ability of this lower Al_2O_3, higher alkali glass to maintain glass
components in solution. Note that although ThO_2 was on high in this glass,

4.34
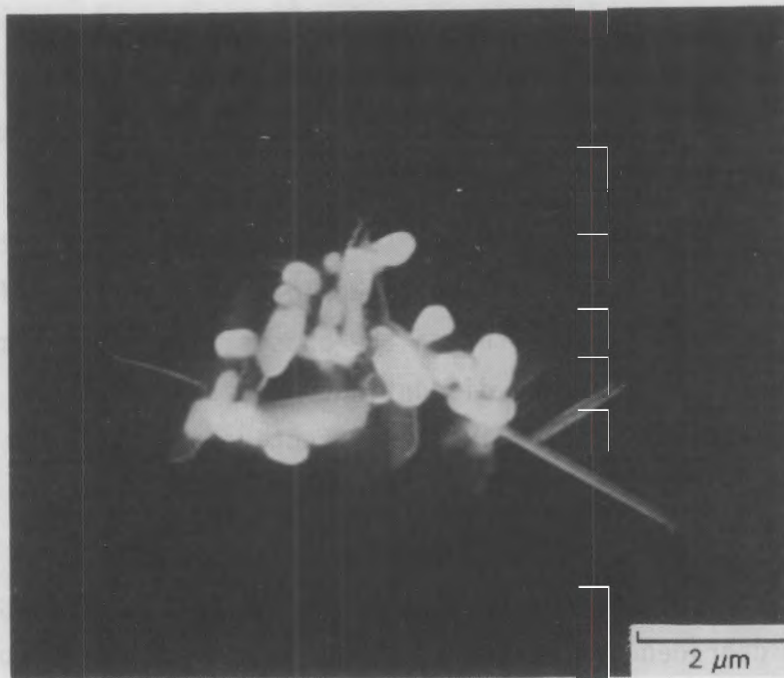
FIGURE 4.14. SEM Micrograph of DG-WV44 Showing Metallic Surrounded by Acicular Crystals, Plus Spheroids in Surrounding Glass Which May be Evidence of Liquid-Liquid Phase Separation (10,000 X)
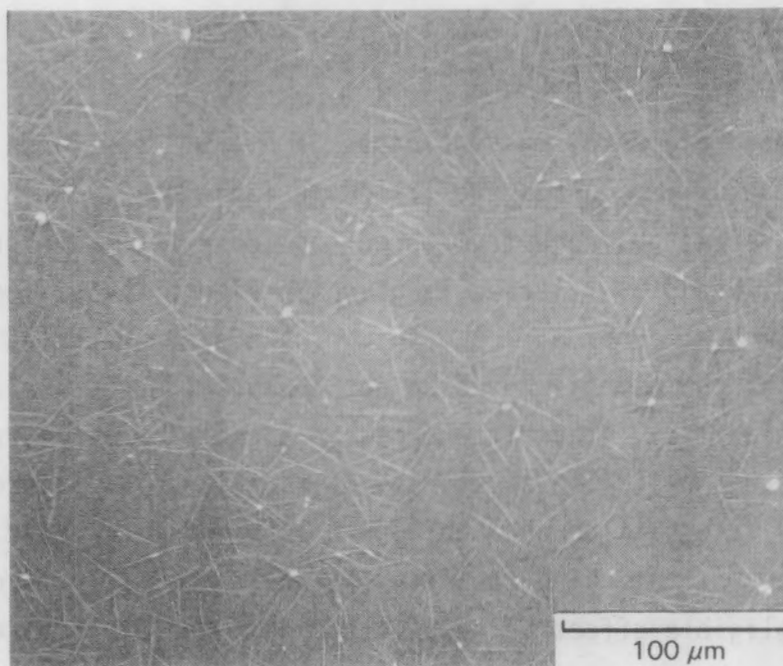
FIGURE 4.15. SEM Micrograph of DG-WV47 Showing Abundance of Metallics Surrounded by Acicular Crystals (300 X)

all of it was dissolved. Also, this glass was relatively low in Fe, probably decreasing its propensity to form Fe-bearing crystals. The lack of noble of metal phases may be related to the low concentrations of noble metals in the glass (they are part of the "others" component in Table 4.7).

From a practical point of view, it is unlikely that the scattered small crystalline phases noted in these samples would have a marked effect on durability. The materials constituting the phases are probably more durable than the host glass, and they are discontinuous in any event, so they do not provide a means of grossly increasing the effective surface area of the glasses.

However, if a sufficient amount of these phases form during the melting process (rather than during cooling), it is possible that processability of the glass may be degraded or that these phases might settle out of the glass and accumulate in the melter as a sludge. The examination of batch melting sequences and eludge accumulation, which is a complex matter dependent on melter shape and throughput and particle size, shape, and density, are beyond the scope of this work. Further study of the formation of these crystals should be undertaken.

4.6 GLASS REDOX ADJUSTMENT EFFECTS

The normalized elemental mass releases of Al, B, Cs, Li, Na, Si, Th, and U for the redox-adjusted glasses are listed in Table 4.12. Each value given represents the average obtained from three replicate tests. A graphical representation of B and Si releases is given in Figure 4.16. The error bars represent experimental error of ± two sds. The sds are based on replicate tests performed at the same time and do not include the time-related component of variability. The differences in B and Si releases among the glasses tested are small. The similarity of the Si and B releases suggests that the glasses have similar chemical durability and that redox state has negligible effect on chemical durability. Statistical analysis of variance confirms the negligible effect of redox state on B and Si releases.

The final pH of the leachate appears to increase with the increasing Fe^{2+}/Fe^{3+} of the glass leached. This could be caused by the oxidation of

4.36

TABLE 4.12. Average Normalized Elemental Mass Releases of Redox Adjusted Glasses (7-day MCC-3, 90°C, Deaerated DIW), g/m$_2$

| Element | Fe^{2+}/Fe^{3+} | | | |
	0.068	0.126	0.236	0.424
Al	0.119	0.113	0.114	0.121
B	0.212	0.209	0.212	0.237
Cs	0.092	0.101	0.081	0.067
Fe	0.003	0.002	0.003	0.003
K	0.020	0.056	0.026	0.095
Li	0.274	0.269	0.269	0.295
Mg	0.000	0.000	0.000	0.003
Mn	0.002	0.002	0.002	0.003
Na	0.209	0.203	0.215	0.249
P	0.177	0.173	0.171	0.182
Si	0.116	0.112	0.112	0.121
Th	0.000	0.000	0.000	0.000
Ti	0.001	0.001	0.000	0.001
U	0.024	0.023	0.021	0.025
pH[a]	9.64	9.76	9.82	9.91

(a) pH measured at test termination at 25°C.

Fe^{2+} in the leachate. As Fe^{2+} goes into solution, it is oxidized by dissolved O_2 in the following reaction:

$$O_2 + 4H^+ + 4Fe^{2+} \rightarrow 4Fe^{3+} + 2H_2O \qquad (4.7)$$
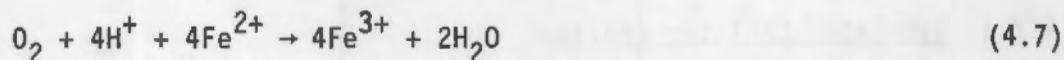
This reaction consumes H^+ which in turn increases the pH. With greater Fe^{2+}/Fe^{3+} ratios, more Fe^{2+} is available for oxidation. The greater the amount of Fe^{2+} oxidized, the greater the increase in solution pH. Calculations comparing available Fe^{2+} concentrations and H^+ consumption support this theory.

4.37
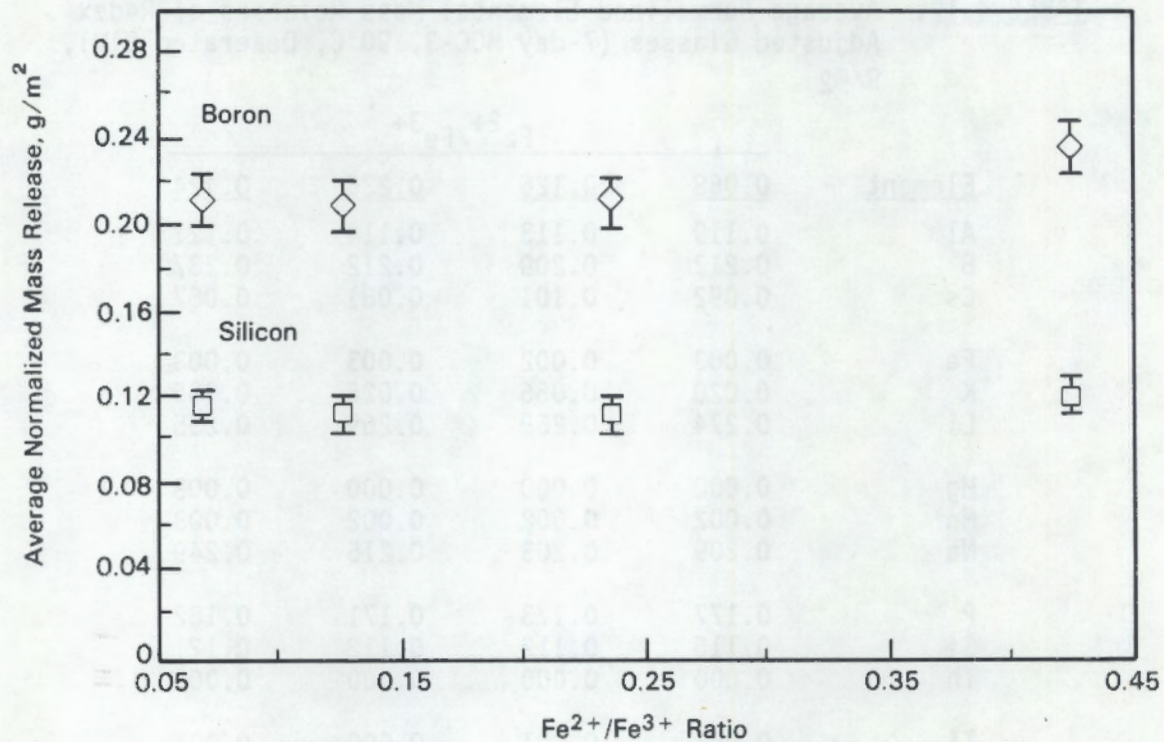
FIGURE 4.16. Comparison of Si and B Normalized Mass Releases from Redox-Adjusted Glasses. Modified MCC-3 test, 90°C, deaerated deionized water, 7-day.

4.7 THERMAL HISTORY EFFECTS

Glasses DG-WV11R through DG-WV14R were heat treated under simulated canister and isothermal conditions and then leach tested to determine glass durability.

4.7.1 Simulated Canister Cooling

The glass microstructure and durability were determined from normalized element release data, for glasses subjected to slow-cooling. The glass microstructure and durability results are discussed below.

Glass Microstructure

Cubic spinel-type crystals [$(Fe,Ni)(Cr,Fe)_2O_4$] were observed in all heat-treated glasses with SEM/EDX and verified with XRD. These crystals contained Cr, Ni, and Fe. Some also contained small amounts of Mn. These crystals were scattered evenly throughout the glass. They ranged in size

4.38

from approximately 5 to 10 μm. Ruthenium inclusions and fluorite crystals (ThO_2+UO_2) were also observed in all glasses. The Ru inclusions appeared to act as nucleation sites for crystal growth. The fluorite crystals measured approximately 25 to 50 μm across; the Ru inclusions measured approximately 0.3 to 0.8 μm. Crystals which appear to be hematite [$(Cr,Fe)_2O_3$] were observed in all glasses with SEM/EDX. They were not detected in four of the samples with XRD, probably due to relatively low crystalline concentrations.

The XRD analysis results are given in Table 4.13. This table lists approximate amounts of crystals identified. A total crystalline content of roughly 15 to 20 wt% was estimated by the analysis to be in the glass samples.

Glass Chemical Durability

Table 4.14 lists the normalized elemental mass releases of B, Cs, Na, Si, Th, U, and those elements whose oxide contributed at least 1 wt% of the glass composition. Each value given represents the average obtained from three replicate tests. Normalized elemental mass releases of DG-WV11R and DG-WV14R are given in Table 4.13 also for comparison. DG-WV11R may be treated as a control glass as its redox state is fairly close to that of the heat-treated glasses.

TABLE 4.13. Amounts of Crystals Identified by XRD in Heat-Treated Glasses[a]

Sample[b]	%Spinel[c]	%Hematite[d]	%Fluorite[e]
HT-S-3	12.00	<0.75	3.00
HT-S-4	12.00	1.50	1.50
HT-S-2	13.50	<0.75	1.50
HT-S-5	12.75	<0.75	1.50
HT-S-6	14.24	<0.75	0.74
HT-S-1	6.00	6.00	3.00

(a) Based on total crystalline content of 15.0 wt%.
(b) Ordered from fastest to slowest overall cooling rates.
(c) $(Fe,Ni)(Cr,Fe)_2O_4$
(d) $(Cr,Fe)_2O_3$, less than values based on 5 wt% detection limit.
(e) ThO_2

4.39

TABLE 4.14. Average Normalized Elemental Mass Releases of Glasses Heat-Treated with Simulated Canister Cooling Rates (7-Day, MCC-3, 90°C, Deaerated DIW), g/m^2

Element	Glass Code							
	HT-S-1	HT-S-2	HT-S-3	HT-S-4	HT-S-5	HT-S-6	DG-WV11R	DG-WV14R
Al	0.144	0.131	0.121	0.114	0.148	0.142	0.119	0.121
B	0.246	0.204	0.192	0.175	0.228	0.218	0.212	0.237
Cs	0.113	0.123	0.119	0.158	0.133	0.132	0.092	0.067
Fe	0.005	0.003	0.002	0.002	0.005	0.005	0.003	0.003
K	0.132	0.121	0.097	0.125	0.116	0.164	0.020	0.095
Li	1.030	0.581	0.408	0.295	1.000	0.930	0.274	0.295
Mg	0.025	0.015	0.007	0.006	0.022	0.023	0.000	0.003
Mn	0.009	0.004	0.003	0.002	0.006	0.005	0.002	0.003
Na	0.265	0.217	0.206	0.188	0.249	0.237	0.209	0.249
P	1.472	0.749	0.461	0.294	1.450	1.329	0.177	0.182
Si	0.142	0.124	0.117	0.109	0.141	0.136	0.116	0.121
Th	0.009	0.004	0.003	0.003	0.007	0.007	0.000	0.000
Ti	0.007	0.004	0.003	0.002	0.007	0.007	0.001	0.001
U	0.062	0.045	0.039	0.048	0.070	0.073	0.024	0.025
pH[a]	10.14	9.89	9.81	9.77	10.20	10.14	9.64	9.91

(a) pH measured at test termination at 25°C.

A graphical representation of B and Si releases for the heat-treated glasses is given in Figure 4.17. The error bars represent ± two sds. The sds are based on replicate tests performed at the same time and do not include the time-related component of variability. The figure demonstrates that the heat treatments have a slight effect on the chemical durability of the glass. A maximum decrease of 15%, based on B release, over that of the reference glass is shown. Furthermore, Figure 4.17 shows the average normalized mass releases of B and Si from the heat-treated samples and DG-V11R and DG-WV14R. The DG-WV11R may be treated as a control glass as its redox state is fairly close to that of the heat-treated glasses. Statistical analyses of variance methods were used to compare the six heat-treated glasses (Specimens HT-S-1 through HT-6-S) with each other and with DG-WV11R and DG-WV14R. The B and Si releases for the more quickly cooled specimens (HT-S-2, -3, and -4)

4.40
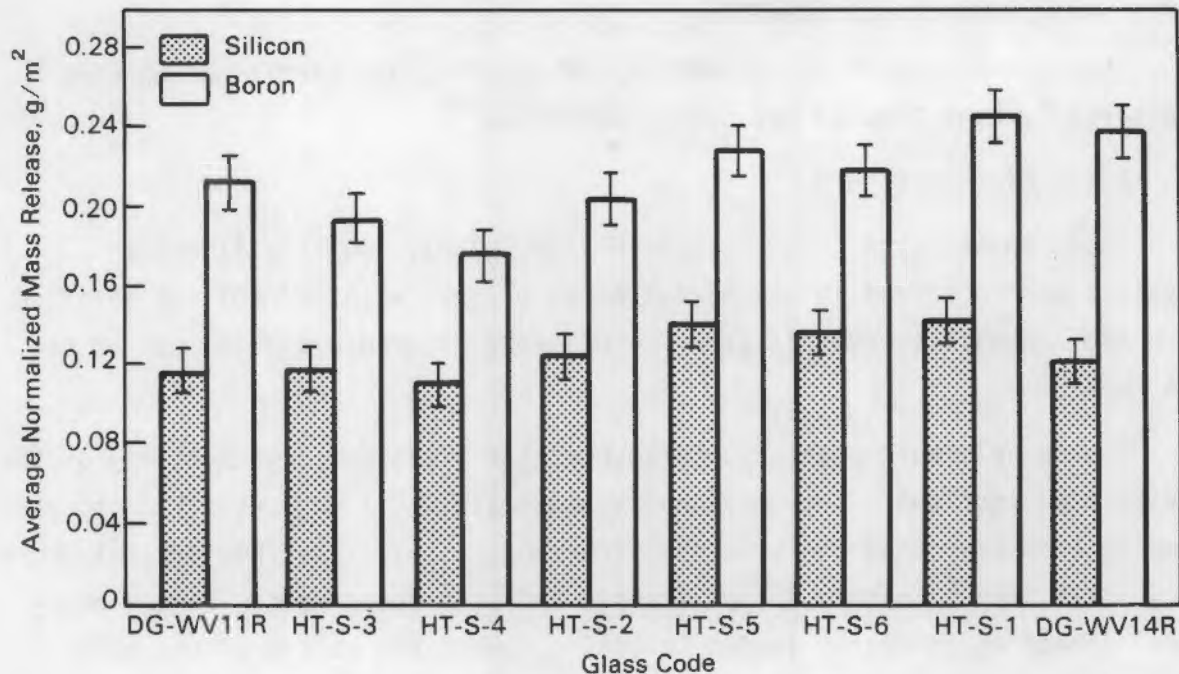
FIGURE 4.17. Comparison of Si and B Normalized Mass Releases from Slow-Cool Heat-Treated Glasses. (Heat-treated glasses are arranged in order from fastest to slowest relative cooling rates. Modified MCC-3 test, 90°C, deaerated deionized water, 7-day.)

differ significantly from the releases for the more slowly cooled specimens (HT-S-1, -5, and -6), but the releases within these two groups do not differ significantly.

The B and Si releases of DG-WV11R are not significantly different from those for the quickly cooled glasses, indicating that this cooling does not affect chemical durability any more than slight glass reduction does. The B releases of DG-WV14R and the more slowly cooled glasses are similar, which indicates that their chemical durabilities also are not significantly different.

The observed microstructure provides no further insight into the effect of the slow cooling treatments on chemical durability. There appears to be no correlation between type and amount of crystalline formation and chemical durability or heat treatment.

4.7.2 Isothermal Heat Treatment

The microstructure and durability of the 15 glass samples which were isothermally heat treated are described below.

Glass Microstructure

Cubic spinel-type crystals [(Fe,Ni)(Cr,Fe)$_2$O$_4$] and ThO$_2$ fluorite crystals were observed in all heat-treated glasses with SEM/EDX and verified with XRD. Hematite crystals [(Cr,Fe)$_2$O$_3$] were also observed in most of the specimens.

The spinels were scattered throughout the glass and some settling of the crystals was noticed. They measured approximately 0.3 μm across--an order of magnitude smaller than the slow-cool treated glasses. The ThO$_2$ crystals were very small, approximately 0.1 μm across, and were found mainly in agglomerates. These agglomerates tended to settle toward the bottom of the melt. Most of the hematite crystals measured approximately 1.0 μm across and appeared in greater amounts at temperatures greater than or equal to 725°C and holding times greater than 12 hours.

The glasses treated at 725°C for greater than or equal to 12 hours also contained a P-rich phase, possibly Li$_3$PO$_4$, and a separate calcium phosphate phase (Ca$_3$(PO$_4$)$_2$), in addition to the crystalline phases described above. The amount of these phases increased with holding time.

The XRD analysis results are given in Table 4.15. This table lists approximate amounts of crystals identified by XRD, by wt% relative to the standard (HT-S-22). The types of crystals listed are spinel, hematite, and fluorite (contains ThO$_2$). The approximate amounts of spinel, hematite, and fluorite crystals in the standard are 7, 0.3, and 1.5 wt% respectively. The amounts of the crystals relative to the standard were obtained by ratioing specimen peak intensities to those of the standard. Therefore a value over one in Table 4.15 indicates the presence of a greater total amount, by weight, of that crystal than found in the standard and conversely, a value less than one indicates a lesser amount. A value of one indicates that the same wt% of the particular crystal is present in the specimen and the standard.

TABLE 4.15. Amounts of Crystals Identified by XRD in Heat Treated Glasses Relative to Amounts in Standard Specimen (HT-S-22)[a]

Sample	Temp/Time[b]	Spinel[c]	Hematite[d]	Fluorite[e]
HT-S-22	500°C/2 h	1.0	1.0	1.0
HT-S-7	500°C/120 h	0.48	1.01	0.13
HT-S-8	500°C/240 h	0.70	0.0	0.26
HT-S-9	600°C/12 h	0.91	0.77	0.29
HT-S-10	600°C/48 h	1.10	0.0	0.34
HT-S-11	600°C/240 h	0.88	0.98	0.36
HT-S-12	725°C/6 h	1.25	0.0	0.32
HT-S-13	725°C/12 h	0.99	0.79	0.61
HT-S-14	725°C/48 h	1.26	2.26	1.15
HT-S-15	725°C/120 h	1.03	2.18	0.80
HT-S-16	725°C/240 h	0.79	2.80	1.24
HT-S-17	800°C/12 h	0.97	0.0	1.04
HT-S-18	800°C/48 h	0.79	5.66	0.74
HT-S-19	800°C/240 h	0.41	4.77	0.81
HT-S-20	900°C/120 h	0.39	2.54	1.13
HT-S-21	900°C/240 h	0.41	2.93	1.49

(a) Relative amounts = (amount in glass, wt%)/(amount in HT-S-22, wt%).
(b) Temperature and holding time of heat treatment.
(c) $(Fe,Ni)(Cr,Fe)_2O_4$; Approximately 7 wt% in HT-S-22.
(d) $(Cr,Fe)_2O_3$; Approximately 0.3 wt% in HT-S-22.
(e) ThO_2; Approximately 1.5 wt% in HT-S-22.

Table 4.15 shows that, at temperatures of greater than or equal to 725°C and holding times of 48 h or more, hematite crystals are formed to a greater extent than in the standard as observed with SEM/EDX. Treatment temperatures less than 725°C appear to either have little effect on the glass crystallinity. The relative amount of fluorite is low and the presence of hematite is not detected in two of the specimens. The relative amount of spinel is less than that of the standard in the 500°C treated specimens.

Glass Chemical Durability

Tables 4.16, 4.17, and 4.18 list the normalized elemental mass releases of B, Na, Si, Th, U, and those elements whose oxide contributed at least

4.43

TABLE 4.16. Average Normalized Mass Releases of Specimens Isothermally Treated at 500 and 600°C (7-day MCC-3, 90°C, Deaerated DIW) - g/m²

	Glass Code, Treatment Temperature, and Holding Time					
	HT-S-22[a]	HT-S-7	HT-S-8	HT-S-9	HT-S-10	HT-S-11
	500°C	500°C	500°C	600°C	600°C	600°C
Element	2 h	120 h	240 h	12 h	48 h	240 h
Al	0.108	0.110	0.110	0.113	0.120	0.154
B	0.182	0.190	0.187	0.198	0.212	0.364
Fe	0.002	0.003	0.002	0.002	0.003	0.008
K	0.087	0.120	0.110	0.109	0.128	0.133
Li	0.219	0.250	0.241	0.293	0.367	0.783
Mg	0.003	0.005	0.005	0.012	0.017	0.013
Mn	0.002	0.002	0.002	0.003	0.006	0.021
Na	0.186	0.183	0.172	0.192	0.211	0.286
P	0.151	0.182	0.182	0.312	0.441	1.147
Si	0.120	0.119	0.119	0.126	0.131	0.145
Th	0.001	0.002	0.002	0.002	0.004	0.032
Ti	0.002	0.002	0.002	0.003	0.005	0.021
U	0.031	0.034	0.032	0.039	0.051	0.123
pH[b]	9.22	9.18	9.21	9.39	9.42	9.36

(a) Prepared standard.
(b) pH measured at test termination at 25°C.

1 wt% of the glass composition. Each value given represents the average obtained from three replicate tests. The three replicate tests were performed at the same time under the same conditions, and the resulting leachates were chemically analyzed at the same time under the same conditions. Hence, the replicates only include short-term variations in the leach testing and leachate analysis processes.

Figure 4.18 shows the B release data for the isothermally heat-treated glasses plotted as a function of heat treatment time and treatment temperature on a time-temperature-transformation diagram. The B release values for each sample are shown, as well as the approximate locations of a series of constant leaching isopleths.

4.44

TABLE 4.17. Average Normalized Mass Releases of Specimens Isothermally Treated at 725°C (7-day MCC-3, 90°C, Deaerated DIW), g/m^2

	HT-S-22[a] 500°C	Glass Code, Treatment Temperature, and Holding Time				
		HT-S-12 725°C	HT-S-13 725°C	HT-S-14 725°C	HT-S-15 725°C	HT-S-16 725°C
Element	2 h	120 h	240 h	12 h	48 h	240 h
Al	0.108	0.124	0.155	0.159	0.160	0.160
B	0.182	0.212	0.261	0.262	0.262	0.263
Fe	0.002	0.004	0.011	0.014	0.014	0.014
K	0.087	0.109	0.154	0.176	0.153	0.161
Li	0.219	0.582	1.500	1.545	1.515	1.543
Mg	0.003	0.019	0.035	0.039	0.040	0.039
Mn	0.002	0.005	0.014	0.017	0.017	0.018
Na	0.186	0.205	0.270	0.267	0.263	0.272
P	0.151	0.791	2.377	2.472	2.309	2.377
Si	0.120	0.138	0.169	0.172	0.170	0.171
Th	0.001	0.003	0.009	0.011	0.016	0.017
Ti	0.002	0.004	0.020	0.026	0.028	0.025
U	0.031	0.046	0.088	0.110	0.113	0.096
pH[b]	9.22	9.47	10.08	10.02	9.94	9.92

(a) Prepared standard.
(b) pH measured at test termination at 25°C.

The appearance of this diagram is essentially identical to what would be expected if crystallinity were plotted instead of chemical durability. This similarity is not surprising because devitrification of (growth of crystallinity in) the glass causes the decrease in durability. A maximum decrease in durability by a factor of two was found for the isothermally heat-treated samples (500°C for 2 h versus 600°C for 240 h). This type of behavior for a similar glass, SRL-165, was found in another study (Jantzen, Bickford, and Karraker 1984). In that study, the decrease in glass durability was attributed to the formation of acmite, $NaFeSi_2O_6$, as one of the devitrification products.

4.45

TABLE 4.18. Average Normalized Mass Releases of Specimens Isothermally Treated at 800°C and 900°C (7-day MCC-3, 90°C, Deaerated DIW), g/m^2

		Glass Code, Treatment Temperature, and Holding Time				
	HT-S-22(a)	HT-S-17	HT-S-18	HT-S-19	HT-S-20	HT-S-21
	500°C	800°C	800°C	800°C	900°C	900°C
Element	2 h	120 h	240 h	12 h	48 h	240 h
Al	0.108	0.141	0.112	0.124	0.112	0.112
B	0.182	0.238	0.186	0.222	0.203	0.204
Fe	0.002	0.010	0.003	0.004	0.002	0.002
K	0.087	0.145	0.113	0.026	0.091	0.102
Li	0.219	1.106	0.267	0.537	0.253	0.265
Mg	0.003	0.032	0.013	0.009	0.005	0.007
Mn	0.002	0.011	0.004	0.005	0.003	0.003
Na	0.186	0.251	0.187	0.219	0.186	0.193
P	0.151	1.657	0.231	0.643	0.164	0.172
Si	0.120	0.154	0.122	0.135	0.120	0.122
Th	0.001	0.007	0.001	0.002	0.001	0.001
Ti	0.002	0.014	0.003	0.003	0.002	0.002
U	0.031	0.070	0.034	0.045	0.031	0.033
pH(b)	9.22	9.87	9.26	9.40	9.22	9.42

(a) Prepared standard.
(b) pH measured at test termination at 25°C.

4.8 GROUNDWATER EFFECTS

Table 4.19 lists the normalized elemental mass releases of B, Cs, Na, Si, Th, U, and those elements whose oxide contributed at least 1 wt% of the glass composition. Calcium and Mg releases are not included because corrections of the leachate concentrations could not be made with the test blanks see above). Each value given represents the average obtained from three replicate tests. The average normalized mass releases of DG-WV11R are given in Table 4.19 to provide a comparison.

Graphical representation of B and Si releases are given in Figure 4.19. The error bars represent ± two sds. The sds are based on replicate tests performed at the same time and do not include the time-related component of variability. The releases of DG-WV11R are included in the figure to provide

4.46
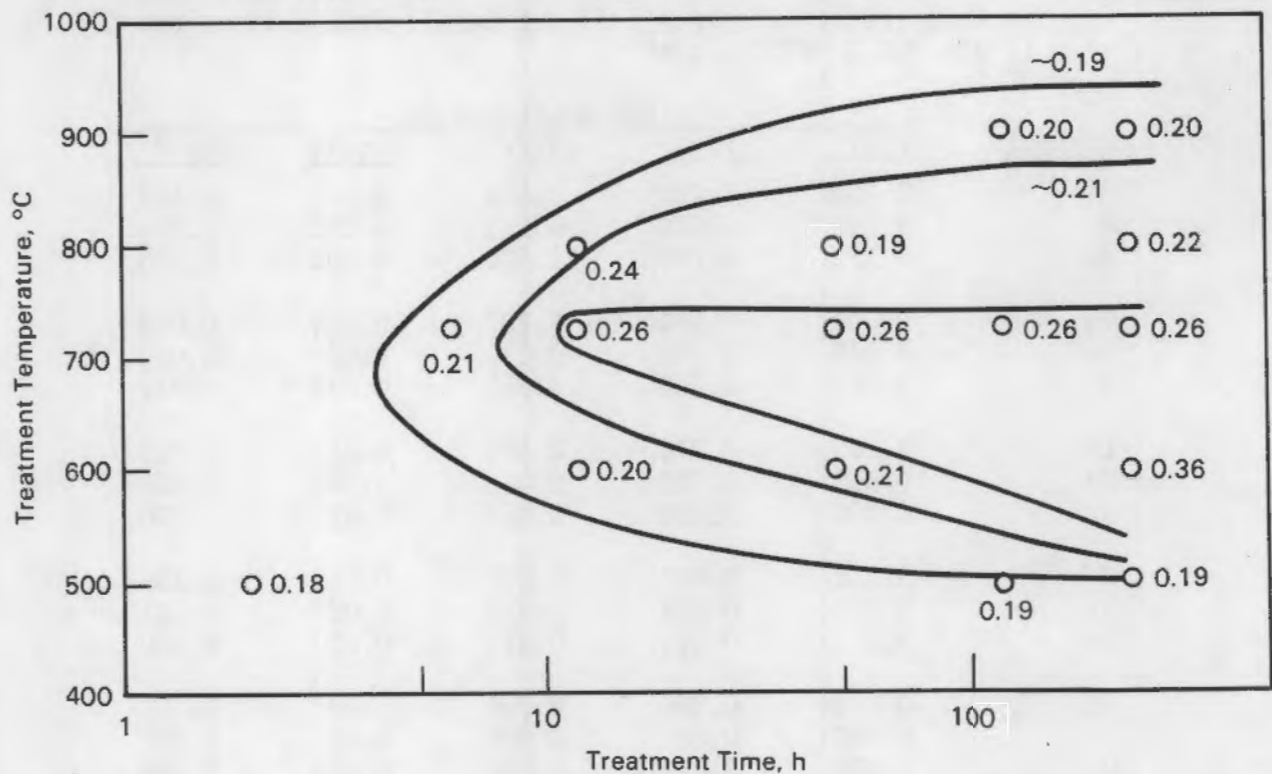
FIGURE 4.18. Time-Temperature-Transformation Diagram for B Releases from Isothermally Heat-Treated Reference Glass (WVCM-50). (Numbers in graph are B releases in g/m^2.) 7-day MCC-3, deaerated DIW, 90°C.

a comparison between glass chemical durability in DIW versus groundwater. The tests were conducted under the exact same conditions except that the redox adjusted glass was leached under CO_2-free conditions, while the groundwater leached glass was leached in a standard air atmosphere.

Figure 4.19 shows that groundwater type has a definite effect on the chemical durability of the glass and that the glass appears to be more chemically durable in the groundwaters tested than in deaerated DIW, under CO_2-free conditions. Specifically, Figure 4.19 demonstrates that the glass is most chemically durable in PBB1 and least chemically durable in DIW. The difference in durability, based on B release, is greater than in DIW by approximately a factor of 5 in PBB1, 4 in PBB3, 3 in J-13 well water, and 2 in GR-4.

4.47

TABLE 4.19. Average Normalized Mass Releases of West Valley Reference Glass in PBB1, PBB3, Reference Tuff and Basalt Groundwaters and DIW (7-day MCC-3, 90°C), g/m^2

	Groundwater Type				
Element	PBB1	PBB3	Tuff	Basalt	DIW[a]
Al	0.000	0.000	0.014	0.028	0.113
B	0.045	0.060	0.076	0.092	0.209
Ba	0.127	0.206	0.000	0.000	0.000
Cs	0.000	0.000	0.107	0.114	0.069
Fe	0.000	0.000	0.000	0.009	0.000
K	0.252	0.000	0.055	0.044	0.017
Li	0.205	0.216	0.191	0.214	0.259
Mn	0.000	0.000	0.000	0.008	0.000
Na	0.000	0.000	0.094	0.025	0.200
P	0.000	0.000	0.000	0.058	0.168
Si	0.010	0.025	0.015	0.027	0.111
Sr	0.311	0.000	0.013	0.000	0.000
Th	0.000	0.000	0.000	0.001	0.000
Ti	0.000	0.000	0.000	0.002	0.000
U	0.006	0.022	0.032	0.045	0.019
pH[b]	8.25	6.47	8.85	9.84	9.91

(a) Normalized mass release of DG-WV11R glass, slightly redox adjusted glass, leached in deaerated water, CO_2-free conditions.

(b) pH measured at test termination at 25°C.

That the brines, PBB1 and PBB3, caused the lowest amount of leaching is consistent with a known decreased solubility of SiO_2-bearing solids in solutions of high ionic strength. The relative saturation fraction of silicic acid in the leachant plays an important role in determining the glass reactivity (Strachan, Pederson, and Lokken 1985). This explains why the groundwater (composition close to that of GR-4), and to a smaller extent in brine at 90°C. The glass was found to leach more readily in DIW than the synthetic groundwater at 40°C. The results reported here also agree with this outcome.

4.48
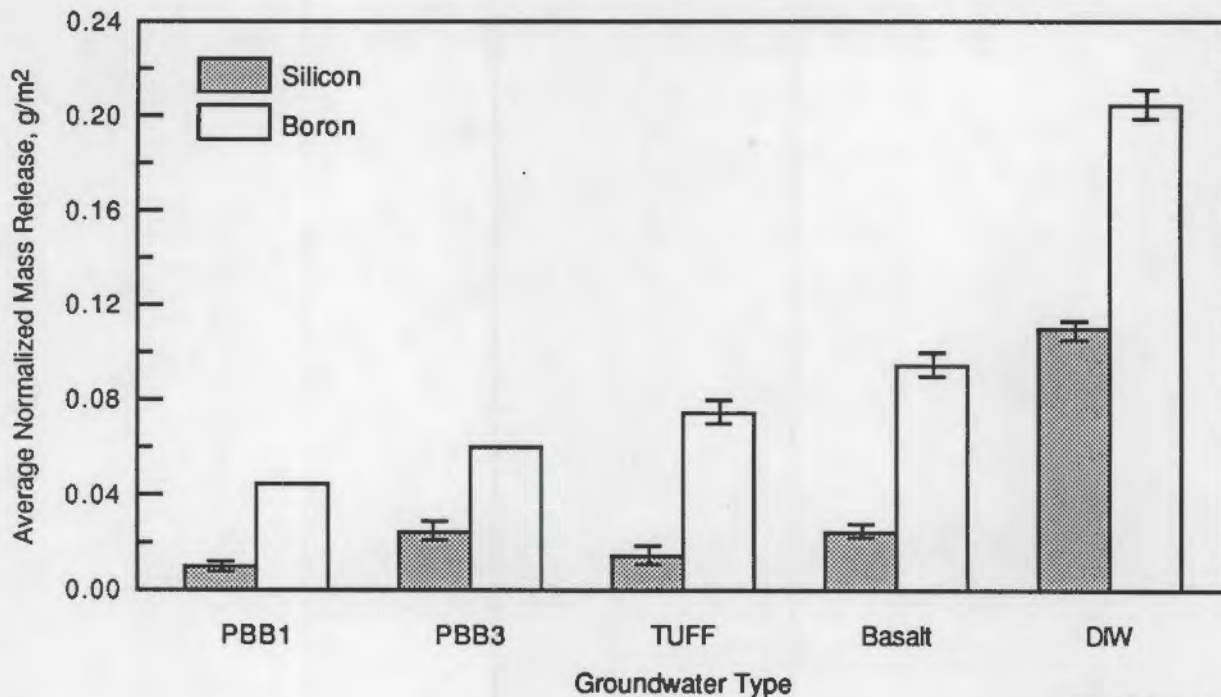
R8808 022 001

FIGURE 4.19. Comparison of B and Si Normalized Mass Releases from Reference Glass in Different Groundwaters (7-day MCC-3, deaerated DIW, 90°C)

Figure 4.19 also demonstrates that glass dissolution is greater in PBB3 than PBB1 and that dissolution is greater in basalt groundwater than in tuff groundwater. The brine-caused durability difference agrees with results found in the literature. The major difference between the brine compositions is Mg concentration, which is higher in PBB3. Early leaching studies conducted in brine solutions (Braithwaite 1980) concluded that glass dissolution increases with an increasing Mg content in the brine. The researchers attributed this effect to Mg causing a decrease in pH and substituting for divalent oxides like CaO and SrO in the glass matrix. However, other brine leaching studies (McGrail and Reimus 1987) have shown that the kinetics of dissolution of a defense waste glass were not affected by the difference in brine composition. The difference in durability observed between basalt and tuff groundwater is most probably caused by the higher initial pH of the basalt groundwater (10.18 versus 8.20) allowing for greater glass network attack.

4.49

FIGURE 4.16. Comparison of B and Si Normalized Mass Release from Reference Glass in Different Groundwaters (7-day MCC-1, measured at 90 C).

Figure 4.16 also demonstrates that glass dissolution is greater in PBB1 than PBB2, and that dissolution is greater in basalt groundwater than in tuff groundwater. The brine-caused durability difference agrees with results found in the literature. The major difference between the brine compositions is the Na concentration, which is higher in PBB2. Early leaching studies conducted in brine solutions (Devils Lake 1980) contained that glass dissolution increases with an increase in Na content in the brine. The researchers attributed this effect to increased leaching of alkali and substitution, for instance, of alkalis like CaO and SrO in the glass matrix. However, other brine-leaching studies (McGrail and Peters 1985) have shown that the kinetics of dissolution of aluminosilicate glass were not affected by the difference in brine composition. The difference in durability caused between basalt and tuff groundwater is most probably caused by the higher initial pH of the basalt groundwater (10.16 versus 8.20) allowing for greater glass network attack.

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APPENDIX A

AVERAGE NORMALIZED MASS RELEASES OF DG-WV1

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AVERAGE NORMALIZED MASS RELEASES OF DG-WV1

TABLE A.1. DG-WV1 Average Normalized Mass Releases and Corresponding Uncertainties (7-day MCC-3, deaerated DIW, 90°C)

	Normalized Mass Release, g/m^2				Test Standard Deviation[f]	% RSD[g]
Element	A[a]	B[b]	C[c]	D[d]		
Al	0.106	0.096	0.103	0.107	4.94E-03	4.8
B	0.186	0.148	0.154	0.177	1.80E-02	10.8
Ba	0.000	0.000	0.000	0.001	(h)	(h)
Ca	0.002	0.002	0.009	0.005	3.40E-03	76.4
Ce	0.000	0.000	0.000	0.000	0.00E+00	0.0
Cr	0.000	0.000	0.000	0.000	0.00E+00	0.0
Cs	0.104	0.107	0.073	0.108	1.81E-02	18.3
Fe	0.002	0.002	0.003	0.003	0.56E-03	23.6
K	0.021	0.081	0.082	0.045	3.06E-02	53.5
La	0.000	0.000	0.000	0.000	0.00E+00	0.0
Li	0.301	0.221	0.214	0.263	4.06E-02	16.2
Mg	0.000	0.003	0.007	0.000	3.40E-02	142.6
Mn	0.001	0.001	0.003	0.002	0.57E-03	31.2
Mo	0.181	0.082	0.149	0.149	5.16E-02	36.5
Na	0.158	0.134	0.139	0.156	1.22E-02	8.3
P	0.105	0.063	0.055	0.088	2.32E-02	29.9
Si	0.116	0.103	0.109	0.117	6.58E-03	5.9
Sr	0.000	0.000	0.000	0.000	0.00E+00	0.0
Th	0.001	0.002	0.003	0.002	0.83E-03	38.9
Ti	0.001	0.001	0.002	0.002	0.35E-03	24.5
U	0.026	0.039	0.038	0.034	6.22E-03	18.0
Zr	0.032	0.002	0.003	0.003	1.47E-02	145.0
pH[e]	9.15	9.22	8.42	9.38		

(a) Average of triplicate data, test run began 1-15-87.
(b) Average of triplicate data, test run began 4-13-87.
(c) Average of triplicate data, test run began 5-21-87.
(d) Average of triplicate data, test run began 6-3-87.
(e) pH at test termination at 25°C.
(f) Combined short- and long-term variation in the leach testing and leachate analysis processes.
(g) The test standard deviation expressed as a percentage of the overall mean release for each element.
(h) Not computed.

APPENDIX B

<u>FORMULAS FOR CONFIDENCE AND TOLERANCE BANDS</u>

APPENDIX B

FORMULAS FOR CONFIDENCE AND TOLERANCE BANDS

Formulas for $(1-\alpha)100\%$ one-sided upper and two-sided confidence bands and $(1-\alpha)100\%$ / $(1-\gamma)100\%$ one- and two-sided upper tolerance bands on a fitted (least squares) model are presented here.

In general, let the model be represented in vector notation by

$$y = \underset{\sim}{x}' \, \underset{\sim}{b} \tag{B.1}$$

where y = normalized boron release (NBR)

$\underset{\sim}{b}$ = a p x 1 column vector of estimated parameters

$\underset{\sim}{x}'$ = a 1 x p row vector whose elements are functions of the oxide component proportions.

For the linear mixture models given by Equations (4), (5), (6), and (7) in this report, $\underset{\sim}{x}$ is just the vector of the eleven oxide component weight fractions, and p = 11.

Now let $\underset{\sim}{X}$ represent the n x p matrix of $\underset{\sim}{x}$ vectors for which we have data, where n is the number of data points. The matrix $\underset{\sim}{X}$ is sometimes referred to as the design or test matrix. Then, for the design matrix $\underset{\sim}{X}$, Eq. (B.1) can be written in the form

$$\underset{\sim}{y} = \underset{\sim}{X} \, \underset{\sim}{b}$$

where $\underset{\sim}{x}$ is an n x 1 column vector containing the NBR value for each data point. The least squares estimate of the parameter vector is

$$\hat{\underset{\sim}{b}} = (\underset{\sim}{X}'\underset{\sim}{X})^{-1} \, \underset{\sim}{X}'\underset{\sim}{y} \tag{B.2}$$

and the predicted NBR at any composition $\underline{x}$ is given by

$$\hat{y}(\underline{x}) = \underline{x}' \ \hat{\underline{b}} \tag{B.3}$$

The $(1-\alpha)100\%$ one-sided upper and two-sided confidence bands on the fitted models are given by Equations (B.4) and (B.5) respectively,

$$\hat{y}(x) + \sqrt{p \ F_{1-2\alpha}(p,q) \ x'(X'X)^{-1}x \ \hat{\sigma}^2} \tag{B.4}$$

$$\hat{y}(x) \pm \sqrt{p \ F_{1-\alpha}(p,q) \ x'(X'X)^{-1}x \ \hat{\sigma}^2} \tag{B.5}$$

where $\hat{y}(x)$ = the predicted value from the fitted model at composition $\underline{x}$

$\underline{x}$ = a $p \times 1$ vector of oxide component weight fractions corresponding to any glass within the compositional region

$F_{1-2\alpha}(p,q)$ = $(1-2\alpha)100$th percentile of the central F-distribution with p numerator and q denominator degrees of freedom

$F_{1-\alpha}(p,q)$ = $(1-\alpha)100$th percentile of the central F-distribution with p numerator and q denominator degrees of freedom

p = the number of parameters in the model

q = the degrees of freedom associated with the estimate of σ

$\hat{\sigma}^2$ = estimate of experimental error variance.

The $(1-\alpha)100\%$ / $(1-\gamma)100\%$ one-sided upper and two-sided tolerance bands on the fitted models are given by Equations (B.6) and (B.7) respectively,

$$\hat{y}(\underline{x}) + \hat{\sigma} \left\{ \sqrt{p \ F_{1-\alpha}(p,q) \ \underline{x}' \ (\underline{X}'\underline{X})^{-1}\underline{x}} + z_{1-\gamma} \left[\frac{q}{\chi^2_\alpha \ (q)} \right]^{1/2} \right\} \tag{B.6}$$

B.2

$$\hat{y}(\underline{x}) \pm \hat{\sigma} \left\{ \overline{p\, F_{1-\alpha/2}(p,q)\, \underline{x}'\, (\underline{X}'\underline{X})^{-1}\underline{x}} + z_{1-\gamma/2} \left[\frac{q}{\chi^2_{\alpha/2}(q)} \right]^{1/2} \right\} \quad (B.7)$$

where $z_{1-\gamma}$ = the $(1 - \gamma)100$th percentile of the standard normal distribution

$\chi^2_{\alpha}(q)$ = the (αth) percentile of the central chi-square distribution with q degrees of freedom

$z_{1-\gamma/2}$ = the $(1 - \gamma/2)100$th percentile of the standard normal distribution

$\chi^2_{\alpha/2}(q)$ = the ($\alpha/2$th) percentile of the central chi-square distribution with q degrees of freedom.

Formulas (B.4) through (B.7) are extensions of the formulas given by Miller (1981, p. 124).

For 95% one-sided upper and two-sided confidence bands and 95%/95% one-sided upper and two-sided tolerance bands, $\alpha = 0.05$ and $\gamma = 0.05$. The quantity $\hat{\sigma}$ in equations (B.4) through (B.7) used to produce the confidence and tolerance band-based results given in Table 27 of this report were obtained via

$$\hat{\sigma} = \hat{y}(x) * \%RSD \quad (B.8)$$

where %RSD is either the within-lab or within-lab and lab-to-lab %RSD from Table 4.9 of this report.

APPENDIX C

<u>SHORT-TERM, LONG-TERM, AND LAB-TO-LAB VARIATIONS IN</u>
<u>GLASS ANALYSES, LEACH TESTING, AND LEACHATE ANALYSES</u>

APPENDIX C

SHORT-TERM, LONG-TERM, AND LAB-TO-LAB VARIATIONS IN
GLASS ANALYSES, LEACH TESTING, AND LEACHATE ANALYSES

C.1 INTRODUCTION

In order to carry out the statistical approach for characterizing normalized boron release over the WV-8801-based compositional region, it was necessary to obtain estimates of the short-term within-lab, long-term within-lab, and lab-to-lab standard deviations for the leach testing (including test preparation), leachate analysis, and glass analysis processes. To obtain information on the three lab-to-lab standard deviations and additional information on the six short- and long-term within-lab standard deviations, a limited "literature review" was performed. The results of the review are summarized in this appendix and an evaluation made regarding the uncertainty in normalized boron releases.

C.2 STANDARD DEVIATION OF NORMALIZED BORON RELEASE

The normalized boron releases (NBR) from the 7-day MCC-3 and 28-day MCC-1 and tests were computed as per Equations (1) and (2), respectively. The basic formula is repeated here for convenience:

$$NBR = C / (F * (W * SA)/V) \tag{C.1}$$

where NBR = normalized boron release (g/m^2)

C = concentration of boron in the leachate (ppm or g/m^3)

F = fraction of boron in glass = $(.311\ g\ B/g\ B_2O_3) * wt\%\ B_2O_3$ in glass)

W = weight of glass sample leached

SA = surface area of glass/g of glass (m^2/g)

V = volume of leachant (m^3).

Within the West Valley Support Task (WVST), it has been the practice to use the nominal SA/V value selected for the tests (10 m^{-1} for MCC-1 tests and

2000 m^{-1} for MCC-3 tests). This is acceptable provided the actual SA/V values vary randomly around the nominal value, in which case the variation in SA/V in different tests will be observed as a variation in the elemental release concentrations, C, and thus be accounted for in the standard deviation formula below. However, the variability of NBR due to variations in SA/V cannot be separately estimated.

The standard deviation of a single normalized release value (i.e., the value from a single analysis of leachate from a single leach test performed at a single lab) can be obtained via the general formula:

$$SD(NBR) = NBR \left\{ [SD(C)/C]^2 + [SD(W)/W]^2 \right\}^{0.5} \tag{C.2}$$

The quantity SD(C) in (C.2) is given by the formula

$$SD(C) = (s_1^2 + s_2^2 + \ldots + s_6^2)^{0.5} \tag{C.3}$$

where s_1 = short-term leach test standard deviation

s_2 = long-term leach test standard deviation

s_3 = lab-to-lab leach test standard deviation

s_4 = short-term leachate analysis standard deviation

s_5 = long-term leachate analysis standard deviation

s_6 = lab-to-lab leachate analysis standard deviation.

and it is assumed that the short-term, long-term, and lab-to-lab random errors in the leach testing (including sample preparation) and leachate analysis processes are independent.

The quantity SD(W) in (C.2) is given by the formula

$$SD(W) = (s_7^2 + s_8^2 + s_9^2)^{0.5} \tag{C.4}$$

where s_7 = short-term glass analysis standard deviation for B_2O_3 in the glass

s_8 = long-term glass analysis standard deviation for B_2O_3 in the glass

C.2

s_9 = lab-to-lab glass analysis standard deviation for B_2O_3
in the glass

and it is assumed that the short-term, long-term, and lab-to-lab random errors in the glass analysis process are independent. Note that s_7, s_8, and s_9 have values for each oxide component in the glass, but only B_2O_3 is of concern here relative to computing the uncertainty in normalized boron releases.

In the following section, the results of the literature review to collect information on previous estimates of s_1 through s_9 are given.

C.3 RESULTS OF LITERATURE REVIEW

Tables C.1 to C.7 contain the results of the literature review for estimates of short-term within-lab, long-term within-lab, and lab-to-lab standard deviations. Leach testing (including specimen preparation) and leachate analysis standard deviations are given in Tables C.1 to C.4, while glass analysis standard deviations are given in Tables C.5 to C.7. Results in Tables C.1 to C.4 are given for "as-analyzed" concentrations and normalized releases of boron. Because boron is the element of most interest, literature review efforts focused on collecting B information. The "as-analyzed" B concentration values are the ones directly applicable to Equation (C.3), but the normalized release values can also be used when working with % relative standard deviation (%RSD) versions of Equations (C.2) and (C.3). Specific discussions of each table are given below.

Tables C.1 and C.2 summarize short-term within-lab standard deviations for the leach testing and leachate analysis processes. Table C.1 presents results for MCC-1 testing of several glasses, while Table C.2 presents results for MCC-3 testing of several glasses. The "Proc. SD" and "Anal. SD" columns in Tables C.1 and C.2 contain estimates of s_1 and s_4, respectively.

TABLE C.1. Short-Term Procedural and Analytic Uncertainties in Boron Concentrations from MCC-1 Testing at 90°C in DIW

Glass	# Days	Date Test Began	Report	As Analyzed (mg/L)					Blank Corrected and Normalized (g/m^2)				
				Average Release	Proc. SD	Anal. SD	Total SD	Total % RSD	Average Release	Proc. SD	Anal. SD	Total SD	Total % RSD
ARM-1	3	11/15/83	MCC-D5	2.23					6.31	0.100	0.054	0.130	2.1
	7	10/28/83	MCC-D5	2.98					8.48	0.249	0.025	0.258	3.0
	7	2/28/86	WV/MCC-1	3.12	0.032	0.148	0.152	4.9	8.87			0.319*	3.6*
	14	10/28/83	MCC-D5	3.74					10.5	0.242	0.040	0.257	2.4
	27	2/28/86	WV/MCC-1	4.36	0.121	0.034	0.126	2.9	12.5			0.364*	2.9*
	28	10/31/83	MCC-D5	4.21	0.054	0.029	0.061	1.5	11.8				
	26	7/1/85	MCC-D5	4.46	0.032	0.047	0.057	1.3	12.6				
	28	6/26/86	WV/MCC-1	4.10	---	---	0.086	2.1	11.6	---	---	0.255	2.2
	28	5/29/87	APP A	4.64	---	---	0.191	4.1	13.2	---	---	0.552	4.2
	55	2/28/86	WV/MCC-1	4.72	0.038	0.026	0.046	1.0	13.4			0.154*	1.2*
	56	11/22/83	MCC-D5	5.39	0.398	0.046	0.401	7.4	15.0				
	56	7/1/85	MCC-D5	4.83	0.059	0.032	0.087	1.4	13.6				
	91	10/28/83	MCC-D5	4.88					13.6	0.090	0.055	0.115	0.8
	91	5/29/87	APP A	5.43	---	---	0.042	0.8	15.4	---		0.163	1.1
	182	10/28/83	MCC-D5	5.50					14.9	0.090	0.182	0.210	1.4
	364	10/28/83	MCC-D5	6.20					16.2	0.409	0.105	0.437	2.7
	546	11/22/83	MCC-D5	6.05					16.5	0.193	0.260	0.344	2.1
CUA aka WVCM-50	28	5/29/87	APP A	3.98	---	---	0.364	9.2	10.8	---	---	1.03	9.5
	56	5/29/87	APP A	5.35	---	---	0.620	11.6	14.6	---	---	1.73	11.8
	91	5/29/87	APP A	6.37	---	---	0.828	13.0	17.3	---	---	2.28	13.3
CTS	28	6/26/88	WV/MCC-1	6.32	---	---	0.202	3.2	19.5	---	---	0.633	3.3
	71	4/11/87	WV/MCC-1	8.58	---	---	0.055	0.6	26.5	---	---	0.226	0.8
	91	4/11/87	WV/MCC-1	8.80	---	---	0.110	1.2	27.2	---	---	0.373	1.4
ATM-10	28	11/10/86	WV/MCC-1	3.19	---	---	0.086	2.7	11.1	---	---	0.293	2.6
	57	11/10/86	WV/MCC-1	4.18	---	---	0.254	6.1	14.5	---	---	0.885	6.1
	91	11/10/86	WV/MCC-1	4.97	---	---	0.411	8.3	16.2	---	---	1.36	8.4
SRL-131	28	3/31/82	MCC-D2	10.1	---	---	0.197	1.9	32.4	---	---	1.18	3.6
	91	3/24/82	MCC-D2	20.2	---	---	0.757	3.7	61.2	---	---	1.72	2.8
	182	3/24/82	MCC-D2	28.0	---	---	0.566	2.0	86.7	---	---	2.33	2.7
	365	3/24/82	MCC-D2	40.2	---	---	1.563	3.9	119.0	---	---	4.98	4.2
PNL 76-68	28	9/26/80	MCC-D1	11.4	---	---	2.25	19.7	46.7	---	---	9.24	20.2
	56	10/15/80	MCC-D1	15.1	---	---	0.76	5.0	54.1	---	---	3.31	6.1
	91	10/15/80	MCC-D1	24.0	---	---	5.59	23.3	85.6	---	---	20.0	23.4
	182	10/15/80	MCC-D1	33.1	---	---	0.15	0.5	106.7	---	---	7.0	6.6
	365	10/15/80	MCC-D1	37.0	---	---	0.61	1.6	111.3	---	---	5.7	5.1

Notes: (1) All entries (except those marked "*") are estimates of short-term uncertainty in boron release from a single analysis of a single MCC-1 test at 90oC in DIW. "Short-term" with respect to the Analytic SD refers to the fact that repeat analyses were usually performed within a few mintues, while with respect to the Procedural SD it refers to the fact that the replicate MCC-1 tests were conducted at the same time. Where only one analysis per leachate was performed, the analyses for the replicate-test leachates were analyzed within minutes of each other.

(2) Entries marked "*" are based on boron concentrations averaged over the repeat leachate analyses. Hence, they underestimate the uncertainty desired (the uncertainty in a single analysis value from a single test).

(3) Entries of "---" indicate that it was not possible to separate the procedural and analytic sources of variation.

(4) Blank entries were not computed due to lack of time or the required data. All such entries could be computed given time and the appropriate data.

TABLE C.2. Short-Term Procedural and Analytic Uncertainties in Boron Concentrations from MCC-3 Testing at 90°C in DIW

Test & Glass	# Days	Date Test Began	Report	As Analyzed (mg/L)					Blank Corrected and Normalized (g/m^2)				
				Average Release	Proc. SD	Anal. SD	Total SD	Total % RSD	Average Release	Proc. SD	Anal. SD	Total SD	Total % RSD
Modified MCC-3													
WV-1	7	1/8/87	na	14.00	---	---	0.100	0.71	0.186	---	---	0.0013	0.70
WV-1	7	4/6/87	na	11.20	---	---	0.100	0.89	0.148	---	---	0.0013	0.88
WV-1	7	5/14/87	na	11.33	---	---	0.231	2.04	0.154	---	---	0.0031	2.03
WV-1	7	5/27/87	na	12.93	---	---	0.252	1.95	0.176	---	---	0.0034	1.94
WV-2	7	1/8/87	na	14.40	---	---	0.100	0.69	0.191	---	---	0.0013	0.68
WV-3	7	1/8/87	na	13.70	---	---	0.0	0.0	0.236	---	---	0.0	0.0
WV-4	7	1/8/87	na	17.43	---	---	0.289	1.66	0.239	---	---	0.0039	1.65
WV-5	7	1/8/87	na	17.53	---	---	0.115	0.66	0.229	---	---	0.0015	0.66
WV-6	7	1/8/87	na	14.17	---	---	0.058	0.41	0.188	---	---	0.0008	0.43
WV-7	7	1/8/87	na	14.20	---	---	0.173	1.22	0.188	---	---	0.0023	1.22
WV-8	7	1/8/87	na	8.72	---	---	0.020	0.23	0.167	---	---	0.0004	0.24
WV-15	7	5/14/87	na	20.63	---	---	0.153	0.74	0.264	---	---	0.0019	0.74
WV-16	7	5/14/87	na	14.17	---	---	0.208	1.47	0.181	---	---	0.0027	1.50
WV-17	7	5/14/87	na	16.60	---	---	0.173	1.04	0.273	---	---	0.0028	1.04
WV-18	7	5/14/87	na	13.87	---	---	0.058	0.42	0.210	---	---	0.0009	0.42
WV-19	7	5/14/87	na	12.93	---	---	0.321	2.48	0.206	---	---	0.0051	2.49
WV-20	7	5/14/87	na	9.79	---	---	0.269	2.75	0.148	---	---	0.0041	2.75
WV-21	7	5/14/87	na	12.80	---	---	0.300	2.34	0.205	---	---	0.0048	2.36
WV-22	7	5/14/87	na	13.27	---	---	0.379	2.85	0.185	---	---	0.0052	2.84
WV-23	7	5/27/87	na	18.00	---	---	0.300	1.67	0.232	---	---	0.0039	1.68
WV-24	7	5/27/87	na	15.83	---	---	0.115	0.73	0.193	---	---	0.0014	0.72
WV-25	7	5/27/87	na	12.10	---	---	0.100	0.83	0.179	---	---	0.0015	0.84
WV-26	7	5/27/87	na	14.30	---	---	0.100	0.70	0.172	---	---	0.0012	0.70
WV-27	7	5/27/87	na	19.53	---	---	0.404	2.07	0.250	---	---	0.0052	2.08
WV-28	7	5/27/87	na	12.43	---	---	0.208	1.67	0.188	---	---	0.0031	1.66
WV-29	7	5/27/87	na	14.70	---	---	0.0	0.0	0.207	---	---	0.0	0.0
WV-30	7	5/27/87	na	15.10	---	---	0.173	1.15	0.204	---	---	0.0023	1.13
AVG.	7	na	na	14.59	---	---	0.206	1.41	0.206	---	---	0.0029	1.41

TABLE C.2. (contd)

Test & Glass	# Days	Date Test Began	Report	As Analyzed (mg/L)					Blank Corrected and Normalized (g/m^2)				
				Average Release	Proc. SD	Anal. SD	Total SD	Total % RSD	Average Release	Proc. SD	Anal. SD	Total SD	Total % RSD
MCC-3 & ARM-1	18	8/26/84	MCC-D6	12.8	---	---	0.168	1.3					
	30	8/26/84	MCC-D6	14.0	---	---	0.132	0.9					
	56	10/2/84	MCC-D6	17.1	0.000	0.385	0.393	2.3					
	122	10/19/84	MCC-D6	21.3	0.611	0.236	0.656	3.1					
	182	8/9/84	MCC-D6	21.4	1.31	0.066	1.31	6.1					
MCC-3 & ARM-1	7	5/28/87	WV/MCC-3	12.1	---	---	0.566	4.7	0.458	---	---	0.022	4.7
MCC-3M & ARM-1	7	6/10/87	WV/MCC-3	11.4	---	---	---	---	0.432	---	---	---	---
	28	6/10/87	WV/MCC-3	15.3	---	---	0.990	6.5	0.580	---	---	0.017	2.9
MCC-3 & CUA	7	5/28/87	WV/MCC-3	11.0	---	---	0.116	1.1	0.401	---	---	0.011	2.6
MCC-3M & CUA	7	6/10/87	WV/MCC-3	10.1	---	---	0.058	0.6	0.368	---	---	0.009	2.5
	28	6/10/87	WV/MCC-3	14.9	---	---	0.231	1.6	0.542	---	---	0.015	2.9

Notes: (1) All entries are estimates of short-term uncertainty in boron release from a single analysis of a single MCC-3 test at 90oC in DIW. "Short-term" with respect to the Analytic SD refers to fact that repeat analyses were usually performed within a few mintues, while with respect to the Procedural SD it refers to the fact that replicate MCC-3 tests were conducted at the same time. Where only one analysis per leachate was performed, the analyses for the replicate-test leachates were analyzed within minutes of each other.

(2) Entries of "---" indicate that it was not possible to separate the procedural and analytic sources of variation.

(3) Blank entries were not computed due to lack of time or the required data. All such entries could be computed given time and the appropriate data.

(4) The MCC-3 test calls for continuous agitation, while the modified MCC-3 test (MCC-3M) involved agitation only once a day.

(5) For the MCC-3S results on ARM-1, the "As Analyzed" results are actually based on blank corrected and volume normalized values.

TABLE C.3. Long-Term Procedural Plus Analytic, Short-Term Procedural, and Short-Term Analytic Uncertainties in Boron Concentrations from MCC-1 and MCC-3 Testing at 90°C in DIW

Test & Glass	Days	As Analyzed (mg/L)						Blank Corrected and Normalized (g/m^2)					
		Average Release	Long-Term SD	----Short-term---- Proc. SD	Anal. SD	Total SD	Total % RSD	Average Release	Long-Term SD	----Short-term---- Proc. SD	Anal. SD	Total SD	Total % RSD
MCC-1 & ARM-1	7												
	28	4.33	0.176	0.084	0.038	0.193	4.5						
	56	4.98	0.317	0.204	0.035	0.379	7.6						
	91												
MCC-3 & WV-1	7	12.37	1.340	---- 0.185 ----		1.352	10.9	0.166	0.018	---- 0.0025 -----		0.018	10.8

Notes: (1) Long-term SDs are estimates of the uncertainty in boron release due to time-related random variations in the MCC-1 test procedure and in the leachate analysis procedure. Although a test may only be performed once and the resulting leachate analyzed once, the boron release is still subject to long-term variation. The fact that tests were performed at several times on replicate specimens with repeat leachate analyses allowed the separation of the long-term procedural plus analytic, short-term procedural, and short-term analytic standard deviations. The short-term variations are interpreted as explained in Note (1) of Table 1.

(2) Results from five times were used to develop the ARM-1, 28-day MCC-1 standard deviations above. The 27-day results from 2/28/86 (see Table 1) were treated as 28-day results, since they fell within the range of the other 28-day results.

(3) Results from three times were used to develop the ARM-1, 56-day MCC-1 standard deviations above. The 55-day results from 2/28/86 (see Table 1) were treated as 56-day results, since they fell within the range of the other 56-day results.

(4) Results from four times were used to develop the WV-1, 7-day MCC-3 standard deviations above.

(5) Entries marked by "---" indicate that the short-term procedural and analytic standard deviations could not be separately estimated because only one analysis per leachate was performed.

(6) Blank entries were not computed due to lack of time or the required data. All such entries could be computed given time and the appropriate data.

TABLE C.4. Lab-to-Lab Uncertainties in Boron Concentrations from 28-Day MCC-1 Testing of NBS Glass, MCC 76-68 Glass, and UK209 Glass at 90°C in DIW

Round Robin (a)	Concentration Range (ppm)	Average Norm. Release (g/m^2)	Within-Lab SD	Within-Lab %RSD	Between-Labs SD	Between-Labs %RSD	Total SD	Total %RSD
MCC 76-68	7.6 - 19.0	36.0	3.02	8.4	11.2	31.6	11.6	32.1
MCC NBS		17.8	2.88	16.2	11.4	63.9	11.8	66.0
CEC UK 209	2.4 - 4.9	10.5	0.42	4.0	2.0	19.0	2.1	19.4

Notes: (1) The concentration range and average release information is with respect to all labs participating in the round robin.

(2) The within-lab SD and %RSD above involves only short-term variation to the extent that the replicate tests performed by a given lab were conducted and leachates analyzed at the same time. The round robin test plan did not provide for estimating the long-term within-lab variation. Thus, an unknown portion of the between-labs SD and %RSD may be attributable to long-term within-lab variation.

TABLE C.5. Short-Term Uncertainties in Boron Glass Analyses by ICP[a]

Oxide	ARW-1 (b) Mean Wt%	SD	% RSD	ATM-10 (c) Mean Wt%	SD	% RSD	CTS (d) Mean Wt%	SD	% RSD	CUA (e) Mean Wt%	SD	% RSD
Al203	6.90	0.04	0.7	6.846	0.0209	0.3	4.36	0.03	0.7	10.09	0.207	2.9
B203	11.8	0.06	0.5	9.166	0.082	0.9	10.4	0.1	1.0	11.80	0.283	2.4
BaO	0.66	0.00	0.0	0.046	0.0013	2.9	0.16	0.01	6.3	0.13	0.0021	1.6
CaO	2.28	0.01	0.4	0.604	0.035	5.8	0.57	0.03	5.3	1.02	0.028	2.8
Ce02	1.37	0.01	0.7	0.072	0.0013	1.8	0.21	0.01	4.0	0.61	0.021	3.5
Cr203	----	----	---	0.237	0.011	4.6	0.41	0.01	2.4	0.26	0.0072	2.8
Cs20	1.1	----	---	0.072	0.0015	2.1	0.007	0.002	2.3	----	----	---
Fe203	----	----	---	11.527	0.21	1.8	11.3	0.1	0.9	11.05	0.071	0.7
K20	----	----	---	3.344	0.13	3.9	3.4	0.2	5.0	2.75	0.071	2.6
La203	----	----	---	0.025	0.002	9.0	0.09	0.01	11.1	0.05	0.0029	5.9
Li20	5.08	0.06	1.2	2.891	0.028	1.0	2.97	0.05	1.7	2.31	0.035	1.5
MgO	----	----	---	1.153	0.0298	2.6	1.25	0.01	0.8	1.12	0.021	1.9
Mn02	----	----	---	1.293	0.0219	1.7	1.66	0.02	1.2	1.27	0.0071	0.6
Mo03	1.88	0.02	1.1	---	---	---	----	----	---	0.05	0.000	0.0
Na20	9.82	0.08	0.8	10.526	0.50	4.8	11.0	0.1	0.9	9.59	0.170	1.8
NiO	----	----	---	0.298	0.0135	4.6	0.05	0.01	1.5	0.33	0.022	6.6
Nd203	5.83	0.04	0.7	0.168	0.0023	1.4	----	----	---	0.15	0.0073	4.9
P205	0.57	0.01	1.8	2.340	0.259	11.0	2.51	0.01	0.4	2.20	0.142	6.4
Rh02	----	----	---	0.012	0.0018	15.0	----	----	---	----	----	---
Ru02	----	----	---	0.001	0.0108	17.7	----	----	---	----	----	---
S03	----	----	---	0.307	0.0896	29.2	----	----	---	----	----	---
Si02	46.1	0.23	0.5	45.839	2.39	5.2	44.0	0.6	1.4	40.65	0.919	2.3
SrO	0.47	0.00	0.0	0.025	0.0010	4.0	0.11	0.01	9.1	0.03	0.0030	10.1
Th02	----	----	---	3.290	0.0336	1.0	----	----	---	2.59	0.190	7.0
Ti02	3.43	0.02	0.6	0.858	0.0245	2.9	0.95	0.02	2.1	0.01	0.0071	0.9
U02	----	----	---	0.527	0.0171	3.2	----	----	---	0.49	0.022	4.5
Y203	----	----	---	0.017	0.0008	4.7	----	----	---	0.02	0.000	0.0
ZnO	1.52	0.01	0.7	---	----	---	----	----	---	----	----	---
Zr02	1.96	0.02	1.0	0.247	0.0018	0.7	2.97	0.07	2.4	0.49	0.014	2.9

(a) Results in this table are based on as-analyzed weight percent values, obtained by ICP. In a few cases the results were obtained by AA or EDXRF.

(b) Based on duplicate analyses of three samples (except only one analysis for Cs). The duplicate analyses may have been averaged before computing SD and %RSD, which would lead to an underestimate of the uncertainty in a single analysis of a single specimen.

(c) Based on duplicate analyses of six samples. The duplicate analyses may have been averaged before computing SD and %RSD, which would lead to an underestimate of the uncertainty in a single analysis of a single specimen.

(d) Based on one analysis each of three samples.

(e) Based on one analysis each of two samples.

TABLE C.5. (contd)

Oxide	SRL-131 (b) Mean Wt%	SD	% RSD	MCC 76-68 (b) Mean Wt%	SD	% RSD
Al2O3	3.65	0.19	6.2	0.73	0.01	1.4
B2O3	9.84	0.16	1.6	9.26	0.08	0.9
BaO	0.01	0.00	0.0	0.53	0.01	1.9
CaO	1.04	0.04	3.8	2.42	0.03	1.2
CeO2	0.24	0.01	4.2	0.94	0.02	2.1
Cr2O3	0.18	0.04	22.2	0.50	0.04	8.0
Cs2O	0.30	0.01	3.3	0.93	0.01	1.1
Fe2O3	14.28	0.64	4.5	9.33	0.12	1.3
K2O	0.12	----	5.9	----	----	---
La2O3	0.33	0.01	3.0	----	----	---
Li2O	3.69	0.05	1.3	----	----	---
MgO	1.24	0.02	1.6	----	----	---
MnO2	4.17	0.16	3.8	0.04	0.01	25.0
MoO3	----	----	---	1.86	0.02	1.1
Na2O	14.77	0.22	1.5	13.90	0.32	2.3
NiO	1.54	0.07	4.5	0.24	0.02	8.3
Nd2O3	0.45	0.01	2.2	1.44	0.02	1.4
P2O6	0.10	0.01	10.0	0.70	0.06	8.6
RhO2	----	----	---	----	----	---
RuO2	----	----	---	----	----	---
SO3	----	----	---	----	----	---
SiO2	38.60	0.41	1.1	41.50	0.32	0.8
SrO	0.14	0.01	7.1	0.39	0.01	2.6
ThO2	----	----	---	----	----	---
TiO2	0.75	0.01	1.3	3.02	0.02	0.7
UO2	1.62	0.04	2.5	----	----	---
Y2O3	----	----	---	----	----	---
ZnO	----	----	---	4.57	0.03	0.7
ZrO2	0.31	0.01	3.2	1.76	0.07	4.0

(a) Results in this table are based on as-analyzed weight percent values, obtained by ICP. In a few cases the results were obtained by AA or EDXRF.

(b) Based on a single analysis of each of three samples.

TABLE C.6. Combined Short- Plus Long-Term[a] Within Lab
Uncertainties in Normalized[b] Glass Analyses
for Glasses WV-1, WV-2, and WV-15 to WV-30

Oxide	WVCM-50/ WV-30 Wt%	Largest SD (c)	Pooled SD	Largest %RSD (c)	Pooled %RSD (d)
Al2O3	10.265	0.438	0.196	3.6	1.8
B2O3	11.820	0.233	0.126	1.7	1.1
BaO	0.200	0.007	0.005	9.7	5.4
CaO	0.825	0.177	0.049	21.2	6.7
CeO2	0.670	0.085	0.043	39.9	22.7
Cr2O3	0.145	0.035	0.012	20.2	8.0
Cs2O	0.045	0.014	0.009	28.3	18.1
Fe2O3	11.470	0.375	0.159	3.1	1.4
K2O	1.810	0.643	0.395	59.8	24.3
Li2O	2.125	0.205	0.066	12.4	3.7
MgO	0.945	0.106	0.053	13.8	6.3
MnO2	1.205	0.071	0.025	2.9	1.2
Na2O	9.640	0.757	0.422	7.9	4.4
NiO	0.340	0.240	0.055	68.7	16.1
P2O5	2.465	0.318	0.160	20.4	7.8
SiO2	40.040	0.566	0.282	1.5	0.7
ThO2	3.125	0.848	0.239	22.6	7.4
TiO2	0.820	0.049	0.024	7.1	2.6
UO2	0.620	0.134	0.047	22.3	8.7
ZrO2	0.615	0.198	0.088	26.6	14.9

(a) WV-1 (WVCM-47) was analyzed twice each on 1/2/87 and 6/3/87, and once
each on 6/11/87 and 7/7/87. WV-2 was analyzed twice on 1/2/87.
Glasses WV-15 to WV-22 were analyzed once each on 6/3/87 and 6/11/87.
Glasses WV-23 to WV-30 were analyzed once each on 6/3/87 and 7/7/87.
While it is possible to separately estimate short-term (i.e., within
day) uncertainty for WV-1 and WV-2, it is not possible to do so for
the other glasses. For simplicity, all analyses for each glass were
treated as if they incorporate both short- and long-term uncertainty.
This results in a combined estimate of short- plus long-term uncertainty
for each oxide component.

(b) Results in this table are based on normalized (to 100%) weight percent
values obtained from the as-analyzed weight percents. The results are
quite similar for the as-analyzed (unnormalized) data.

(c) The largest values of SD and %RSD indicate the range of values for each
quantity over the 18 glasses considered. The %RSD values are relative to
the mean composition of each glass, not relative to the WVCM-50 (WV-30)
composition given above. The WVCM-50 (WV-30) composition is listed as
representative of the region of compositions covered by these glasses.

(d) The pooled SD and %RSD values are "combined" estimates over the
individual SDs and %RSDs for each glass.

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TABLE C.7. Lab-to-Lab Uncertainties in ARM-1 Glass Analyses at Three PNL Labs

Oxide	Mean Wt%	SD Labs	%RSD Labs	SD Days	%RSD Days	Total SD	Total %RSD
Al2O3	5.B9	0.128	2.2	0.102	1.7	0.164	2.8
B2O3	11.85	0.459	3.9	0.225	1.9	0.511	4.3
BaO	0.66	0.013	2.0	0.009	1.4	0.016	2.4
CaO	2.22	0.050	2.2	0.036	1.6	0.062	2.8
CeO2	1.27	0.0	0.0	0.121	9.5	0.121	9.5
Li2O	4.95	0.237	4.B	0.074	1.5	0.24B	5.0
MoO3	1.83	0.0	0.0	0.036	2.0	0.036	2.0
Na2O	9.55	0.220	2.3	0.377	3.9	0.436	4.6
Nd2O3	5.80	0.064	1.1	0.074	1.3	0.098	1.7
P2O5	0.55	0.033	6.1	0.079	14.4	0.086	15.6
SiO2	44.52	1.41	3.2	0.800	1.8	1.62	3.6
SrO	0.46	0.006	1.4	0.007	1.5	0.009	2.0
TiO2	3.36	0.095	2.8	0.054	1.6	0.109	3.3
ZnO	1.48	0.012	0.8	0.027	1.8	0.030	2.0
ZrO2	1.99	0.093	4.7	0.048	2.4	0.105	5.3

Note: Results in this table are based on as-analyzed (not normalized to 100) weight percent values. Each lab analyzed ARM-1 glass several times a day on four or five days over a two week period during April 1986. The results were not previously published, and it is unclear whether the "Days SD" includes within day uncertainty with respect to single determinations, or with respect to the average for the day. Thus, although it is clear that the Total SD and Total %RSD contain lab-to-lab and long-term (between days) uncertainty, it is not clear whether the short-term (within day) uncertainty is fully represented.

Where it was not possible to separately estimate s_1 and s_4, the "Total SD" column contains combined estimates of $(s_1^2 + s_4^2)^{0.5}$.

Table C.3 contains estimates of long-term within-lab standard deviations for the leach testing and leachate analysis processes. It was not possible to separately estimate the long-term standard deviations for these two processes, so a combined estimate [i.e., $(s_2^2 + s_5^2)^{0.5}$] is given in the "Long-Term SD" column. The "Short-Term" column contains pooled estimates of s_1 and s_4 (over the multiple times a given glass was tested).

Table C.4 contains results on lab-to-lab standard deviations from 28-day MCC-1 tests at 90°C in DIW (or the equivalent thereof in the case of the CEC

results). The results are for normalized releases, and do not separate out the leach testing, leachate analysis, and glass analysis standard deviations. Because each lab only performed the leach testing (including specimen and leachant preparation) and leachate analysis, the results in Table C.4 do not include an estimate of glass analysis uncertainty. Roughly speaking then, the "Between-Labs" columns in Table C.4 provide estimates of the contributions of s_3 and s_5. However, it is not clear to what extent this lab-to-lab variation (which is very large) is actually composed of long-term within-lab variation. The "Within-Lab" columns only deal with short-term within-lab variation.

Table C.5 contains short-term glass analysis standard deviations (i.e., s_7) by oxide for six glasses. Although some of the glasses contain similar weight percents of certain oxides, the standard deviations vary quite a bit (e.g., the SiO_2 values range from approximately 39 to 46%, but have relative standard deviations ranging from 0.5 to 5.2%).

Table C.6 contains combined estimates of short- and long-term glass analysis standard deviations [i.e., $(s_7^2 + s_8^2)^{0.5}$]. Seventeen different glasses were analyzed twice each at different times, and another glass was analyzed six times. The maximum standard deviation (for each oxide component) over the 18 glasses is listed (the minimum was nearly always zero). The results were also "pooled" over the 18 glasses to give an idea of the "average" standard deviation for each oxide.

Table C.7 contains estimates of lab-to-lab glass analysis standard deviations (i.e., s_9) by oxide. The estimates are based on analyses of ARM-1 glass by three different PNL labs. Because the three labs used similar procedures and performed the analyses in the same time frame, the variation observed may be less than what would have been observed if the labs were not "related" and the analyses were spread further apart in time.

C.4 EVALUATION OF LITERATURE REVIEW RESULTS

Table C.8 contains a summary of the standard deviations contained in Tables C.1 through C.7, presented as %RSDs to simplify the presentation. The results vary quite a bit from study to study and glass to glass, so ranges

TABLE C.8. Summary of Relative Standard Deviations from Tables C.1-C.7 and Estimation of the Uncertainty in a Single Normalized Boron Release Value

Process & Source of Uncertainty	% Relative Standard Deviation	
	MCC-1, 28-day	MCC-3, 7-day
Short-Term Within-Lab Leach Testing and Leachate Analysis	1 - 16% "Avg"= 2-3%	0.7 - 4.7% "Avg"= 1.5-3%
Long-Term Within-Lab Leach Testing and Leachate Analysis	4 - 6% (a)	11% (a)
Lab-to-Lab Leach Testing and Leachate Analysis	19 - 64% (a),(c)	(b)
Short-Term Within-Lab Glass Analysis--B2O3	---------- 0.5 - 2.5% -----------	
Long-Term Within-Lab Glass Analysis--B2O3	---------- 0.5 - 1.5% (a) -------	
Lab-to-Lab Glass Analysis--B2O3	-------------- 5% (a),(c) -------	
Total Standard Deviation of Normalized Boron Release	20 - 66%	22 - 65%

(a) These values are fairly uncertain as they are based on limited data.

(b) No studies with multiple labs conducting MCC-3 tests have been performed. For purposes of computing the normalized boron release total standard deviation, the range of 19 - 64% from the MCC-1 tests was used.

(c) The lab-to-lab variation may also include long-term within-lab variation. It was not possible to separately estimate these two sources of variation.

have been presented in Table C.8. It is clear that the total uncertainty (including all short- and long-term within-lab and lab-to-lab variations) in normalized boron release is probably at least 20% for both the 28-day MCC-1 and 7-day MCC-3 tests. The total uncertainty may be as high as 60 to 70%.

Analyzing glasses more than once, performing leach tests on a glass more than once, and performing more than one analysis per leachate--and then averaging the normalized releases--can be done to reduce the uncertainty. However, these repeated activities would have to be performed at different times at different labs to reduce the long-term within-lab and lab-to-lab contributions to the total uncertainty. The usual practice of repeating leach tests and leachate analyses at the same time at the same lab (and averaging the results) only reduces short-term within-lab uncertainties, which appear to be a small contributor to the total uncertainty. Lab-to-lab and long-term within-lab variations are the main contributors to the total uncertainty.
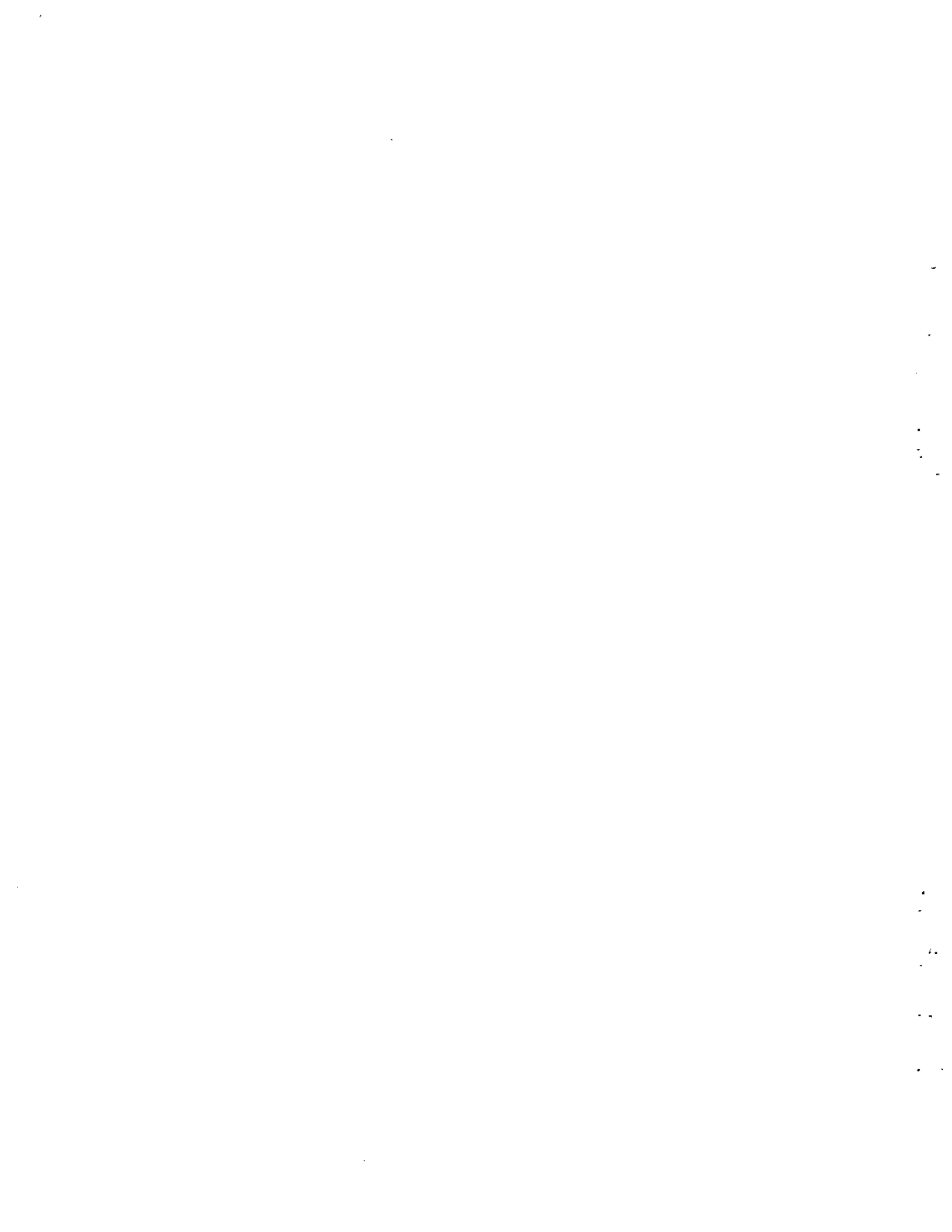
APPENDIX D

ESTIMATES OF SHORT- AND LONG-TERM WITHIN-LAB UNCERTAINTIES BASED ON REPEAT GLASS ANALYSES, REPEAT LEACHATE ANALYSES, AND REPEAT LEACH TESTS

APPENDIX D

ESTIMATES OF SHORT- AND LONG-TERM WITHIN-LAB UNCERTAINTIES BASED ON REPEAT GLASS ANALYSES, REPEAT LEACHATE ANALYSES, AND REPEAT LEACH TESTS

This appendix contains estimates of short- and long-term within-lab percent relative standard deviations (%RSD) associated with the glass analysis, leachate analysis, and leach testing processes. These results were obtained from FY 1988 work in which certain glass analyses, leachate analyses, and leach tests were repeated over time.

Tables D.1 through D.3 contain %RSDs from repeated compositional analyses of three glasses: Corning-A, ARM-1, and NBS-SRM-1411. These results are not of direct interest, but provide supporting information for the %RSDs of the repeat analyses of three FY 1988 composition variation glasses, DG-WV33, DG-WV34, and DG-WV44. The %RSDs for these three glasses are given in Table D.4. Details on the number of repeat analyses and the interpretation of the %RSDs reported are given as footnotes in Tables D.1 through D.4.

Table D.5 contains the %RSDs from repeat analyses of leachates from 7-day MCC-3 and 28-day MCC-1 tests of glasses DG-WV33, DG-WV34, and DG-WV44. Note that aliquots of the same leachate for each glass were analyzed repeatedly, so that only leachate analysis uncertainty is estimated.

On the other hand, Table D.6 contains %RSDs from repeat 7-day MCC-3 and 28-day MCC-1 leach tests. Hence, these %RSDs include variations in the leach testing procedures as well as in the leachate analysis procedure. It is interesting to observe that the %RSDs in Table D.6 are of approximately the same magnitude as those in Table D.5. This indicates that the variation in results due to the leach testing process is very small compared to the variation in leachate analysis results.

Short-Term, Long-Term, and Total Within-Lab %RSD in As-Analyzed (Unnormalized) ICP Analyses of Corning-A Glass

Oxide Component	Mean[a] Wt%	Short-Term Within-Lab %RSD[b]	Long-Term Within-Lab %RSD[c]	Total Within-Lab %RSD[d]	Total Within-Lab %RSE[e]
Al_2O_3	10.53	0.00	1.10	1.10	0.64
B_2O_3	8.77	0.14	1.33	1.34	0.77
CaO	0.48	0.84	14.31	14.33	8.27
Fe_2O_3	12.75	0.32	2.17	2.20	1.26
K_2O	1.08	19.02	35.81	40.55	22.08
Li_2O	2.01	0.61	2.74	2.80	1.60
MgO	0.82	0.50	5.64	5.66	3.26
MnO_2	1.30	0.31	2.10	2.13	1.22
Na_2O	7.79	1.64	4.90	5.17	2.91
P_2O_5	2.35	3.88	4.91	6.26	3.25
SiO_2	45.08	0.49	1.03	1.14	0.63
TiO_2	0.81	1.13	0.50	1.24	0.54
ZrO_2	2.20	0.87	6.99	7.05	4.05

(a) The glass was analyzed for composition two times on each of three dates (5/24/88, 7/15/88, and 8/15/88) for a total of six analyses. The mean weight percent oxides are averages of the six values obtained for each oxide.

(b) The short-term within-lab percent relative standard deviation quantifies the variation in analyses performed on the same day. The standard deviation of an individual analysis is reported, not the standard deviation of the mean weight percent oxide. Also, note that the short-term %RSDs are based on only three degrees of freedom (i.e., duplicate analyses were performed on only three days), and hence are <u>uncertain</u>.

(c) The long-term within-lab percent relative standard deviation quantifies the variation in analyses performed over the space of a few months. The standard deviation of an individual analysis is reported, not the standard deviation of the mean weight percent oxide. Also, note that the long-term %RSDs are based on only two degrees of freedom (i.e., analyses were only made on three different dates), and hence are <u>quite uncertain</u>.

(d) The total within-lab percent relative standard deviation includes both short- and long-term within-lab variation in glass analyses, and quantifies the total within-lab uncertainty in a single ICP analysis.

(e) The total within-lab percent relative standard error includes both short- and long-term within-lab variation in glass analyses, and quantifies the total within-lab uncertainty in the estimated Corning-A composition (obtained as an average of six analyses).

TABLE D.2. Short-Term, Long-Term, and Total Within-Lab %RSD in As-Analyzed (Unnormalized) ICP Analyses of ARM-1 Glass

Oxide Component	Mean[a] Wt%	Short-Term[b] Within-Lab %RSD	Long-Term[c] Within-Lab %RSD	Total[d] Within-Lab %RSD
Al_2O_3	5.68	0.28	3.18	3.19
B_2O_3	11.68	1.35	1.97	2.39
BaO	0.64	1.58	3.42	3.77
CaO	2.35	0.48	5.63	5.65
Ce_2O	1.44	1.10	2.95	3.15
Cs_2O	1.11	3.23	6.97	7.69
Li_2O	4.70	0.75	7.55	7.59
MoO_3	1.91	0.78	1.66	1.83
Na_2O	9.55	1.48	4.26	4.51
Nd_2O_3	5.39	1.60	4.34	4.62
P_2O_5	0.56	8.51	41.76	42.62
SiO_2	44.98	1.75	3.01	3.48
SrO	0.46	0.00	3.96	3.96
TiO_2	3.29	0.48	2.05	2.11
ZnO	1.52	1.04	5.95	6.04
ZrO_2	1.91	2.07	8.18	8.44

(a) The glass was analyzed for composition two times each on 4/1/88 and 5/13/88, and once each on 5/24/88, 6/8/88, 7/15/88, and 8/15/88, for a total of eight analyses. The mean weight percent oxides were obtained by computing the mean for each day, and then averaging the values from the six days.

(b) The short-term within-lab percent relative standard deviation quantifies the variation in analyses performed on the same day. The standard deviation of an individual analysis is reported, not the standard deviation of the mean weight percent oxide. Also, note that the short-term %RSDs are based on only two degrees of freedom (i.e., analyses were repeated on only two days), and hence are quite uncertain.

(c) The long-term within-lab percent relative standard deviation quantifies the variation in analyses performed over the space of a few months. The standard deviation of an individual analysis is reported, not the standard deviation of the mean weight percent oxide. Also, note that the long-term %RSDs are based on only 5 degrees of freedom (i.e., analyses were repeated on only 6 different dates), and hence are uncertain.

(d) The total within-lab percent relative standard deviation includes both the short- and long-term within-lab variation in glass analyses.

TABLE D.3. Short-Term, Long-Term, and Total Within-Lab %RSD in As-Analyzed (Unnormalized) ICP Analyses of NBS-SRM-1411 Glass

Oxide Component	Mean[a] Wt%	Short-Term[b] Within-Lab %RSD	Long-Term[c] Within-Lab %RSD	Total[d] Within-Lab %RSD
Al_2O_3	5.63	0.48	6.28	6.30
B_2O_3	10.65	0.94	1.51	1.78
BaO	4.68	0.11	3.81	3.81
CaO	2.18	1.17	4.79	4.93
Fe_2O_3	0.11	22.73	14.32	26.86
K_2O	3.90	6.54	19.91	20.96
MgO	0.33	1.52	11.41	11.51
Na_2O	9.55	1.11	3.16	3.35
SiO_2	55.64	0.58	3.19	3.24
TiO_2	0.45	35.14	34.18	49.02
ZnO	3.84	0.39	1.88	1.92

(a) The glass was analyzed for composition two times each on 4/1/88 and 5/13/88, and once each on 5/24/88, 6/8/88, 7/15/88, and 8/15/88, for a total of eight analyses. The mean weight percent oxides were obtained by computing the mean for each day, and then averaging the values from the six days.

(b) The short-term within-lab percent relative standard deviation quantifies the variation in analyses performed on the same day. The standard deviation of an individual analysis is reported, not the standard deviation of the mean weight percent oxide. Also, note that the short-term %RSDs are based on only two degrees of freedom (i.e., duplicate analyses were made on only two dates), and hence are very uncertain.

(c) The long-term within-lab percent relative standard deviation quantifies the variation in analyses performed over the space of a few months. The standard deviation of an individual analysis is reported, not the standard deviation of the mean weight percent oxide. Also, note that the long-term %RSDs are based on only five degrees of freedom (i.e., analyses were repeated on six different dates), and hence are uncertain.

(d) The total within-lab percent relative standard deviation includes both the short- and long-term within-lab variation in glass analyses.

TABLE D.4. Short-Term, Long-Term, and Total Within-Lab %RSD in As-Analyzed (Unnormalized) ICP Analyses of West Valley Glasses DG-WV33, DG-WV34, and DG-WV44

Oxide Component	Mean[a] Wt%			Short-Term[b] Within-Lab %RSD			Long-Term[c] Within-Lab %RSD			Total[d] Within-Lab %RSD		
	DG-WV33	DG-WV34	DG-WV44	DG-WV33	DG-WV34	DG-WV44	DG-WV33	DG-WV34	DG-WV44	DG-WV33	DG-WV34	DG-WV44
Al_2O_3	8.22	5.34	8.30	2.23	0.47	0.79	2.32	3.19	3.35	3.22	3.22	3.44
B_2O_3	9.09[e]	11.14	11.30[e]	0.67	0.00	1.40	2.45	2.42	2.42	2.54	2.42	2.80
CaO	0.54[e]	0.21	0.20[e]	7.86	7.21	8.11	7.10	13.65	20.99	10.59	15.44	22.50
Fe_2O_3	11.66	9.82	15.46	0.00	1.77	1.02	1.29	0.00	0.97	1.29	1.77	1.41
K_2O	4.82	4.84	4.76	1.04	4.38	13.70	15.81	15.29	12.38	15.84	15.90	18.46
Li_2O	2.63	2.82	2.80	7.97	1.67	1.82	0.00	4.40	5.47	7.97	4.71	5.77
MgO	1.25	0.44	0.54	3.12	4.64	1.87	0.00	5.66	3.16	3.12	7.32	3.67
MnO_2	1.30	2.00	0.13	0.54	1.95	3.79	2.69	0.00	0.00	2.75	1.95	3.79
Na_2O	9.78	10.22	10.33	4.19	4.32	2.23	2.84	1.46	4.85	5.06	4.56	5.33
P_2O_5	2.54	2.02	0.66	0.00	0.00	10.71	2.41	6.06	0.00	2.41	6.06	10.71
SiO_2	40.40	38.54	37.16	1.67	1.20	0.00	1.08	1.99	4.13	1.99	2.32	4.13
ThO_2	3.34	1.83	3.56	4.55	4.40	0.20	3.94	0.00	6.10	6.01	4.40	6.10
TiO_2	0.86	2.78	0.38[e]	1.16	1.21	1.85	1.74	1.07	1.85	2.09	1.61	2.62
ZrO_2	0.51	1.89	1.86	7.78	5.64	5.44	0.00	3.45	7.06	7.78	6.61	8.91
Alk Earths	1.87[e]	0.68	0.74[e]	4.54	4.74	3.42	0.00	4.39	7.20	4.54	6.46	7.97
Alkalis	17.24	17.88	17.89	3.89	2.18	2.21	3.97	0.57	4.51	5.55	2.25	5.02

(a) The three glasses were analyzed for composition two times each on 4/1/88 and 5/13/88, and once on 6/8/88, for a total of five analyses. The mean weight percent oxides are averages of the five values obtained for each oxide.

(b) The short-term within-lab percent relative standard deviation quantifies the variation in analyses performed on the same day. The standard deviation of an individual analysis is reported, not the standard deviation of the mean weight percent oxide. Also, note that the short-term %RSDs are based on only two degrees of freedom (i.e., duplicate analyses were performed on only two dates), and hence are <u>quite uncertain</u>.

(c) The long-term within-lab percent relative standard deviation quantifies the variation in analyses performed over the space of a few months. The standard deviation of an individual analysis is reported, not the standard deviation of the mean weight percent oxide. Also, note that the long-term %RSDs are based on only two degrees of freedom (i.e., analyses were repeated on only three different dates), and hence are <u>quite uncertain</u>.

(d) The total within-lab % RSD includes both the short- and long-term within-lab variation in glass analyses.

(e) An outlier was deleted from the data prior to obtaining the mean and standard deviations.

TABLE D.5. Short-Term, Long-Term, and Total Within-lab %RSD of Elemental Boron Releases from Repeated Leachate Analyses of Leachates from 7-Day MCC-3 and 28-Day MCC-1 Leach Tests of West Valley Glasses DG-WV33, DG-WV34, and DG-WV44

I. REPEAT LEACHATE ANALYSES[e]

Leach Test	Mean Boron Release[a] ppm and (normalized)			Short-Term[b] Within-Lab %RSD			Long-Term[c] Within-Lab %RSD			Total[d] Within-Lab %RSD		
	DG-WV33	DG-WV34	DG-WV44	DG-WV33	DG-WV34	DG-WV44	DG-WV33	DG-WV34	DG-WV44	DG-WV33	DG-WV34	DG-WV44
MCC-3, 7-day	14.51 (0.251)	24.15 (0.351)	21.30 (0.294)	1.46	1.17	0.66	17.03	3.04	7.99	17.10	3.26	8.02
MCC-1, 28-day	4.60 (15.94)	6.83 (19.83)	6.84 (18.90)	0.46	0.21	0.31	6.59	6.69	7.75	6.61	6.70	7.75

(a) The three leachates from each test were analyzed for composition two times each on 5/16/88, and once each on three other dates (approximately 5/2/88, 5/5/88, and 7/25/88 for the MCC-1 leachates and 3/19/88, 5/5/88, and 7/25/88 for the MCC-3 leachates), for a total of five analyses per leachate. The mean boron releases were obtained by averaging the two 5/16/88 values and then averaging the resulting value with the single values (for each leachate) from the other three days.

(b) The short-term within-lab percent relative standard deviation quantifies the variation in leachate analyses performed on the same day. The standard deviation of an individual analysis is reported, not the standard deviation of the mean boron release. Note that the %RSDs apply to boron release in both ppm and normalized units. Also, note that the short-term %RSDs are based on only one degree of freedom (i.e., computed from two values), and hence are very uncertain.

(c) The long-term within-lab percent relative standard deviation quantifies the variation in leachate analyses performed over the space of a few months. The standard deviation of an individual analysis is reported, not the standard deviation of the mean boron release. Note that the %RSDs apply to boron release in both ppm and normalized units. Also, note that the long-term %RSDs are based on only three degrees of freedom (data from four times were used), and hence are uncertain.

(d) The total within-lab percent relative standard deviation includes both the short- and long-term within-lab variation in leachate analyses.

(e) The %RSDs in this table are based on repeated leachate analyses of leachate from a single leach test for each of the glass and leach test combinations. Hence, the %RSDs contain variation only from the leachate analysis process, and not from the leach testing process.

TABLE D.6. Short-Term, Long-Term, and Total Within-Lab %RSD of Elemental Boron Releases from Repeated 7-Day MCC-3 and 28-Day MCC-1 Leach Tests of West Valley Glasses DG-WV33, DG-WV34, and DG-WV44

II. REPEAT LEACH TESTS

Leach Test	Mean Boron Release[a] ppm and (normalized)			Short-Term[b] Within-Lab %RSD			Long-Term[c] Within-Lab %RSD			Total[d] Within-Lab %RSD		
	DG-WV33	DG-WV34	DG-WV44	DG-WV33	DG-WV34	DG-WV44	DG-WV33	DG-WV34	DG-WV44	DG-WV33	DG-WV34	DG-WV44
MCC-3, 7-day	12.72 (0.220)	23.53 (0.342)	21.52 (0.297)	0.72	1.59	1.79	6.02	6.16	7.28	6.06	6.37	7.50
MCC-1, 28-day	4.64 (16.07)	6.92 (20.11)	6.71 (18.56)	3.68	2.98	3.05	4.02	4.63	6.66	5.45	5.51	7.33

(a) The two leach tests (for each of the three glasses) were performed starting at three different times. At each of the three times, the tests were run in duplicate. Hence, there were a total of six runs for each glass and leach test combination. The three different times each test was performed were approximately equally spaced over a three month period. The mean boron releases were obtained by averaging the six boron release values for each glass and leach test combination.

(b) The short-term within-lab percent relative standard deviation quantifies the variation in leach tests performed at the same time and in leachate analyses performed on the same day. The standard deviation of an individual analysis is reported, not the standard deviation of the mean boron release. Note that the %RSDs apply to boron release in both ppm and normalized units. Also, note that the short-term %RSDs are based on only three degrees of freedom (i.e., the tests were performed in duplicate three times), and hence are quite uncertain.

(c) The long-term within-lab percent relative standard deviation quantifies the variation in leach tests and leachate analyses performed over the space of a few months. The standard deviation of an individual boron release is reported, not the standard deviation of the mean boron release. Note that the %RSDs apply to boron release in both ppm and normalized units. Also, note that the long-term %RSDs are based on only two degrees of freedom (i.e., data from three times were used), and hence are quite uncertain.

(d) The total within-lab percent relative standard deviation includes both the short- and long-term within-lab variation in the leach testing and leachate analysis processes.

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Albuquerque, NM 87185

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Joint Integration Office
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4308 Carlisle N.E.
Suite 101
Albuquerque, NM 87107

E. Maestas
DOE West Valley Project
P.O. Box 191
West Valley, NY 14171

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