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M-AREA MIXED WASTE GLASSES: II. DURABILITY AND VISCOSITY TESTING OF HIGH ALUMINUM AND URANIUM CONTAINING BOROSILICATE WASTE GLASSES

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November 2018

SRNL-STI-2011-00702 Revision 0

*Retired

SRNL.DOE.GOV

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Printed in the United States of America

Prepared for
U.S. Department of Energy

SRNL-STI-2011-00702
Revision 0

Keywords: mixed waste, high alumina waste, high uranium wastes, treatability study, durability testing, TCLP, durability modeling

Retention:

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Prepared for the U.S. Department of Energy under contract number DE-AC09-08SR22470.

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EXECUTIVE SUMMARY

Radioactive waste sludges that were high in Al_2O_3 (14.17 to 29.02 wt%) and U_3O_8 (2.93 to 5.66 wt%) while being simultaneously low in Fe_2O_3 (1.26 to 2.01 wt%) were vitrified into borosilicate glass in the Savannah River Site's (SRS) M-Area. The overall Na_2O concentrations of borosilicate and soda-lime-silica (SLS) glasses studied at the Savannah River National Laboratory (then the Savannah River Technology Center) prior to startup of the M-Area melter ranged from 6.80 to 27.09 wt%, while the B_2O_3 concentrations ranged from 0.04 to 32.62 wt%. These glass formulations and measured durability's may, therefore, be useful for formulation and testing of high Al_2O_3 and U_3O_8 sludges to be vitrified in the Defense Waste Processing Facility (DWPF) or the Hanford Tank Waste Treatment and Immobilization Plant (WTP).

Initial glass formulations for the high Al_2O_3 and U_3O_8 M-Area waste sludges were proposed by Savannah River National Laboratory (SRNL) in the 1990-1994 timeframe. The M-Area wastes were both radioactive and Resource Conservation and Recovery Act (RCRA) hazardous "listed" mixed wastes. The wastes were F006 listed as they were nickel plating line wastes. The initial SRNL glass formulations were used as the basis for privatization of a vitrification Vendor Treatment Facility (VTF). Once the waste was vitrified, it was delisted and buried on the SRS.

Extensive durability testing was performed on forty-three high Al_2O_3 and U_3O_8 glasses made in crucibles with the actual M-Area waste during a treatability study at SRNL. Thirty-three glasses were borosilicate glasses and ten glasses were SLS glasses. The durability testing of the crucible glasses included American Society for Testing and Materials (ASTM) C1285 (Product Consistency Testing) at 90°C in deionized water for 7 days duration in deionized water and longer-term testing at 25°C in E-Area groundwater since the actual M-Area waste glass was eventually buried in the E-Area burial ground. Analysis of the homogeneity of the laboratory glasses was assessed by X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM). Measurement of selected glass viscosities and densities are also reported.

Examination of the Al_2O_3 solubility limit in the M-Area glasses was used to define new compositional regions of technological importance for DWPF and WTP. The data indicates that the P_2O_5 limit of 2.25 wt% (3 wt% PO_4) set for DWPF glass in 1987 may not apply for high alumina glasses, especially those with no Li_2O or minimal Li_2O in the frit. This is based on the data presented in this study for homogeneous and durable borosilicate glasses (SLS glasses were excluded) and the following:

- the DWPF P_2O_5 limit was set based on a simulated Stage 1 waste glass at 28 wt% waste loading: the glass contained only 4.01 wt% Al_2O_3
- the DWPF P_2O_5 limit was set using frit 165 and a 72 wt% frit loading: the glass contained 5.04 wt% Li_2O and 10.82 wt% Na_2O
- the simulated glass contained no U_3O_8 like the glasses in this study (range of U_3O_8 was 2.93-5.25 wt% in this study).
- the 3 wt% PO_4 limit agreed with data in literature which cited solubility limits in silicate and borosilicate glasses between 3-4 wt% PO_4.

Therefore, combinations of low Li_2O and P_2O_5 appear to allow high Al_2O_3 glass loadings up to 25-26 wt% without compromising glass durability. This was confirmed for two glasses that were made in a 2007 DWPF study that achieved 26.6 wt% Al_2O_3 without compromising glass durability. A potential means of accomplishing this goal would be to add a source of phosphate to the waste or to the frit/glass forming chemicals. The DWPF design basis sludges were projected to only contain ~0.22 (Purex High Activity Waste, HAW), 0.16 (Average Waste), and 0.13 (HM HAW) wt% PO_4 which at 28 wt% waste loading in glass is projected to be only 0.04-0.06 wt% PO_4 in glass. In reality, the PO_4 concentrations in the glasses made from Sludge Batch (SB) SB1b, SB2, SB3, SB4, SB5, SB6, and SB7a have been 0.47, 0.36, 0.22, 0.19, 0.16, 0.15, <0.13, and <0.29 wt%, respectively. Therefore, small concentrations of P_2O_5 up to 1-2 wt% as an additive should be investigated as a mechanism to increase the Al_2O_3 loadings of HM sludges and allow the amount of Al-dissolution to be optimized. This data could have applicability to Hanford's WTP as well.

Glass durability modeling was performed using the 90°C ASTM C1285 data and average dissolution activation energy of 75 kJ/mole from the literature was used to extrapolate to 25°C conditions to complete a Performance Assessment (PA) for burial in the E-Area trenches on the SRS site once the waste was delisted. This data is reported elsewhere but discussed in the current study and compared to the actual testing at 25°C that was completed in SRS E-Area ground water to confirm the PA extrapolations from 90°C to 25°C. The PA data was reassessed in this study to provide information about glass formulations which can minimize uranium leaching from high alumina containing glasses.

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AA	Atomic Absorption
ANL	Argonne National Laboratory
APS	Amorphous Phase Separation
ASME	American Society of Mechanical Engineers
ASTM	American Society for Testing and Materials
CIF	Consolidated Incinerator Facility
CPS	Crystalline Phase Separation
CTF	Chemical Transfer Facility
DETF	Dilute Effluent Treatment Facility
DOE	Department of Energy
DWPF	Defense Waste Processing Facility
EA	Environmental Assessment
EPA	Environmental Protection Agency
ETF	Effluent Test Facility
GEL	General Engineering Laboratory
HAW	High Activity Waste
HSi	High Silica
HLW	High Level Waste
IC	Ion Chromatography
ICP-ES	Inductively Coupled Plasma – Emission Spectroscopy
ICP-MS	Inductively Coupled Plasma – Mass Spectroscopy
ISE	Ion Selective Electrode
IT/SF	Interim Treatment/Storage Facility
KPA	Kinetic Phosphorescence Analyzer
LETF	Liquid Effluent Treatment Facility
LSi	Low Silica
MEP	Multiple Extraction Procedure
N	Nominal
NPDES	National Pollution Discharge Elimination System
OCRWM	Office of Civilian Radioactive Waste Management
PA	Performance Assessment
PCT	Product Consistency Test
PPC	Professional Planning Commission
PNNL	Pacific Northwest National Laboratory
QA	Quality Assurance
QARD	Quality Assurance Requirements Document
RCRA	Resource Conservation and Recovery Act
RFP	Request for Proposal
SA	Surface Area
SB	Sludge Batch
SEM	Scanning Electron Microscopy
SCDHEC	South Carolina Department of Health and Environmental Control
SLLS	Soda Lime Lithia Silica
SLS	Soda Lime Silica
spg	Specific gravity
SRS	Savannah River Site
SRAT	Sludge Receipt and Adjustment Tank

SRNL	Savannah River National Laboratory
SRTC	Savannah River Technology Center
TCLP	Toxicity Characteristic Leaching Procedure
TTT	Time-Temperature-Transformation
VFT	Vogel-Fulcher-Tammann equation
VTF	Vendor Treatment Facility
WCP	Waste Compliance Plan
WSRC	Washington Savannah River Company
WL	Waste Loading
WTP	Hanford Tank Waste Treatment and Immobilization Plant
XRD	X-Ray Diffraction

1.0 INTRODUCTION

The initial concept of solidification of M-Area's high Al_2O_3 (14.17 to 29.02 wt.%) and high U_3O_8 (2.93 to 5.66 wt.%) containing mixed (hazardous and radioactive) waste into glass began in 1987 when the sludge and supernates were first analyzed and documented at the SRNL which was then the Savannah River Technology Center (SRTC). [1,2] In 1989, the Professional Planning Committee (PPC) formally recommended that high nitrate containing (low-level mixed) wastes, such as those existing in M-Area, be considered for vitrification. [3] The investigation of vitrification of low-level high nitrate containing wastes was considered timely because of the potential for large waste volume reduction compared to alternative solidification into cement. [2]

The M-Area operations at the SRS in Aiken, South Carolina, produced reactor components for nuclear weapons materials for the U.S. Department of Energy (DOE). The resulting waste was stored in nine tanks. The total volume in storage was initially ~1,200,000 gallons of which ~300,000 gallons were gelatinous hydroxide sludges and the other 900,000 a supernate. The supernate in the tanks was treated in a wastewater treatment facility and the resulting effluent released to a National Pollution Discharge Elimination System (NPDES) permitted outfall stream on the SRS. [4] Removing the uranium from the supernate created ~275,000 gallons of spent filter aids rich in SiO_2. After supernate treatment, approximately 425,000 gallons of waste sludge comingled with leftover supernate remained. The sludge/supernate was enriched in aluminum, sodium, uranium, and nitrate. The type of filter aid used in the wastewater treatment plant varied over the years, e.g. diatomaceous earth, perlite, and/or perflo, but all the filter aids were SiO_2 enriched and were of high surface area, e.g. $>50m^2/g$.

Vitrification into glass was chosen as the preferred stabilization option for the remaining sludge and contaminated filter aid because it reduced the volume of sludge/filter aid by ~85%. Moreover, when compared to alternative stabilization technologies (e.g. cement) the final disposal volume could be reduced by 96% using vitrification where the alternative would increase volume. The large volume reductions allowed for large associated savings in disposal and/or long-term storage costs once the vitrified waste form was delisted. [5,6,7]

Since the M-Area waste contained high concentrations of Al_2O_3 and U_3O_8, glass formulations that were high in B_2O_3 were used to flux the high Al_2O_3 content of the waste. The durability performance of these glasses during ASTM C1285 testing (Product Consistency Test or PCT, 8) is of interest to High Level Waste (HLW) glass formulations for high Al_2O_3 containing tank wastes, e.g. SRS HM wastes which, when too high in Al and other sludge is not available for blending, are aluminum dissolved to remove a fraction of the alumina through caustic dissolution. The M-Area glass formulations may help determine the limits to which HM wastes need to be aluminum dissolved. The high Al_2O_3 waste loadings should also be of interest to Hanford WTP vitrification. Moreover, the modeling of the M-Area glass dissolution rate in deionized water, as summarized in this study, provides a validated dissolution rate constant for high Al_2O_3 and U_3O_8 containing alkali borosilicate glasses.

2.0 BACKGROUND

The Liquid Effluent Treatment Facility (LETF) in M-Area was constructed in 1985 to process M-Area chemical wastes due to the federally mandated closure of the M-Area seepage basin. The LETF consisted of three facilities: the Dilute Effluent Treatment Facility (DETF), the Chemical Transfer Facility (CTF), and the Interim Treatment/Storage Facility (IT/SF). The DETF processed dilute wastewaters from the M-Area processes and released the clarified liquid to Tim's Branch. [4] The DETF was a conventional water treatment facility that used precipitation, flocculation, and filtration to remove dissolved metals. These solids were transferred through the CTF to the IT/SF.

While the M-Area waste was stored in the IT/SF tanks, it separated into a sludge fraction and a supernate. In May 1990, South Carolina Department of Health and Environmental Control (SCDHEC) approved a permit to operate the DETF- IT/SF Supernate Transfer Facility. [4] The permit allowed the DETF to be used to treat the supernate from the M-Area IT/SF tanks in addition to the dilute wastewaters from the M-Area processes. When the DETF- IT/SF Supernate Transfer Facility concept for treatment of M-Area's supernate and subsequent discharge to Tim's branch was initiated, M-Area's waste solidification strategy was altered from solidification of sludge plus supernates, to solidification of only the sludge and spent filter aid. Supernate treatment was completed in 1994.

Samples of M-Area sludge and supernate were obtained by SRNL in September 1986 from Tank 6 and 8 which were being continuously agitated at that time. Sludge samples from Tanks 1 through 6, and Tank 8 were obtained in January of 1988 after agitation. Analyses of these tank samples were documented previously. [1,2] These M-Area samples were used to demonstrate that a low temperature borophosphate glass could be produced from the M-Area waste [1] since at that time the sludge and the high nitrate containing supernate were to be treated together. The document containing the sludge and supernate analyses and proof that it could be made into a low temperature glass was subsequently used to support a request for pre-proposals to stabilize the M-Area waste by independent contractors. [9]

In 1989 when the sludge/supernate analyses were performed and two borophosphate glasses made [1], the DETF was not permitted to treat the M-Area supernate. Approval to use filtration to clean up the supernate along with other dilute wastewaters in M-Area was not received until May 1990. [4] The filter media would get contaminated with uranium in the process and the filter media would have to be co-disposed along with the sludge. Since the filter aid was primarily fine SiO_2 in the form of perlite, perflo, and diatomaceous earth, [2] the combined sludge/filter aid lent itself to vitrification in either borosilicate glass or soda-lime-silica (SLS) glass.

Sludge samples from Tank 7 and filter aid samples from Tank 10 were obtained by SRNL in March of 1992. Additional filter aid from Tank 10 was obtained in November of 1992 and the results of these tank analyses are documented elsewhere. [2] During the treatability study [10], mixtures of the Tank 8 sludge and the Tank 10 filter aid were used to make durable and processable glass compositions using the durability and process models developed for the DWPF. [11]

Results from the treatability study and subsequent sample analyses were used to support the request for proposals (RFP) and subsequent vitrification in a VTF from 1996-1999 [12], and the up-front and final delisting petitions. [6,7,13] The final delisting petition for the vitrified waste was approved by the Environmental Protection Agency (EPA) in 2000. [5] This allowed the delisted vitrified waste to be disposed of in the SRS E-Area trenches.

The results of the treatability study and the subsequent durability testing of the treatability study samples is documented in this report since this information may be useful to glass formulations related to high Al_2O_3 and high U_3O_8 containing HLW sludges currently scheduled for vitrification in the DWPF or at the WTP.

3.0 QUALITY ASSURANCE (QA)

All analyses were conducted at SRNL (then SRTC) in accordance with DOE/RW-0214 (Quality Assurance Requirements Document (QARD) for technical documents prepared by Office of Civilian Radioactive Waste Management (OCRWM), program participants, and OCRWM managed contractors that are submitted for review, acceptance, and release by OCRWM) and American Society of Mechanical Engineers (ASME) NQA-1 based quality assurance program in use at the time the work was performed. The analytic results are recorded in laboratory notebooks DPSTN-4695, WSRC-NB-95-139, WSRC-NB-95-140, WSRC-NB-96-394, WSRC-NB-96-396, and WSRC-NB-96-609 where WSRC is Washington

Savannah River Company. The vitrification was performed under waste treatability and Quality Assurance (QA) Task Plan entitled “Solidification of M-Area and Consolidated Incinerator Facility (CIF) Wastes into Glass.” [14] The samples were characterized, and durability tested for several years after the treatability study ended under the sample exclusion law.

4.0 EXPERIMENAL

4.1 Defining the M-Area Waste Variability Envelope

The Tank 8 sludge represented the average sludge composition of Tanks 1-8 in M-Area and was readily available. The composition of Tank 8 sludge is given in Reference 2 and Section 5.1 of this report. Tank 10 contained mostly spent filter aid which was SiO_2 rich. The processing strategy was to blend the Tank 10 filter aid with the high sodium nitrate and alumina rich sludge wastes from the various tanks. The addition of glass formers would then be used to vitrify the sludge/filter aid into borosilicate waste glass.

When the treatability study was conducted in 1993, the M-Area Effluent Treatment Facility (ETF) was in the process of treating the supernates in Tanks 7 and 8 and returning the spent filter aid to Tank 10. The volume of the sludge remaining after supernate treatment would be completed was predicted to be ~244,000 gallons, with a density of 1.25 kg/L and ~38 dry wt. % solids. The predicted volume of filter aid in Tank 10 was ~412,000 gallons with a density of 1.1 kg/L and ~17 dry wt. % solids. These predicted volumes were used to prepare a “nominal blend (N),” mixture of 6,100 mL of Tank 8 sludge with 10,540 mL from Tank 10 (see Table 4-1).

In order to bracket the potential final volumes of waste, a high SiO_2 (HSi) and low SiO_2 (LSi) mixture was prepared. The LSi mixture, assumed a final volume of filter aid in Tank 10 of 200,000 gallons, a density of 1.1 Kg/L, and 17 wt. % solids. Density and wt. % solids for Tank 8 were the same as in the nominal blend. The LSi mixture was prepared by blending 4,600 mL of Tank 8 sludge with 3,740 mL of Tank 10 sludge (see Table 4-1). The HSi mixture was prepared by assuming a higher volume (450,000 gallons) in Tank 10 with a density of 1.2 wt.% and 30 wt.% solids. This mixture was prepared using 1,190 mL of Tank 8 sludge and 4,600 mL of Tank 10 filter aid (see Table 4-1).[§]

The volume ratios given in Table 4-1 correspond to mass ratios of Tank 8:Tank 10 waste of 0.67, 0.52, and 1.39 for the nominal, high SiO_2, and low SiO_2 blends, respectively, using the sludge and filter aid densities given in Reference 2. It is interesting to note that the final tank volumes, when measured in 1995, were most similar to the “LSi” SRNL blend, i.e., 385,000 gallons of plating line sludge and 228,000 gallons of Tank 10 filter aid or a Tank 8/Tank 10 volume ratio of 1.69.

[§] More Tank 10 material was used in the HSi mixture to compensate for the higher estimated solids loading (30% vs. 17%) than for the other two mixtures (LSi and N).

Table 4-1. Nominal, High SiO_2 and Low SiO_2 Waste Mixtures Representing the M-Area Compositional Envelope.

Mixtures Made On 03/18/93	Tank 1-8 Sludge / Tank 10 Spent Filter Aid Volume Ratio (M-Area Tank Farm in gallons)	Tank 8 Sludge (for Tanks 1-8) / Tank 10 Spent Filter Aid Volume Ratio (Treatability Mixtures in mL)	Tank 8 / Tank 10 Mass* Ratios
Low Si (LSi) (low Tank 10)	$\frac{244{,}500 gal}{200{,}000 gal} = 1.22$	$\frac{4{,}600 mL}{3{,}740 mL} = 1.23$	1.39
Nominal (N)	$\frac{244{,}500 gal}{412{,}500 gal} = 0.59$	$\frac{6{,}100 mL}{10{,}540 mL} = 0.58$	0.67
High Si (HSi) (high Tank 10)	$\frac{244{,}500 gal}{450{,}000 gal \bullet \left(\frac{30}{17}\right) \bullet \left(\frac{1.2}{1.1}\right)} = 0.28$	$\frac{1{,}194 mL}{4{,}600 mL} = 0.26$	0.52

* Conversion to mass ratios for Tank 8 sludge = 244,500 gal x 3.78 L/gal x 0.382 wt. % solids @ 105°C x 1.25 (spg of sludge); conversion to mass ratios for Tank 10 nominal and low Si = 412,500 gal x 3.78 L/gal x 0.17 wt.% solids @ 105°C x 1.10 (spg of filter aid); conversion factor for Tank 10 high Si = 412,500 gal x 3.78 L/gal x 0.30 wt.% solids @ 105°C x 1.20 (spg of filter aid) where spg is specific gravity of the sludge.

4.2 Analyses of Sludge-Spent Filter Aid Blend

The chemical analyses of the Tank 8 sludge/Tank 10 filter aid blends were determined in duplicate. The sludge was dried at ~300°C to remove residual hydroxide species and completely analyzed for the remaining cations and ions by the following techniques:

- Dissolution by Na_2O_2 with an HCl uptake
  - Inductively Coupled Plasma-Emission Spectroscopy (ICP-ES) for Al, Ca, Fe, Mg, Mn, Li, Si, Cr, B, Sr, Ti, P, Ba, Pb, Mo, Zn, Cu
  - Atomic Absorption (AA) for Si

- Dissolution by HCl/HF bomb
  - ICP-ES for Na, Ni, Zr
  - AA for Ni, Na, K, Si

- Uranium by Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS)

- Dissolution by Na_2O_2 with a H_2O uptake
  - Ion Chromatography (IC) for SO_4, NO_3, PO_4
  - Ion Selective Electrode (ISE) for Cl and F

Weight loss was measured at 105°C to get moisture loss and at 300°C to remove hydroxide and bound waters of hydration.

4.3 Glass Formulations

4.3.1 Crucible Tests

Glass formulations were made with combinations of only one or two glass forming additives to simplify processing, i.e., eliminate the need for a prefabricated frit and minimize the potential for weighing errors during manual operation of the VTF. Because the waste blends (nominal, HSi, and LSi) were high in Al_2O_3 and SiO_2, and the targeted waste loadings were in the 70-90 wt% range to achieve the largest volume reduction for disposal, only melt fluxes were added to fabricate alkali borosilicate glasses as indicated below and shown in Figure 1:

- Boric Acid (H_3BO_3)
- Borax (30 wt. % Na_2O + 70 wt. % B_2O_3)
- 50 wt. % Na_2O + 50 wt. % B_2O_3
- 50 wt. % Li_2O + 50 wt. % B_2O_3
- 70 wt. % Li_2O + 30 wt. % B_2O_3

In addition, SLS and soda-lime-lithia-silica (SLLS) glasses were fabricated from the following glass forming combinations and shown in Figure 1:

- Calcium Oxide (CaO)
- 50 wt. % Na_2O + 50 wt. % CaO
- 50 wt. % Li_2O + 50 wt. % CaO
- 70 wt. % Na_2O + 30 wt. % CaO

The use of reactive silica (surface area > 50 m^2/g), in this case the Tank 10 filter aid that was part of the blended waste, was shown to extend the known processing range in the SLS glass forming system (Figure 1). [15,16]

The glass formulations and waste loadings are given in Table 4-2 and Table 4-3. The approximate melt temperatures were calculated from the DWPF viscosity model assuming that a given melt needed to be in the 20-100 poise range to pour. The actual melt temperatures are recorded in Figure 1, Table 4-2, and Table 4-3. Additional details of the furnaces used, the furnace calibrations, and the visual observations of the melts are given in Appendix A. Most of the glasses were melted in 500 mL pure Al_2O_3 crucibles as a relatively large quantity of each glass was needed for the durability testing at different surface area to leachate volumes in deionized water and E-Area ground water and for the Toxicity Characteristic Leaching Procedure (TCLP) and repetitive TCLP Multiple Extraction Procedure (MEP) tests discussed below.

4.4 Glass Analyses

The glasses made in crucibles were analyzed by the following methods:

- Dissolution by Na_2O_2 with an HCl uptake
  - ICP-ES for Al, Ca, Fe, Mg, Mn, Li, Si, Cr, B, Sr, Ti, P, Ba, Pb, Mo, Zn, Cu

- Dissolution by HCl/HF bomb
  - ICP-ES for Na, Zr, U
  - AA for K

Anions were not measured as the anion content of the sludge was very low. [2] Glasses were analyzed in duplicate and the Waste Compliance Plan (WCP) Purex glass was used as a glass standard. Glass compositions were bias corrected to the standard glass for all elements analyzed.

All glasses were examined by XRD for crystalline phases. This was important as the glasses contained P_2O_5 from 0.45 to 4.02 wt% P_2O_5 which at concentrations higher than 2.24 P_2O_5 (3 wt. % PO_4) is known to cause crystalline phase separation (CPS) as described in References 17, 18, and 19:

> "In phosphate-containing borosilicate glasses, all three major glass formers are present in structural tetrahedral or trigonal groups, e.g. $(SiO_4)^{-4}$, $(BO_4)^{-5}$, $(BO_3)^{-3}$, and $(PO_4)^{-3}$. The competition for dominant structural roles causes the cation with the highest field strength, P^{5+}, to dominate the de-mixing process. If the difference in the field strengths (ΔF) between the major glass forming (structural) elements exceeds 0.3, then the phase separation will be of a crystalline and not amorphous nature according to Dietzel, [20] e.g. the differences between B and P and Si and P exceed the limit of 0.3 while the ΔF difference between B and Si is only 0.06. Therefore, the phase separation in phosphate systems is of a crystalline nature, CPS. Glasses in these phosphate systems separate to crystalline or partially crystalline solids, depending on quench rate."

In addition, many of the glasses formulated with high B_2O_3 were in the region of the Na_2O-B_2O_3-SiO_2 system where various types of amorphous phase separation (APS) are known to occur (Figure 1-top). These glasses were examined by SEM for glass-in-glass phase separation. The glass-in-glass droplet textures were of large enough scale that acid etching was not necessary. Therefore, glasses were examined for both APS and CPS. [18,19,21]

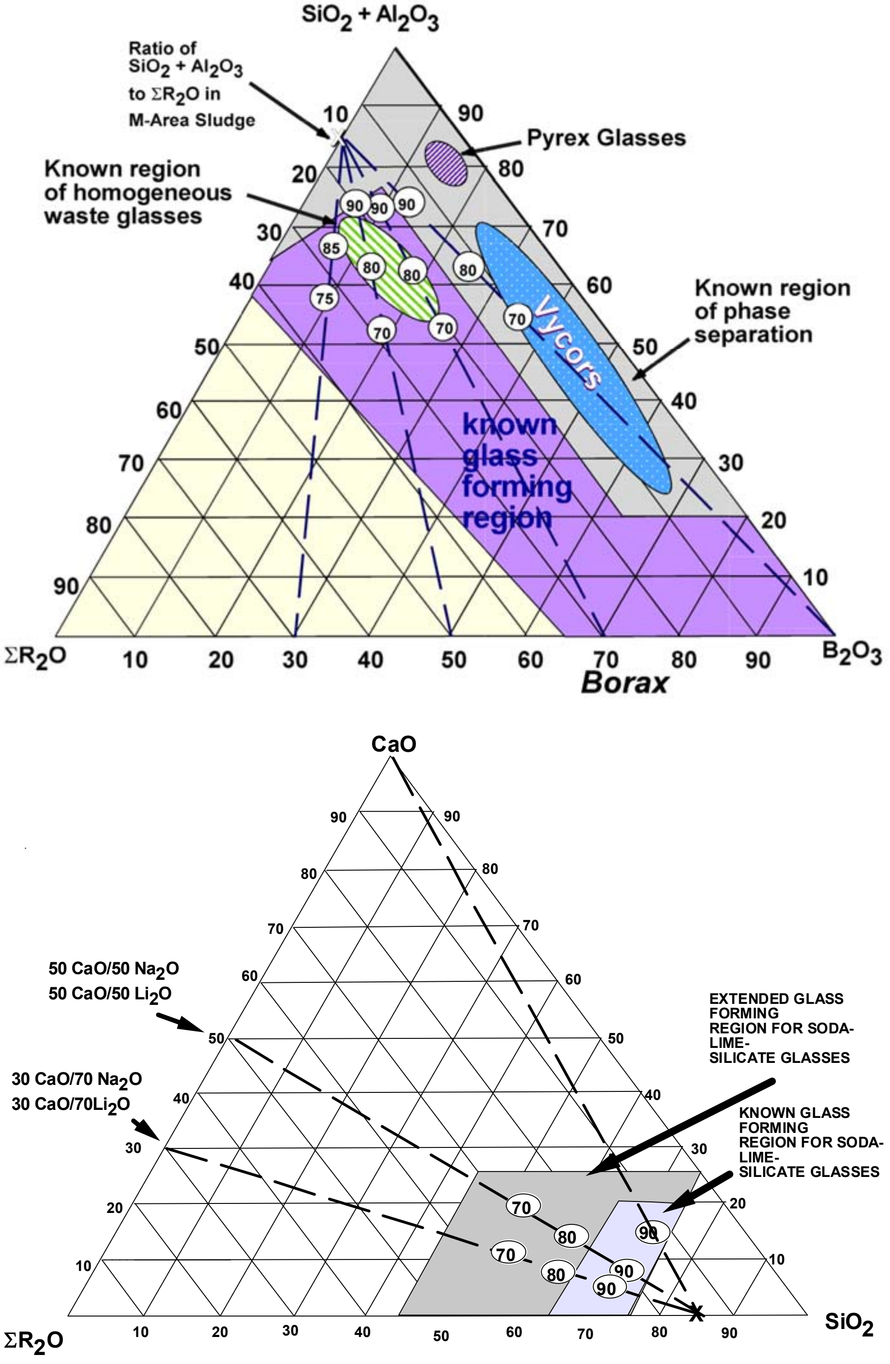


Figure 1. Alkali borosilicate glass forming system in weight percent (top) and the alkali-lime-silica glass forming system in weight percent (bottom).

The composition of the nominal M-Area sludge is shown with an "X", the composition of the glass forming additives are shown along the alkali-borate binary (top) and the alkali-CaO binary (bottom). The glass formulations with the pertinent waste loadings are indicated by the ovals.

Table 4-2. SRNL M-Area Alkali Borosilicate Glass Formulations Made in Crucibles

Glass Family		Sodium Borosilicate		Sodium + Lithium Borosilicate Glasses	
Sample ID	**Waste Blend**	**Waste Loading (wt. %)**	**Melt Temperature (°C)**	**Waste Loading (wt. %)**	**Melt Temperature (°C)**
ADDITION OF B_2O_3 ONLY					
MN-1	Nominal	90	1400	---	---
MN-2	Nominal	80	1260	---	---
MN-3	Nominal	70	1150	---	---
MHSi-1	High Si	90	1400	---	---
MHSi-2	High Si	80	1300	---	---
MHSi-3	High Si	70	1150	---	---
MLSi-1	Low Si	90	1350	---	---
MLSi-2	Low Si	80	1300	---	---
MLSi-3	Low Si	70	1150	---	---
ADDITION OF BORAX (30:70 Na_2O:B_2O_3)					
MN-4	Nominal	90	1400	---	---
MN-15	Nominal	85	1200	---	---
MN-5	Nominal	80	1300	---	---
MN-16	Nominal	75	1150	---	---
MN-6	Nominal	70	1150	---	---
MHSi-4	High Si	90	1400	---	---
MHSi-5	High Si	80	1150	---	---
MHSi-6	High Si	70	1200	---	---
MLSi-4	Low Si	90	1400	---	---
MLSi-5	Low Si	80	1150	---	---
MLSi-6	Low Si	70	1150	---	---
ADDITION OF 50:50 Na_2O:B_2O_3					
MN-7	Nominal	90	1400	---	---
MN-8	Nominal	80	1150	---	---
MN-9	Nominal	70	1200	---	---
MLSi-7	Low Si	90	1400	---	---
MLSi-8	Low Si	80	1150	---	---
MLSi-9	Low Si	70	1150	---	---
ADDITION OF 50:50 Li_2O:B_2O_3					
MN-10	Nominal	---	---	90	1200
MN-11	Nominal	---	---	80	1150
MN-12	Nominal	---	---	70	1150
MHSi-11	High Si	---	---	80	1200
MLSi-10	Low Si	---	---	90	1200
MLSi-11	Low Si	---	---	80	1150
ADDITION OF 70:30 Li_2O:B_2O_3					
MN-13	Nominal	---	---	85	1150
MN-14	Nominal	---	---	75	1150

Table 4-3. SRNL M-Area Soda-Lime-Silica and Soda-Lime-Lithia-Silica Glass Formulations Made in Crucibles.

Glass Family		Soda-Lime-Silica (SLS) Glasses		Sodium + Lithium-Lime-Silica Glasses	
Sample ID	**Waste Blend**	**Waste Loading (wt. %)**	**Melt Temperature (°C)**	**Waste Loading (wt. %)**	**Melt Temperature (°C)**
ADDITION OF 50:50 Na_2O:CaO					
MN-17	Nominal	90	1350	---	---
MN-18	Nominal	80	1150	---	---
MN-19	Nominal	70	1150	---	---
ADDITION OF 50:50 Li_2O:CaO					
MN-20	Nominal	---	---	90	1200
MN-21	Nominal	---	---	80	1150
MN-22	Nominal	---	---	70	1150
ADDITION OF CaO					
MN-23	Nominal	90	1400	---	---
ADDITION OF 70:30 Na_2O:CaO					
MN-24	Nominal	90	1400	---	---
MN-25	Nominal	80	1150	---	---
MN-26	Nominal	70	1150	---	---

4.5 ASTM C1285 Durability Testing

The PCT results can be expressed as a normalized concentration (NC_i) which have units of $g_{\text{waste form}}/L_{\text{leachant}}$, or as a normalized release (NL_i) in $g_{\text{waste form}}/m^2$, or as a normalized rate (NR_i) in $g_{\text{waste form}}/ m^2 \cdot day$ where "i" is the chemical element of interest. The equation for NCi is given in Equation 1. Expression of the PCT test response as NL_i or NR_i necessitates the use of the surface area (SA) of the sample releasing species "i" and the volume (V) of the leachant being used which is expressed as the SA/V ratio. Examples of the calculations are given in Equation 2 and 3

$$NC_i = \frac{c_i(sample)}{f_i} \tag{2}$$

where NC_i is the normalized concentration ($g_{\text{waste form}}/L_{leachant}$)
c_i *(sample)* is the concentration of element *i* in the leachate solution (g_i/L)
f_i is the fraction of element *i* in the unleached waste form (unitless).

$$NL_i = \frac{c_i(sample)}{f_i \cdot (SA/V)} \tag{2}$$

where NL_i is the normalized release ($g_{\text{waste form}}/m^2$)
c_i *(sample)* is the concentration of element *i* in the leachate solution (g_i/L)
f_i is the fraction of element *i* in the unleached waste form (unitless).

and

$$NR_i = \frac{c_i(sample)}{f_i \cdot (SA/V) \cdot t} \tag{3}$$

where NR_i is the normalized release rate ($g_{\text{waste form}}/ m^2 \cdot day$)
SA/V is the surface area of the final waste form divided by the leachate volume (m^2/L)
t is the time duration of test (days).

In this study the durability results are reported in NL_i.. Leachates were analyzed by ICP-ES scan for multiple elements (B, Li, Na, Al, Fe, Ca, Mg, Si, Zn, etc) and by a Chemcheck Kinetic Phosphorescence Analyzer (KPA) which was capable of measuring trace levels of uranium and lanthanides**.** KPA analyses were used at SRNL before ICP-MS.

4.5.1 Nominal Temperature Testing (90°C)

The chemical durability of the M-Area glasses from the crucible studies and the pilot scale studies was determined using ASTM procedure C 1285-02. [8] The glasses were ground and sized between -100 and +200 mesh (74 µm to 149 µm). To remove the electrostatic fines, the sized material was washed six times with 100% ethanol. Water was not used for washing for fear of removing any water-soluble phases prior to leaching as cautioned by the ASTM C1285-02 procedure.

For all samples, ASTM Type I water [22] was used as the leachant, a constant leachant to sample ratio of 10 cm^3/g or 0.01 L/g (V in equations 1 and 2 above) was used, the test temperature was 90°C, and the test duration was seven days. The temperature and 7-day duration are the nominal test conditions used for testing glass waste form performance, e.g. PCT-A. However, Teflon® vessels were used and so rigorously the test is defined as PCT-B. Leachate concentrations are given as NL_i per Equation 1 for B, Si, Na, Li, Ni, and U.

4.5.2 Extrapolation and Confirmation of Dissolution to Performance Assessment Conditions (25°C)

Whited et. al. [23,24,25] used literature values to tabulate the 90°C long term (84-980 days) static dissolution data in both deionized water and Yucca Mountain J13 groundwater for a wide variety of HLW glasses from Europe (SM527 and R7T7), the United States (SRL-131, 165, 200, 202), and a statistical study related to DWPF glasses [26]. Data from 29 different glasses, some tested using the PCT (ASTM C1285) and the MCC-1 (ASTM C-1220) [27] test protocols, were compiled at a wide variety of test parameters, i.e. SA/V and time. The average long-term release rate, expressed as NR_i, was calculated and used in conjunction with an activation energy of dissolution (E_a) to use the SRNL 90°C PCT values to generate a leach rate at 25°C. This 25°C leach rate was then used in determining if the M-Area glasses, once delisted, would pass the SRS E-Area PA. An average E_a of dissolution for borosilicate glasses of 75 KJ/mole was used from White [28] for dissolution of a nuclear waste glass in ASTM Type I water. This was confirmed by more recent (1998) work of Dove [29] for the dissolution of pure SiO_2 in ASTM Type I water which gave an E_a of dissolution of 78.9 KJ/mole. This assessment assumed that uranium was released at a similar rate as boron as a worst-case scenario even though it is likely that uranium release would be solubility limited while boron release would not be solubility limited. [23,24,25]

4.5.3 Confirmatory Dissolution Testing at Performance Assessment Conditions (25°C)

Confirmatory, PCT-B tests were performed in SRS E-Area ground water from well #94 at 25°C at six different SA/V ratios at time durations of 14, 28, and 42 days yielding the (SA/V)•t matrix given in Table 4-4.

Table 4-4. Mesh Sizes and SA/V Ratios and times used for Confirmatory Testing at 25°C in E-Area Ground Water.

Group ID	Mesh*	Mass of glass (g)	Mass of Water (g)	Leachant Volume/Sample Mass (cm^3/g)	Time (days)	(SA/V)•t (m^2/L)•days*
A	60-80	2	20	10	14	14,600
B	60-80	2	10	5	14	29,200
C**	270-400	2	20	10	14	69,100
D**	270-400	2	10	5	14	138,300
E	60-80	2	20	10	28	29,200
F	60-80	2	10	5	28	58,300
G	100-140	2	20	10	28	49,000
H	100-140	2	10	5	28	98,000
I	270-400	2	20	10	42	207,400
J	270-400	2	10	5	42	414,800

* Mesh sizes were used to calculate the glass surface area (SA) as per the Appendix of the ASTM C1285 test protocol

** Groups C and D durability tests were not performed due to lack of funding as the (SA/V)•t range was covered by experiments G, H, and I

Since testing was performed at eight different (SA/V)•t ratios to accelerate the dissolution, large quantities of glass were required. Only three glasses were available in sufficient quantity to be tested (MN-12, MN-13 and MHSi-5) at the time at which this confirmatory study was initiated.

4.6 TCLP Testing

The EPA TCLP was carried out on the glass samples for Ba, Cr, Ni, Pb by General Engineering Laboratories (GEL) in Charleston, SC, an EPA certified laboratory. In addition, GEL measured the TCLP leachates for total U as an indication of the uranium drinking water standard. The results of the standard TCLP and the TCLP MEP testing are given elsewhere. [5,30]

4.7 Viscosity Testing

The SRNL setup and established a Harrop, high-temperature viscometer in 1998 for measuring the viscosity of radioactive glasses. [31] The unit uses approximately 6 grams of glass, which is considerably less than the amount used by commercial laboratories (200-700 grams) and other national laboratories such as the Pacific Northwest National Laboratory (PNNL) which uses 200 grams. Two crucible/spindle sets (Set A and Set B) are used for these measurements. This allows one viscosity measurement per day, since it takes ~ 1 day to clean the crucible and spindle. Set A was calibrated using the NIST 717a borosilicate glass standard. This NIST glass is significantly more viscous than DWPF-type glasses with a viscosity close to 2000 Poise at 1200°C. For comparison, the normal range for DWPF glasses is from 20 to 110 Poise at 1150°C. Due to the high viscosity of the NIST 717a glass, it was decided to measure the viscosities of the HM, Purex, and Batch 1 WCP glasses. The melt viscosities for these glasses had been previously measured by a commercial laboratory, thereby providing an independent measure of glass viscosity for glasses in the range of interest for DWPF.

The melt viscosity was measured according to ASTM-965A. The glass density for each sample was determined since a constant volume of glass is required in the crucible for each glass sample. The mass of glass to be added to the crucible is 2.6 cc • glass density in (g/cc). Viscosity measurements were made at 5 temperatures starting with a temperature of ~ 1190°C. For the high Al_2O_3 containing glasses sometimes higher starting temperatures of ~1300°C were necessary. The temperature was lowered in ~ 50°C intervals and, after equilibration at each temperature, another measurement was made.

Volatilization and crystallization can affect the viscosity results. For example, volatilization of a compound that reduces viscosity will lead to an increase in viscosity with time. On the other hand, crystallization in the melt has the potential to increase the measured viscosity and crystallized glasses are non-Newtonian in behavior [32] and do not obey the Vogel-Fulcher-Tammann (VFT) relationship at temperatures above the glass transition temperature but, instead, obey the Einstein-Smoluchowsky equation for the diffusion of spherical particles through a liquid.[32] Starting the viscosity experiment at temperatures above the liquidus temperature minimizes the effect of crystallization on glass viscosity and ending the viscosity experiment at temperatures of ~850°C, the temperature of maximum crystallization in a time-temperature-transformation (TTT) diagram minimizes the effect of crystallization on glass viscosity. By limiting the temperature range of the viscosity measurement, crystallization does not significantly impact the VFT fit for these data unless a discontinuity is observed in the 1/T (°K) vs. logarithm (base 10) viscosity plot.

The viscosities at a series of temperatures were calculated from the rpm's of the spindle, the %torque on the spindle, and a constant, K, measured from the NIST 717a glass. The K constant actually varies slightly with temperature, and for temperatures between 1050 and 1500 °C it is fit to an equation of the form: a-(b x T in °C) where a and b are constants. Using this equation, which differs for each crucible-spindle set (A or B), the viscosity at a given measurement temperature was then calculated by equation (4):

$$\text{Viscosity (Poise) } \eta = [\%\text{ torque / RPM}] \bullet K \tag{4}$$

5.0 RESULTS

5.1 Waste Blend Characterization

The results of the analyses of Tank 8 and Tank 10 from Reference 2 are given in Table 5-1. In addition, the averaged results of the two separate analyses on each of the Tank 8/Tank 10 blends are given in Table 5-1. The details of the three blend analyses are given in Appendix B.

The Tank 8, Tank 10, and blend compositions in Table 5-1 are given on an element wt% basis. Note that the SiO_2 range for the HSi-LSi blends varies between 42.95-50.23 wt%, the U_3O_8 varies between 4.16-6.44 and the Al_2O_3 is 16.67-17.39 wt% for all three blends.

5.2 Glass Composition and Homogeneity

The M-Area mixed waste treatability study consisted of 43 analyzed glasses from vitrification of SRS M-Area wastes (crucible studies). Thirty-three were borosilicate glasses and ten were SLS glasses. The analyzed average and bias corrected compositions are given in Table 5-2 on an oxide basis. All analyses summed to 100±5 wt% indicating the high quality of the analyses.

The conditions of fabrication and quenching method used for the M-Area treatability glasses are given in Table 5-3 and Appendix A. The M-Area waste glasses had all been melted in 99.99% Al_2O_3 crucibles. Since the waste contained between 4 and 15 wt% Al_2O_3, no interaction with the ceramic crucibles was observed visually and there was no impact noted on the measured Al_2O_3 concentrations as compared to the target values. The M-Area glasses from the crucible treatability study had been allowed to air cool in the ceramic crucibles, undergoing a somewhat slower quench than if the glasses had been poured onto steel blocks or pans for a rapid quench. Most of the crystallization was Li_3PO_4 CPS which develops virtually instantaneous regardless of the quench rate [16, 17, 18] and the other crystallizing species were aluminates indicative of exceeding the alumina solubility in the glass. Both these phenomena are relatively independent of quench rate.

The crystalline phases that formed in the M-Area glasses, including the Li-phosphate CPS phases, were identified by XRD (Table 5-3). Eight of the 41 M-Area glasses crystallized Li_3PO_4 as the primary crystalline phase and three crystallized Li_3PO_4 along with an additional silicate or SiO_2 phase. Only two glasses, MN-5 and MHSi-11 exceeded the Al_2O_3 solubility limit and crystallized α-Al_2O_3 or $LiAlO_2$. Glass MN-26 appeared to have incompletely reacted and sodium carbonate (a glass forming additive) was identified. The data for this sample was not used.

Many of the glasses appeared visually to be amorphous which was confirmed by XRD analyses (Table 5-3). However, it was suspected that several of the glasses had undergone APS that would not have been observed by XRD, i.e., they were either in the range of known phase separation in the borosilicate glass system (Figure 2) or if the glasses were predicted or observed to contain amorphous phase separation [19,21] and contained >14 wt% B_2O_3 [33] (see Table 5-3).

The two glasses that exhibited APS were MN-3 and MN-14. Morphologically, APS may take the form of droplets or channels of various dimensions which have defined boundaries. Glass MN-3 contained 28.25 wt% B_2O_3 and was made with only one frit addition, B_2O_3 (see Figure 1 and Table 4-2). At 70 wt% waste loading of the high Al sludge and high Si filter aid nominal mixture, this glass was in the region of the alkali borosilicate waste glasses where Vycor glasses, which are known to be phase separated, form (Figure 2). MN-3 contained no Li_2O and the only Na_2O in the glass (7.96 wt%) was from the alkali in the M-area sludge (see Table 5-2). The SiO_2-B_2O_3 separation morphology [34] is visible in Figure 3 (top) in the as prepared sample which was not etched with any chemicals or steam.

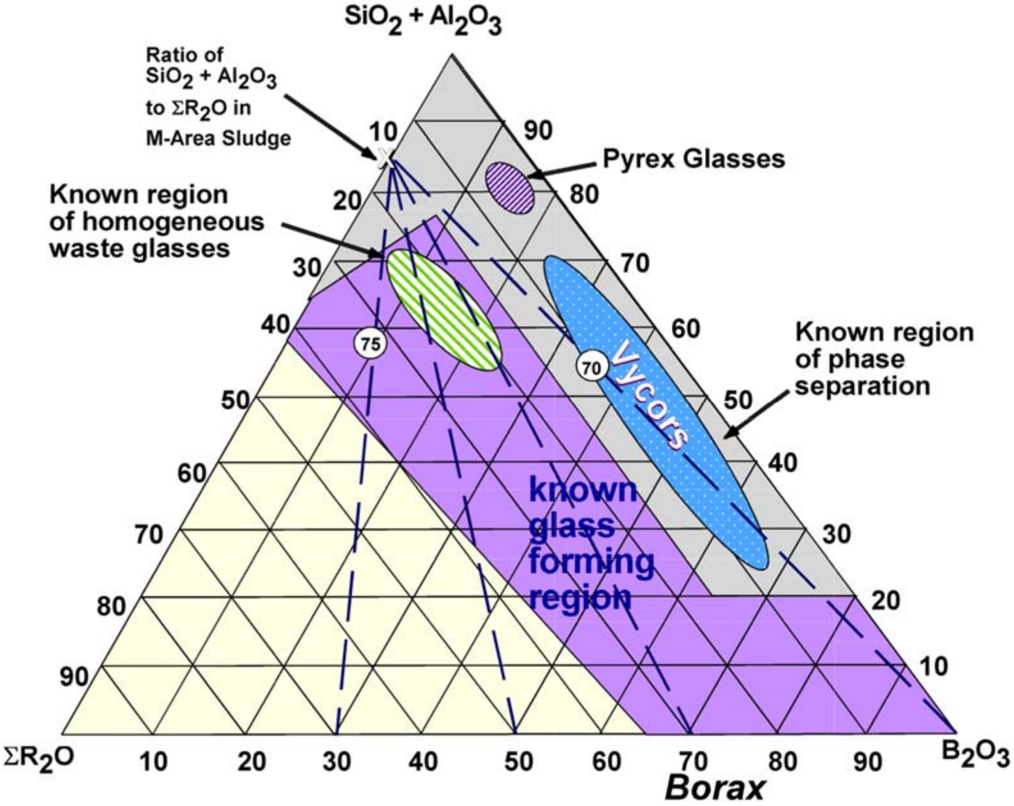
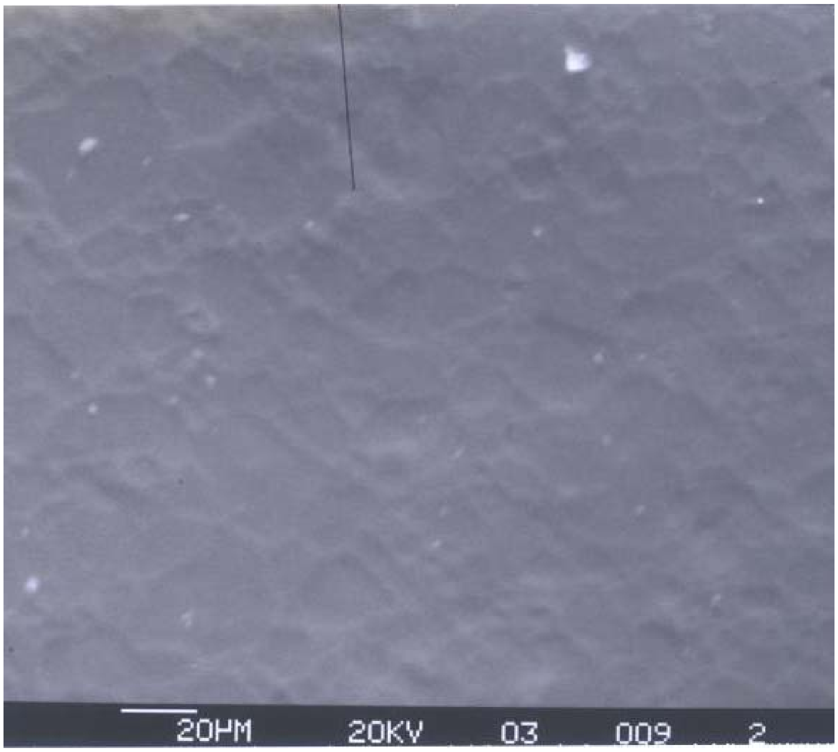
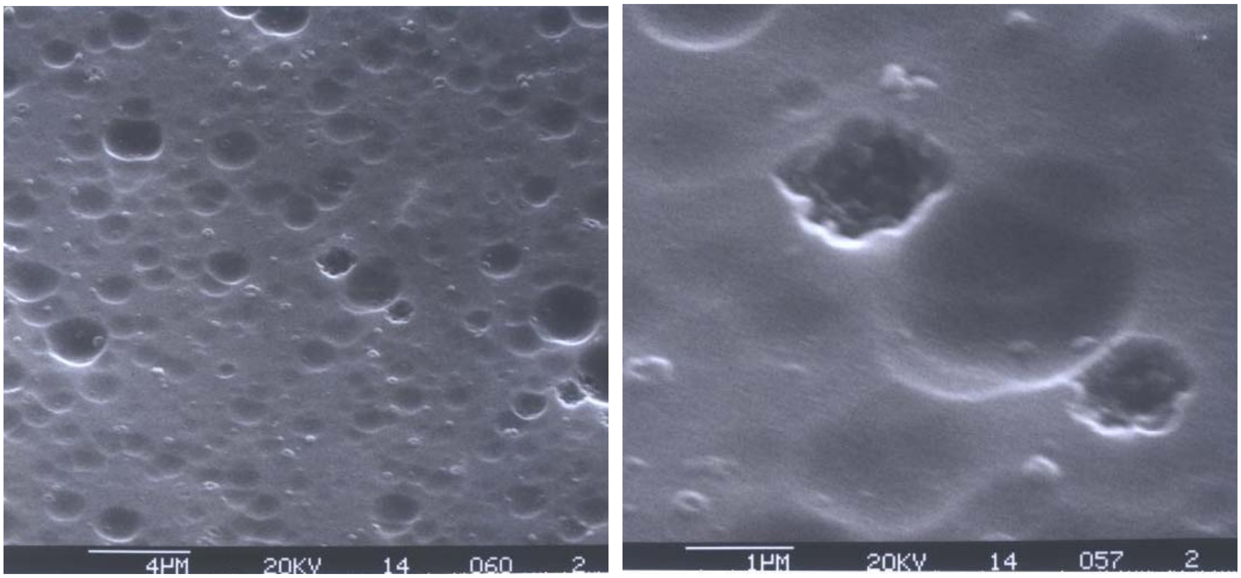


Figure 2. Alkali borosilicate system showing the position of the two glasses, MN-3 and MN-14, which exhibited amorphous phase separation during SEM analyses.

Glass MN-3 contained 28.25 wt% B_2O_3 and is in the region labeled Vycors. Glass MN-14 contained high Li_2O and also exhibits phase separation. Both glasses have < 60 wt% SiO_2.



MN-3



MN-14 MN-14 Enlarged

Figure 3. Phase separation of the glass-in-glass amorphous type observed in MN-3 and MN-14.

Glass MN-14 was made with a two component frit (see Figure 1 and Table 4-2) of 70% Li_2O and 30% B_2O_3. The glass contains 16.86 wt% Li_2O, 17.53 wt% Na_2O, and only 7.45 wt% B_2O_3 (Table 5-2 and Figure 2). Spherical regions of a second phase can be observed in this glass (Figure 3). The regions are about 2 microns in size and are either a different density or have been etched out by SEM preparation techniques.

MN-3 and MN-14 were the only two glasses predicted to be phase separated as APS and the only two glasses that were found to be phase separated by SEM. Both glasses contained <60 wt% SiO_2. Because B and Li cannot be distinguished in the Energy Dispersive X-ray Analysis by SEM, the compositional nature of the phase separation could not be determined.

5.3 Alumina Solubility with P_2O_5

In order to assess the solubility of Al_2O_3 in the high U_3O_8 and P_2O_5 containing borosilicate glasses that could be compositionally useful for DWPF or WTP, a plot was made of all the M-Area glasses that were melted between 1150-1200°C at all the Al_2O_3 concentrations studied. The following conditions were applied:

- SLS glasses were excluded as DWPF and Hanford will vitrify borosilicate glasses (see Table 5-3)
- Glasses with P_2O_5 levels above 2.25 wt% (3 wt% PO_4) from Table 5-2, which is the DWPF phosphate solubility limit, were allowed to evaluate whether the DWPF solubility limit applies to high alumina glasses
- Glasses that failed the ASTM C1285 7 day test at 90°C (data in Table 5-4) at 2 standard deviations (2σ) below the Environmental Assessment (EA) glass limits for B, Li, and Na [35] were excluded
- Glasses that were phase separated (data in Table 5-3) were excluded

Then the logarithms of the PCT B release in g/L were plotted against the Al_2O_3 concentration in the glass (Figure 4). For each data point in Figure 4 a glass ID is given followed by the P_2O_5 concentration in wt%. These 15 glasses contain between 0.45 and 3.08 wt% P_2O_5 and are amorphous as determined by visual observation, XRD, and a calculation using the phase separation discriminator [21]. Glass symbols shown as X's contain Li_2O and Na_2O while the glass symbols shown as squares contain only Na_2O. The U_3O_8 range for these 15 glasses is 2.93-5.25 wt%. Figure 4 indicates the following:

- The P_2O_5 limit of 2.25 wt% P_2O_5 (3 wt% PO_4) may not apply for high alumina glasses, especially those with no Li_2O or minimal Li_2O in the frit
  - the DWPF P_2O_5 limit was set based on a simulated Stage 1 waste glass at 28 wt% waste loading [36]: the glass contained 11.17 wt% Fe_2O_3, 4.01 wt% Al_2O_3 and 53.74 wt% SiO_2 (17, notebook DPSTN E28150[f])
  - the DWPF P_2O_5 limit was set using frit 165 at 72 wt% waste loading: the glass contained 5.04 wt% Li_2O and 10.82 wt% Na_2O (17, notebook DPSTN E28150[f])
  - the simulated glass contained no U_3O_8
  - the 3 wt% PO_4 limit agreed with data in literature which cited solubility limits in silicate and borosilicate glasses between 3-4 wt% PO_4. [17]
- Combinations of low Li_2O and P_2O_5 appear to allow high Al_2O_3 glass loadings up to 25-26 wt% without compromising glass durability

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[f] The notebook number in reference 16 is reported incorrectly as DPSTN-25180 (several numbers are transposed) and thus incorrect

- This implies that DWPF glasses rich in Al_2O_3 might be processed with additional phosphate added as acids, e.g. H_3PO_4 or H_3PO_2 during Sludge Receipt and Adjustment Tank (SRAT) processing, these acids were examined in 1987 for DWPF as a partial replacement for nitric acid [17], since DWPF design basis sludges [17] were projected to only contain ~0.22 (Purex High Activity Waste, HAW), 0.16 (Average Waste), and 0.13 (HM HAW) wt% PO_4 which at 28 wt% waste loading in glass is projected to be only 0.04-0.06 wt% PO_4 in glass. In reality, the PO_4 concentrations in the glasses made from Sludge Batch (SB) SB1b, SB2, SB3, SB4, SB5, SB6, and SB7a have been 0.47, 0.36, 0.22, 0.19, 0.16, 0.15, <0.13, and <0.29 wt%, respectively. Even at higher waste loadings (WL) of 40% the design basis PO_4 concentrations are only 0.06-0.09 wt%
- Small concentrations of P_2O_5 up to 1-2 wt% should be investigated as a mechanism to increase the Al_2O_3 loadings of HM sludges and allow the amount of Al-dissolution to be optimized. These studies may also have applicability to Hanford's WTP as well.

Waste loadings in this range were confirmed for two glasses that were made in a 2007 DWPF study that achieved 26.63-26.64 wt% Al_2O_3 with and without Li_2O and in the presence of 1.1-1.2 wt% P_2O_5. These high Al_2O_3 content glasses did not compromise glass durability either. [37]

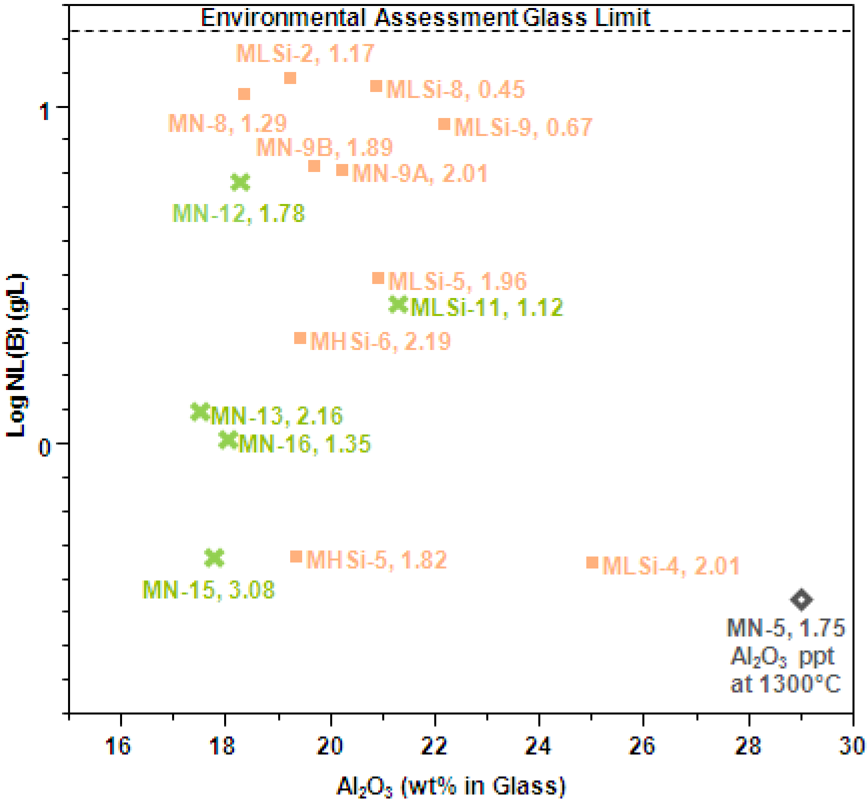


Figure 4. Plot of the M-Area borosilicate glasses that melted between 1150-1200°C. For each data point, a glass ID is given followed by the P_2O_5 concentration in wt%.

Glass symbols shown as X's (green) contain Li_2O and Na_2O while the square (orange) glass symbols contain only Na_2O. One glass which precipitated Al_2O_3 when cooled from a melt temperature of 1300°C is shown for reference at 29 wt% Al_2O_3 which appears to be the limit of Al_2O_3 solubility even at this elevated temperature.

5.4 Glass Viscosity and Density

All the viscosity measurements generated by SRNL are provided in Appendix A. The viscosity (in Poise) of each of these glasses at 1150ºC is to be estimated from a Fulcher equation fitted to these measurements. The functional form of the (three-parameter) Fulcher equation (expressed in Poise) used to fit these data is given by equation (4):

$$\ln \hat{\eta} = A + \frac{B}{(T - C)} \tag{4}$$

where $\ln \hat{\eta}$ represents the natural logarithm of the estimated viscosity (in Poise), $\hat{\eta}$, and A, B, and C represent the parameters of the model that were determined from the available measurements (expressed in Poise) at various temperatures (represented by T, in degrees Celsius). The fitted model was then used to predict the viscosity of the given glass at 1150ºC.

5.5 Glass Durability

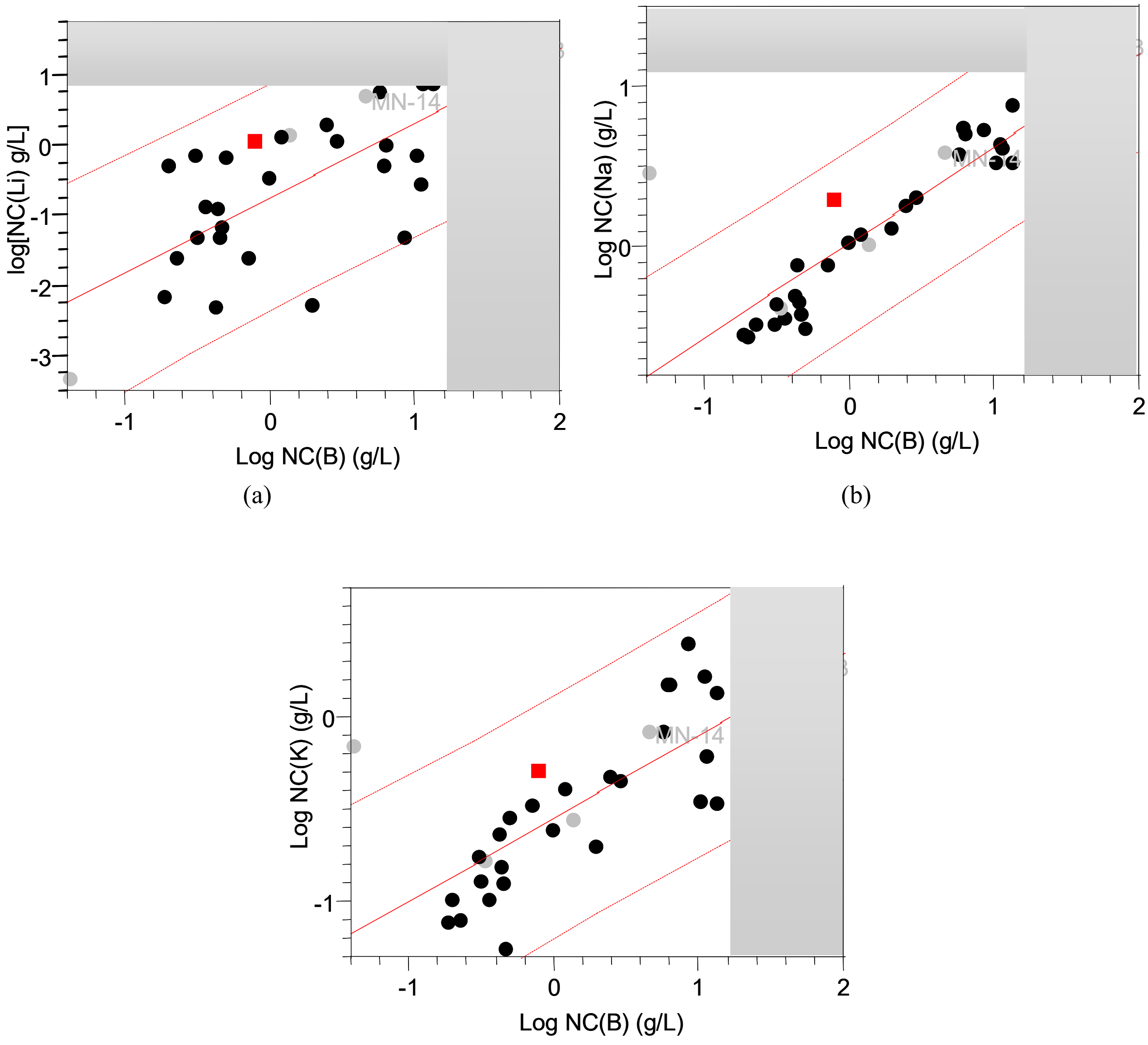
5.5.1 Nominal Temperature Product Consistency Testing (90°C)

The durability of the M-Area waste glasses were tested using ASTM C1285 (Method B for the M-Area glasses in Teflon® at the Method A reference conditions of 7 day duration, 90°C, and 1:10 ratio of mass solids:mass solution). Teflon® was used so that the leachates would be exposed to CO_2 from the atmosphere as they would in groundwater leachants during shallow land burial at the SRS. All glasses were measured in triplicate and the average of the triplicate normalized logarithms is given in Table 5-4. Measured normalized release rates are given in Table 5-4.

The normalized release rates of Li, Na, and K calculated in NC_i from Equation 2 compared to the normalized release rate of B also calculated from Equation 2 demonstrate that the releases are congruent (Figure 5) for glasses that are not crystallized (Table 5-3). Figure 5 plots mainly borosilicate releases and only one SLS glass. It should be noted that the log NC_{Na} is a better linear fit of the data to the log NC_B (Figure 5b) than log NC_{Li} (Figure 5a) and log NC_K (Figure 5c). The poor correlation between log NC_B and log NC_{Li} (Figure 5a) is attributed to the strong interactions between Li and the high concentration of P in these glasses which often caused lithium phosphate CPS to form. The poor correlation between log NC_B and log NC_K is that B is measured by ICP-ES while K is measured by a less accurate AA method. The shaded regions in Figure 5a-c are glasses that are less durable than the DWPF EA glass.

It should be noted that log NC_{Si} and log NC_U are solubility limited and there is little correlation of either with soluble boron (Figure 6). However, log NC_U never rises above log = 0 as it is solubility limited. The use of NC_B, which does rise above log zero, can be used to demonstrate that U leach rate is always much less than the B leach rate (Figure 6b), i.e. if a glass passes the PCT for B release, it will always pass the PCT for U release.

A stepwise regression of the mean uranium ppm values measured in the triplicate PCT's indicated that the Li_2O content of the glass was the single most important parameter in determining the release of uranium to the groundwater. Many of the glasses contained no Li_2O but of the glasses that contained >9 wt% Li_2O, the durability decreased as the Li_2O content increased above 9 wt%.



(a)

(b)

(c)

Figure 5. Correlation of normalized log B release with the log Li, log Na, and log K release in g/L from 90°C for 7 days.

The black circles are homogeneous borosilicate glasses while the gray circles are inhomogeneous borosilicate glasses as determined by XRD and/or SEM. The square is the only homogeneous SLS glass studied. The gray shading indicates glasses that leached greater than the HLW EA glass standard for a given element. Note that the EA glass does not contain K or U and so there is no limit on the K release shown in diagram c.

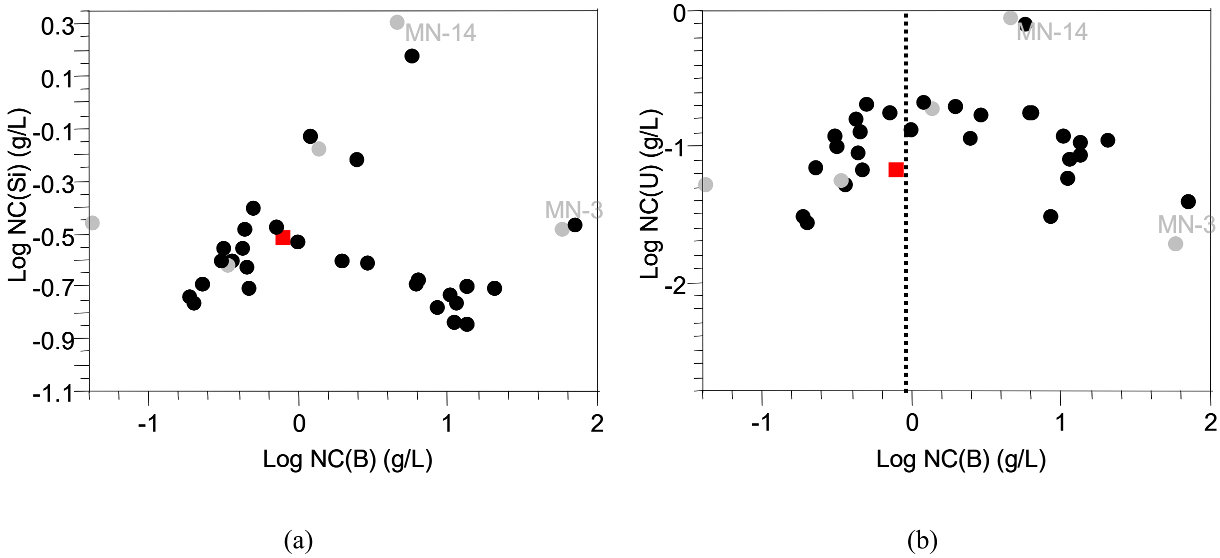


Figure 6. **Correlation of normalized log B release with the log Si and log U release in g/L from 90°C for 7 days.**

The black circles are homogeneous borosilicate glasses while the gray circles are inhomogeneous borosilicate glasses as determined by XRD or SEM. The square is the only homogeneous SLS glass.

Table 5-1. Composition of Tank 8 Sludge and Tank 10 Filter Aids and Blends [1]

Element (dry wt%)	**Tank 8 (11/88)**	**Tank 10 (5/92)**	**Tank 10 (7/93)**	**Nominal Blend**	**High SiO_2 Blend**	**Low SiO_2 Blend**
CATIONS AND ANIONS						
Al (ICP)	10.734	8.896	9.642	8.827	9.147	9.206
Ca (ICP)	0.307	0.351	0.425	0.313	0.332	0.320
Fe (ICP)	0.402	0.870	1.046	0.715	0.852	0.660
Mg (ICP)	0.122	0.122	0.122	0.167	0.150	0.163
Mn (ICP)	0.422	0.035	0.049	0.024	0.029	0.018
Na (ICP)	7.010	7.196	5.132	6.134	5.802	7.028
Na (AA)	7.056	7.433	5.233	7.049	6.552	9.047
Li (ICP)	<0.002	<0.001	<0.001	<0.001	<0.001	<0.001
Ni (ICP	0.728	0.064	0.081	0.551	0.409	0.670
Ni (AA)	0.990	<0.06	<0.06	0.674	0.504	0.785
Si (ICP)	11.301	24.785	25.144	22.977	23.479	20.076
Si (AA*)	*14.715*	*27.445*	*24.845*	*21.765*	*23.380*	*19.093*
Cr (ICP)	0.017	<0.004	<0.004	0.011	<0.004	0.027
B (ICP)	0.010	<0.004	<0.004	<0.004	<0.004	<0.004
U (ICP-MS)	5.133	0.045†	0.222†	4.762	3.524	5.458
Sr (ICP)	0.006	N/A	0.002	0.002	0.002	0.002
Zr (ICP)	0.010	<0.002	<0.002	0.014	<0.002	<0.002
Ti (ICP)	0.029	0.027	0.062	0.057	0.055	0.056
K (AA*)	0.121	2.605	2.053	0.936	0.966	0.687
P (ICP)***	1.896	1.031	0.959	1.338	1.259	1.179
P (Calc IC)**	0.973	1.035	0.997	0.915	1.030	1.081
Ba (ICP)	0.053	N/A	0.016	0.011	0.011	0.009
Pb (ICP)	0.137	0.035	0.032	0.036	0.035	0.041
Mo (ICP)	0.009	<0.004	0.005	0.004	0.005	0.005
Zn (ICP)	0.794	0.172	0.464	0.413	0.328	0.855
Cu (ICP)	0.022	0.003	0.065	0.014	0.014	0.016
F (ISE)	N/A	0.060	1.189	0.551	<0.093	<0.102
Cl (ISE)	0.059	0.310	0.134	0.112	0.100	0.112
SO_4 (IC)	<0.5	<0.2	0.332	0.212	0.133	0.129
NO_3 (IC)	16.376	7.935	6.202	7.197	6.710	10.319
PO_4 (IC)**	2.984	3.175	3.057	2.807	3.160	3.315
PROPERTIES						
wt% SOLIDS (105°C)	38.23	17.56	19.97	26.19	25.25	26.99
wt% SOLIDS (300°C)	NM	NM	18.39	24.38	23.35	24.91
MOLAR MASS BALANCE						
$Al(OH)_3$	25.06	23.12	23.81	22.15	23.27	23.64
$NaNO_3$	22.45	27.48	8.50	9.86	9.20	14.15
Filter Aid	33.07	52.95	53.62	49.02	50.09	42.82
$Na_6U_7O_{24}$	6.75	0.06	0.29	6.25	4.63	7.17
Ca Zeolite-A	2.82	1.30	3.91	2.88	3.05	2.94
$AlPO_4$	5.82	3.16	2.94	4.10	3.86	3.62
SUM	95.96	108.065	95.58	94.26	94.09	94.33

*AA silicon values in italics from HCl/HF dissolution all others with * from Na_2O_2 dissolution; **water soluble phosphate only; *** acid soluble phosphate; NM means Not Measured

Table 5-2. Analyzed Compositions of M-Area Glasses (Wt%)

Sample ID	Al_2O_3	B_2O_3	BaO	CaO	Ce_2O_3	Cr_2O_3	CuO	Fe_2O_3	K_2O	Li_2O	MgO	MnO	MoO_3	Na_2O	Nd_2O_3	NiO	P_2O_5	PbO	SiO_2	TiO_2	U_3O_8	ZnO	ZrO_2	Oxide Sum
MN-1	21.67	10.16	0.00	0.58	0.02	0.08	0.02	1.76	1.50	0.02	0.27	0.04	0.01	10.21	0.01	0.63	1.92	0.02	47.07	0.09	5.04	0.00	0.02	101.15
MN-2	16.85	21.83	0.01	0.37	0.02	0.09	0.02	1.63	1.33	0.01	0.23	0.03	0.01	8.75	0.01	0.55	1.54	0.04	38.76	0.08	4.44	0.03	0.02	96.67
MN-3	14.61	28.26	0.01	0.31	0.02	0.09	0.02	1.55	1.28	0.02	0.21	0.03	0.01	7.96	0.01	0.50	1.14	0.03	35.55	0.08	4.20	0.03	0.02	95.94
MN-4	21.24	7.52	0.01	0.42	0.02	0.09	0.03	1.76	1.51	0.00	0.26	0.04	0.01	12.50	0.01	0.62	2.01	0.03	44.79	0.09	4.99	0.03	0.01	98.00
MN-5	29.02	11.69	0.01	0.29	0.02	0.095	0.02	1.74	1.09	0.00	0.19	0.03	0.01	11.88	0.01	0.48	1.75	0.03	34.15	0.07	3.88	0.02	0.01	96.50
MN-6	16.76	18.89	0.01	0.29	0.02	0.07	0.02	1.43	1.20	0.00	0.21	0.03	0.01	15.28	0.01	0.49	1.10	0.02	35.42	0.07	3.81	0.02	0.02	95.17
MN-7	21.39	5.19	0.01	0.39	0.02	0.07	0.02	1.71	1.48	0.00	0.26	0.03	0.01	14.86	0.01	0.62	2.46	0.02	45.39	0.09	5.00	0.03	0.01	99.07
MN-8	18.38	19.22	0.01	0.33	0.02	0.07	0.01	1.64	1.40	0.03	0.24	0.03	0.01	8.91	0.01	0.56	1.29	0.02	38.92	0.08	4.59	0.03	0.01	95.82
MN-9A	20.26	14.09	0.01	0.35	0.00	0.07	0.02	1.45	0.92	0.00	0.20	0.03	0.00	16.29	0.00	0.49	2.01	0.03	35.98	0.07	3.52	0.03	0.06	95.89
MN-9B	19.70	13.70	0.01	0.34	0.00	0.06	0.02	1.37	0.91	0.00	0.19	0.03	0.00	17.94	0.00	0.47	1.89	0.04	34.97	0.07	3.53	0.03	0.08	95.35
MN-10	18.97	5.68	0.01	0.43	0.02	0.10	0.03	1.86	1.54	4.80	0.27	0.04	0.01	9.71	0.01	0.63	2.19	0.02	45.95	0.09	4.94	0.03	0.02	97.35
MN-11	17.76	10.65	0.00	0.33	0.02	0.08	0.01	1.59	1.30	10.04	0.22	0.03	0.01	8.58	0.01	0.52	1.94	0.02	37.97	0.06	4.20	0.02	0.02	95.39
MN-12	18.33	14.26	0.00	0.30	0.02	0.09	0.01	1.56	1.10	14.67	0.20	0.03	0.01	6.80	0.01	0.47	1.78	0.02	32.77	0.06	3.72	0.02	0.02	96.28
MN-13	17.52	5.09	0.01	0.35	0.02	0.08	0.02	1.81	1.40	11.15	0.25	0.03	0.01	7.87	0.01	0.59	2.16	0.02	43.00	0.08	4.42	0.03	0.02	95.94
MN-14	15.91	7.45	0.00	0.43	0.02	0.08	0.01	1.59	1.24	16.86	0.22	0.03	0.01	7.64	0.01	0.52	2.22	0.00	37.05	0.07	4.07	0.02	0.03	95.50
MN-15	17.79	4.15	0.00	0.39	0.02	0.09	0.01	1.67	1.41	0.17	0.27	0.03	0.01	17.53	0.01	0.63	3.08	0.02	44.52	0.08	4.69	0.03	0.03	96.64
MN-16	18.06	5.85	0.00	0.38	0.02	0.06	0.01	1.61	1.36	0.84	0.26	0.03	0.01	17.27	0.01	0.59	1.35	0.02	44.29	0.08	2.93	0.03	0.02	95.08
MN-17	18.15	0.38	0.00	5.96	0.04	0.07	0.03	1.67	1.54	0.00	0.26	0.03	0.01	15.63	0.02	0.61	2.48	0.04	47.30	0.08	5.14	0.03	0.02	99.50
MN-18	15.77	0.18	0.00	10.23	0.03	0.08	0.02	1.53	1.36	0.01	0.22	0.03	0.01	17.96	0.02	0.56	2.86	0.03	41.67	0.06	4.17	0.03	0.02	96.86
MN-19	14.48	0.42	0.00	13.54	0.02	0.09	0.02	1.56	1.30	0.46	0.27	0.03	0.01	20.80	0.01	0.50	1.17	0.02	38.14	0.06	4.10	0.02	0.02	97.07
MN-20	17.63	0.07	0.00	5.79	0.02	0.08	0.02	1.73	1.58	4.77	0.25	0.03	0.01	9.29	0.01	0.58	2.69	0.02	46.51	0.07	4.90	0.03	0.02	96.11
MN-21	15.88	0.06	0.00	11.62	0.02	0.09	0.02	1.66	1.38	10.48	0.28	0.03	0.01	9.01	0.01	0.55	1.74	0.02	41.30	0.06	4.02	0.03	0.03	98.32
MN-22	15.62	0.11	0.00	14.35	0.02	0.08	0.02	1.55	1.49	13.69	0.27	0.03	0.01	7.92	0.01	0.51	1.56	0.02	38.64	0.06	3.98	0.02	0.01	100.00
MN-23	19.19	0.07	0.00	11.70	0.02	0.09	0.03	1.83	1.44	0.16	0.26	0.04	0.01	9.89	0.01	0.61	2.60	0.03	46.44	0.07	4.91	0.03	0.02	99.46
MN-24	18.80	0.08	0.00	4.76	0.02	0.08	0.02	1.68	1.42	0.00	0.25	0.03	0.01	15.78	0.01	0.59	2.27	0.02	45.60	0.07	4.90	0.03	0.02	96.45
MN-25	15.97	0.04	0.00	6.30	0.02	0.08	0.02	1.62	1.26	0.14	0.23	0.03	0.01	21.08	0.01	0.56	1.87	0.03	42.26	0.07	4.34	0.03	0.02	96.01
MN-26	14.17	0.57	0.00	10.18	0.02	0.08	0.02	1.48	3.22	0.67	0.21	0.03	0.06	26.70	0.01	0.50	1.58	0.03	37.75	0.06	3.84	0.02	0.01	101.22

Sample ID	Al_2O_3	B_2O_3	BaO	CaO	Ce_2O_3	Cr_2O_3	CuO	Fe_2O_3	K_2O	Li_2O	MgO	MnO	MoO_3	Na_2O	Nd_2O_3	NiO	P_2O_5	PbO	SiO_2	TiO_2	U_3O_8	ZnO	ZrO_2	Oxide Sum
MHSi-1	19.93	7.83	0.01	0.42	0.02	0.08	0.02	1.77	2.01	0.02	0.24	0.04	0.01	9.71	0.01	0.51	1.60	0.02	47.81	0.08	3.82	0.03	0.02	96.02
MHSi-2	19.11	15.12	0.01	0.40	0.02	0.08	0.02	1.66	1.89	0.00	0.22	0.04	0.01	9.05	0.01	0.43	2.10	0.02	45.24	0.08	3.52	0.04	0.01	99.12
MHSi-3	16.97	23.46	0.01	0.38	0.02	0.08	0.03	1.58	1.69	0.01	0.21	0.04	0.01	7.99	0.01	0.44	1.55	0.02	41.18	0.07	3.18	0.03	0.01	98.97
MHSi-4	21.95	5.65	0.02	0.42	0.04	0.07	0.03	1.74	1.97	0.00	0.24	0.05	0.01	11.56	0.02	0.48	2.44	0.03	50.12	0.09	3.79	0.03	0.01	100.77
MHSi-5	19.36	11.95	0.01	0.38	0.02	0.08	0.03	1.68	1.83	0.00	0.22	0.04	0.01	13.58	0.01	0.62	1.82	0.03	44.54	0.08	3.39	0.03	0.01	99.72
MHSi-6	19.43	15.79	0.01	0.33	0.02	0.08	0.02	1.67	1.66	0.02	0.20	0.04	0.01	13.30	0.01	0.40	2.19	0.02	40.51	0.07	3.03	0.03	0.09	98.94
MHSi-11	24.35	7.15	0.01	0.39	0.02	0.09	0.03	2.01	1.74	6.82	0.21	0.05	0.01	7.27	0.01	0.42	2.34	0.03	44.54	0.08	3.36	0.03	0.04	100.99
MLSi-1	20.70	11.16	0.01	0.33	0.07	0.08	0.03	1.55	1.13	0.40	0.24	0.03	0.01	12.26	0.04	0.72	1.56	0.04	38.99	0.08	5.66	0.03	0.04	95.17
MLSi-2	19.26	23.20	0.01	0.41	0.12	0.09	0.05	1.48	0.97	0.07	0.22	0.03	0.01	10.50	0.06	0.66	1.17	0.06	35.35	0.08	4.89	0.04	0.03	98.75
MLSi-3	15.44	32.62	0.01	0.25	0.08	0.08	0.02	1.43	0.87	0.06	0.19	0.03	0.01	9.43	0.04	0.60	1.27	0.04	31.44	0.07	4.32	0.02	0.02	98.36
MLSi-4	25.04	8.78	0.01	0.31	0.14	0.08	0.03	1.48	1.01	0.02	0.23	0.03	0.01	13.60	0.07	0.69	2.01	0.06	37.86	0.08	5.24	0.03	0.03	96.86
MLSi-5	20.94	14.32	0.01	0.30	0.08	0.09	0.07	1.53	0.94	0.04	0.22	0.03	0.01	13.45	0.04	0.67	1.96	0.04	36.45	0.08	4.55	0.09	0.02	95.94
MLSi-7	24.87	5.73	0.01	0.37	0.02	0.07	0.02	1.49	0.98	0.00	0.24	0.03	0.01	17.15	0.01	0.68	1.13	0.03	37.79	0.08	5.45	0.03	0.02	96.22
MLSi-8	20.91	15.67	0.01	0.23	0.06	0.18	0.02	1.34	0.77	0.01	0.18	0.03	0.01	22.12	0.03	0.78	0.45	0.02	35.89	0.06	3.57	0.02	0.02	102.39
MLSi-9	22.18	14.47	0.01	0.25	0.02	0.07	0.02	1.26	0.70	0.00	0.18	0.03	0.01	27.09	0.01	0.51	0.67	0.02	28.61	0.06	3.88	0.02	0.01	100.08
MLSi-11	21.33	9.34	0.01	0.32	0.02	0.08	0.02	1.51	0.98	9.30	0.21	0.03	0.01	9.23	0.01	0.75	1.12	0.02	39.90	0.07	5.25	0.02	0.02	99.56

Table 5-3. M-Area Glasses: Fabrication Methods* and Homogeneity

Sample ID	Melt Temp. (°C)	Type of Glass	Analytic Tool Used	Crystalline Phase Separation	Observed Amorphous Phase Separation	Predicted Amorphous Phase Separation [38]
MN-1	1400	Na Borosilicate	XRD	Amorphous	---	No
MN-2	1260	Na Borosilicate	XRD/SEM	Amorphous	No	No
MN-3	1150	Na Borosilicate	XRD/SEM	Amorphous	Yes	Yes
MN-4	1400	Na Borosilicate	XRD	Amorphous	---	No
MN-5	1300	Na Borosilicate	XRD	$\alpha\text{-}Al_2O_3$	---	No
MN-6	1150	Na Borosilicate	XRD	Amorphous	---	No
MN-7	1400	Na Borosilicate	XRD	Amorphous	---	No
MN-8	1150	Na Borosilicate	XRD/SEM	Amorphous	No	No
MN-9A	1200	Na Borosilicate	XRD	Amorphous	---	No
MN-9B	1200	Na Borosilicate	XRD	Amorphous	---	No
MN-10	1200	Na-Li Borosilicate	XRD	Li_3PO_4	---	No
MN-11	1150	Na-Li Borosilicate	XRD	Li_3PO_4	---	No
MN-12	1150	Na-Li Borosilicate	XRD	Amorphous	---	No
MN-13	1150	Na-Li Borosilicate	XRD	Amorphous	---	No
MN-14	1150	Na-Li Borosilicate	XRD/SEM	$Li_{3.2}Mg_{0.4}SiO_4$	Yes	Yes
MN-15	1200	Na Borosilicate	XRD	Amorphous	---	No
MN-16	1150	Na Borosilicate	XRD	Amorphous	---	No
MN-17	1350	SLS	XRD	Li_3PO_4, $Ca_3Mg(SiO_4)_2$	---	No
MN-18	1150	SLS	XRD	Amorphous	---	No
MN-19	1150	SLS	XRD	Amorphous	---	No
MN-20	1200	SLLS	XRD	Li_3PO_4	---	No
MN-21	1150	SLLS	XRD	Amorphous	---	No
MN-22	1150	SLLS	XRD	$Li_{2.8}Mg_{0.6}SiO_4$	---	No
MN-23	1400	SLS	XRD	$Na_2Ca_3Al_2(PO_4)_2(SiO_4)_2$	---	No
MN-24	1400	SLS	XRD	Li_3PO_4	---	No
MN-25	1150	SLS	XRD	Amorphous	---	No
MN-26	1150	SLS	XRD	$Na(HCO_3)_2$	---	No
MHSi-1	1400	Na Borosilicate	XRD	Amorphous	---	No
MHSi-2	1300	Na Borosilicate	XRD	Amorphous	---	No
MHSi-3	1150	Na Borosilicate	XRD/SEM	Amorphous	No	No
MHSi-4	1400	Na Borosilicate	XRD	Amorphous	---	No
MHSi-5	1150	Na Borosilicate	XRD	Amorphous	---	No
MHSi-6	1200	Na Borosilicate	XRD	Amorphous	---	No
MHSi-11	1350	Na-Li Borosilicate	XRD	$LiAlO_2$	---	No
MLSi-1	1300	Na Borosilicate	XRD	Amorphous	---	No
MLSi-2	1150	Na Borosilicate	XRD	Amorphous	---	No
MLSi-3	1400	Na Borosilicate	XRD/SEM	Amorphous	No	No
MLSi-4	1150	Na Borosilicate	XRD	Amorphous	---	No
MLSi-5	1150	Na Borosilicate	XRD	Amorphous	---	No
MLSi-7	1400	Na Borosilicate	XRD	Amorphous	---	No
MLSi-8	1150	Na Borosilicate	XRD	Amorphous	---	No
MLSi-9	1150	Na Borosilicate	XRD	Amorphous	---	No
MLSi-11	1150	Na-Li Borosilicate	XRD	Amorphous	---	No

* all melted and quenched in high purity alumina crucibles

Table 5-4. ASTM C1285 (PCT) Average Durability Responses at 90°C in ASTM Type I Water

Sample ID	Mean pH	$\log_{10}$[NL(i) g/L]					
		B	Li	Na	Si	K	U
MN-1	8.66	-0.69	-0.31	-0.57	-0.77	-0.99	-1.57
MN-2	7.81	1.15	0.85	0.52	-0.70	-0.48	-0.98
MN-3	6.78	1.78	1.06	1.13	-0.49	0.17	-1.71
MN-4	8.36	-0.43	-0.89	-0.44	-0.60	-1.00	-1.01
MN-5	8.74	-0.46	-1.32	-0.38	-0.62	-0.78	-1.26
MN-6	9.03	1.14	0.99	0.88	-0.85	0.13	-1.06
MN-7	9.32	-0.48	-1.32	-0.35	-0.56	-0.90	-1.00
MN-8	8.11	1.03	-0.15	0.52	-0.73	-0.46	-0.94
MN-9A	9.80	0.8	-0.31	0.73	-0.69	0.17	-0.76
MN-9B	9.80	0.82	-0.01	0.69	-0.68	0.17	-0.76
MN-10	11.51	-1.37	-3.35	0.46	-0.46	-0.17	-1.28
MN-11	11.17	0.15	0.12	0.02	-0.18	-0.56	-0.72
MN-12	11.86	0.77	0.74	0.57	0.18	-0.08	-0.10
MN-13	11.54	0.09	0.11	0.08	-0.13	-0.39	-0.68
MN-14	11.94	0.67	0.68	0.59	0.30	-0.08	-0.05
MN-15	10.32	-0.34	-0.93	-0.12	-0.48	-0.82	-1.05
MN-16	10.02	0.01	-0.47	0.03	-0.54	-0.62	-0.89
MN-17	10.09	-0.87	-1.32	-0.36	-0.79	-0.91	-1.88
MN-18	10.72	-0.16	-1.59	0.08	-0.66	-0.52	-1.37
MN-19	11.02	-0.14	0.01	0.28	-0.52	-0.31	-1.19
MN-20	10.12	-1.24	-0.34	-0.38	-0.64	-0.69	-1.81
MN-21	10.94	-0.3	0.16	0.08	-0.49	-0.37	-1.15
MN-22	11.08	-0.12	0.51	0.35	-0.12	-0.20	-0.7
MN-23	10.01	-1.32	-1.23	-0.65	-1.09	-1.02	-2.72
MN-24	10.33	-0.71	-1.32	-0.12	-0.67	-0.81	-2.68
MN-25	10.82	-0.68	-0.55	0.33	-0.25	-0.17	-1.05
MN-26	11.34	-0.36	0.73	0.94	0.08	0.19	-0.22
MHSi-1	8.39	-0.71	-2.17	-0.55	-0.74	-1.12	-1.50
MHSi-2	8.50	-0.31	-1.19	-0.42	-0.71	-1.26	-1.18
MHSi-3	7.76	1.32	0.43	0.66	-0.71	-0.38	-0.95
MHSi-4	8.53	-0.63	-1.62	-0.49	-0.69	-1.10	-1.15
MHSi-5	8.70	-0.33	-1.32	-0.34	-0.63	-0.91	-0.90
MHSi-6	8.73	0.31	-2.28	0.11	-0.60	-0.71	-0.70
MHSi-11	10.38	-0.29	-0.20	-0.53	-0.41	-0.55	-0.70
MLSi-1	8.59	-0.5	-0.16	-0.49	-0.60	-0.76	-0.92
MLSi-2	8.39	1.08	0.86	0.61	-0.76	-0.21	-1.10
MLSi-3	7.02	1.87	1.61	1.42	-0.47	0.66	-1.41
MLSi-4	8.69	-0.35	-2.32	-0.31	-0.56	-0.64	-0.81
MLSi-5	9.01	0.48	0.03	0.30	-0.62	-0.35	-0.77
MLSi-7	9.33	-0.14	-1.62	-0.12	-0.47	-0.49	-0.76
MLSi-8	9.31	1.06	-0.57	0.63	-0.84	0.22	-1.24
MLSi-9	10.20	0.95	-1.32	0.73	-0.79	0.39	-1.52
MLSi-11	11.28	0.41	0.29	0.25	-0.22	-0.33	-1.07

5.5.2 Confirmation of 25°C Dissolution Rates for the E-Area Performance Assessment

Whited et. Al. [23,24,25] estimated the release of uranium to the SRS groundwater from the HLW literature. The 90°C long term (84-980 days) static dissolution data were tabulated in both deionized water and Yucca Mountain J13 groundwater for a wide variety of HLW glasses from Europe (SM527 and R7T7), the United States (SRL-131, 165, 200, 202), and a statistical study related to DWPF glasses [26]. The average long term release rate, expressed as NR_i was calculated and used in conjunction with an E_a of dissolution to generate a leach rate at 25°C for use in determining if the M-Area glasses, once delisted, would pass the SRS burial ground PA. The E_a of dissolution for borosilicate glasses of 75 KJ/mole was used from White [28] for dissolution of a nuclear waste glass in ASTM Type I water. This was confirmed by more recent (1998) work of Dove [29] for the dissolution of pure SiO_2 in ASTM Type I water which gave an E_a of dissolution of 78.9 KJ/mole. This assessment assumed that uranium was released at a similar rate as boron as a worst case scenario even though it is likely that uranium release would be solubility limited while boron release would not be solubility limited. [23,24,25]

Confirmatory, PCT-B tests were performed in SRS E-Area ground water from well #94 at 25°C at six different SA/V ratios at time durations of 14, 28, and 42 days yielding the (SA/V)•t values given in Table 4-4.

Whited tested the eight different (SA/V)•t ratios given in Table 4-4. This required large quantities of glass. Only three homogeneous glasses were available in sufficient quantity to be tested (MN-12, MN-13 and MHSi-5) at the time at which the study was initiated. The positions of these glasses in the alkali borosilicate system are shown in Figure 7. Glass MN-12 was at 70% waste loading and made with a 50:50 two component frit of Li_2O and B_2O_3. Glass MN-13 was at 85% waste loading and made with a two-component frit of 70% Li_2O and 30 wt% B_2O_3. Glass MHSi5 was at 80% waste loading and made with a two-component frit of 30 wt% Na_2O and 70 wt% B_2O_3. Of these three glasses MN-12 (at 70 wt% waste loading) was the least durable and the 80-85% waste loaded MHSi-5 and MN-13 glasses were of comparable durability even though the ratio of alkali (Li_2O in the case of MN-12 and Na_2O in the case of MHSi-5) were highly variable.

For the set of three glasses used as confirmation of the 90°C to 25°C extrapolation, the impacts of glass formulation can be examined since Li_2O, Na_2O, SiO_2 and B_2O_3 were widely varied. Both the B release and the U release seem to be positively correlated (Figure 8a and c) with the Li/Si cation ratio within a narrow composition range, i.e. more Li or less Si makes the glass more durable. Likewise, the durability of the glass in terms of the leach rate release of B and U is negatively correlated with the Na/Al cation ratio (Figure 8b and d), i.e. the most durable glasses are formed when the cation Na/Al or cation Na/(Al+Si) ratio is high.

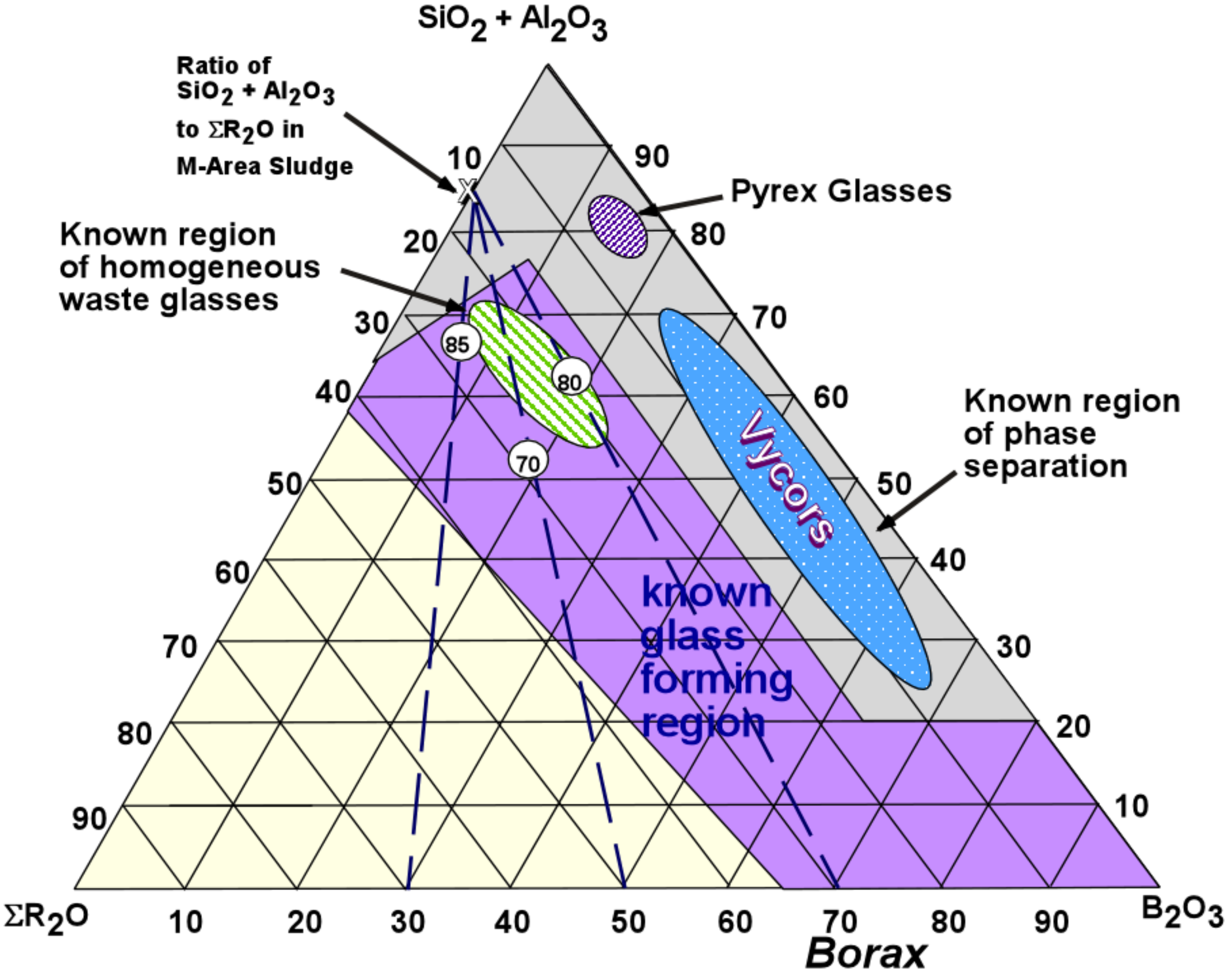
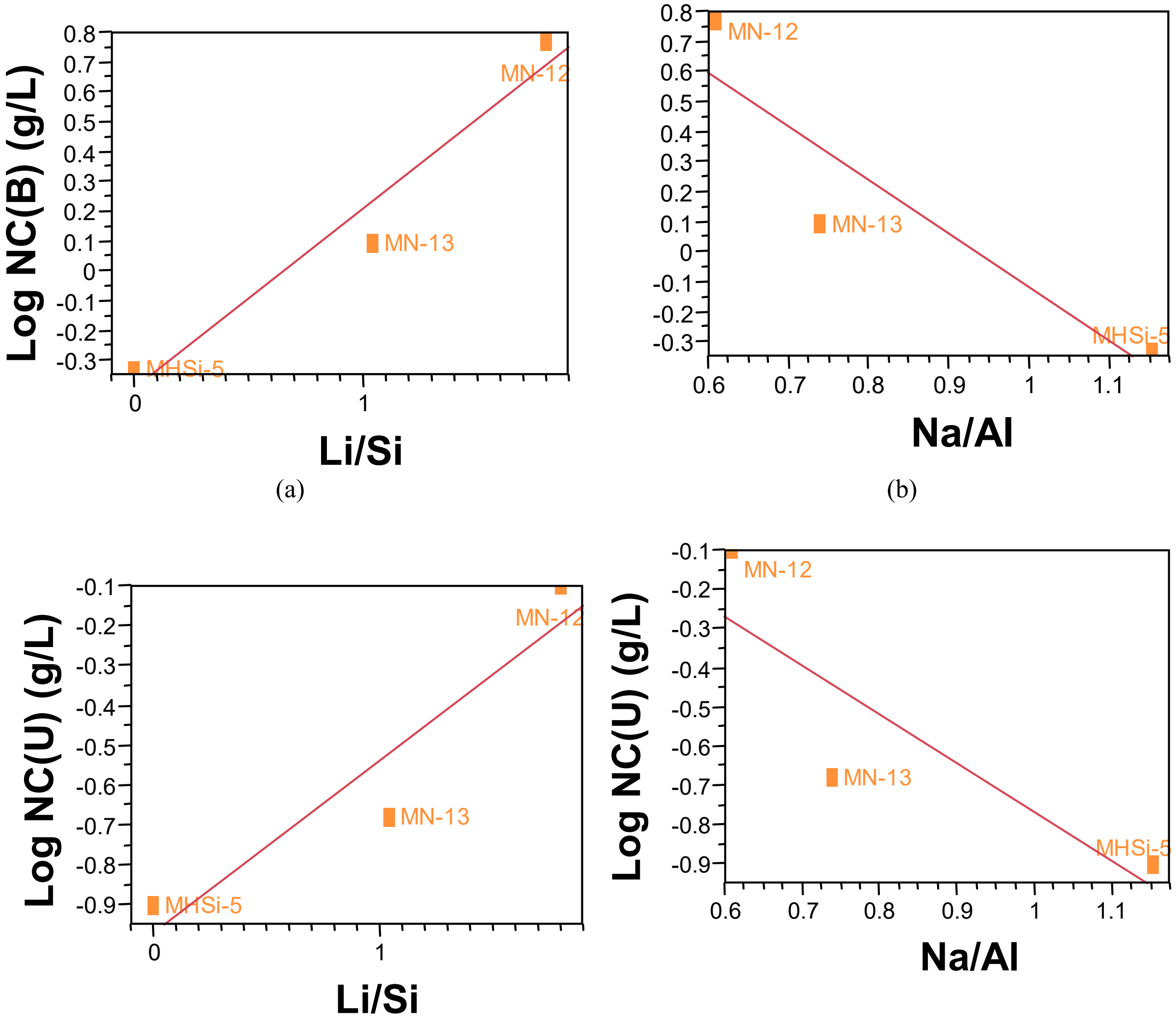


Figure 7. **Positions of MN-12 (70 wt % waste loading), MN-13 (85% waste loaded), and MHSi-5 (80% waste loaded) plotted in their representative positions in the R_2O-B_2O_3-SiO_2 system where R can be Li or Na.**



(a) (b)

(c) (d)

Figure 8. Dependency of 25°C M-Area Glass Durability on Composition.

Moreover, it is noted that for the three glasses studied at 25°C that the log NC_B and log NC_U leaching are linearly related but that the B is released at a much more rapid rate (above the dashed 1:1 correspondence line) in Figure 9. This can also be seen in Figure 8a and b where the B release is greater than the U release in Figure 8c and d. So, the use of B at 90°C to bound U release at 25°C can be justified. In all cases (Figure 8 and Figure 9) MHSi-5 is less durable than MN-13 which is less durable than MN-12.

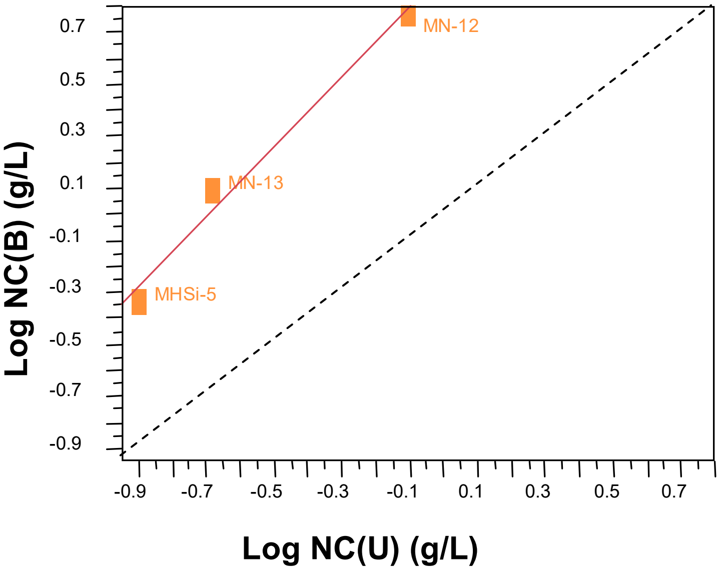


Figure 9. The relative relationship between normalized PCT releases at 90°C for the glasses studied at 25°C and different SA/V ratios. Note that while the B and U releases are linear, the rate of the B release far exceeds the U release. The dashed line indicates the position of the relative releases if they were equal.

The average normalized leaching rate of radionuclide i, NR_i, can be calculated using

$$NR_i = \frac{NL_i}{t},$$

where t is the duration of the test in days and the NL_i is as defined in Equation 2.

A plot of NR_i in g/m^2•day vs time (in cumulative years) follows a square root dependency with time if the leaching is occurring as an ion exchange mechanism rather than by a linear hydrolysis mechanism. This is because the SA/V term in Equation 2 is related to the test duration by a square root dependency. It can be shown that the size fractions and amounts of sample and leachant varied in the E-Area groundwater (see Table 4-4) fall within this square root dependency (Figure 10). In addition, Figure 10 demonstrates that none of the SA/V combinations used for the E-Area ground water testing were in the range of 20,000 m^{-1} where the leaching mechanism may change due to the participation of crystallites formed from back reactions and saturation in the leachate. [39,40]

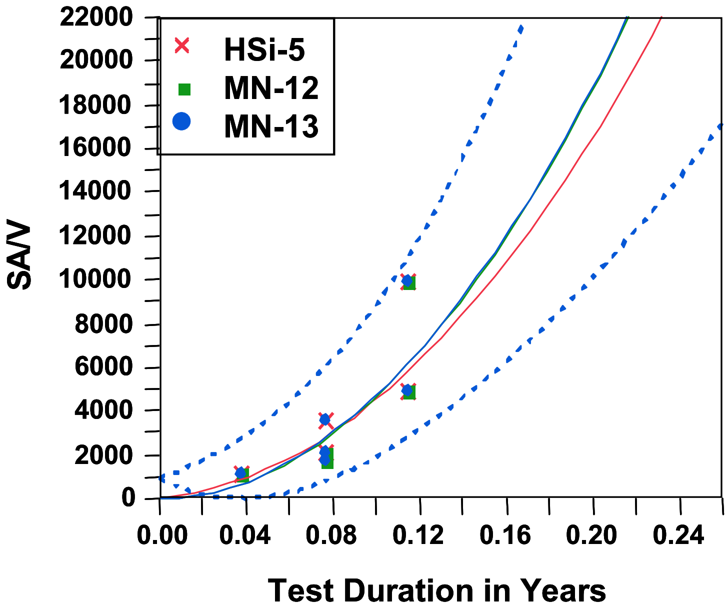


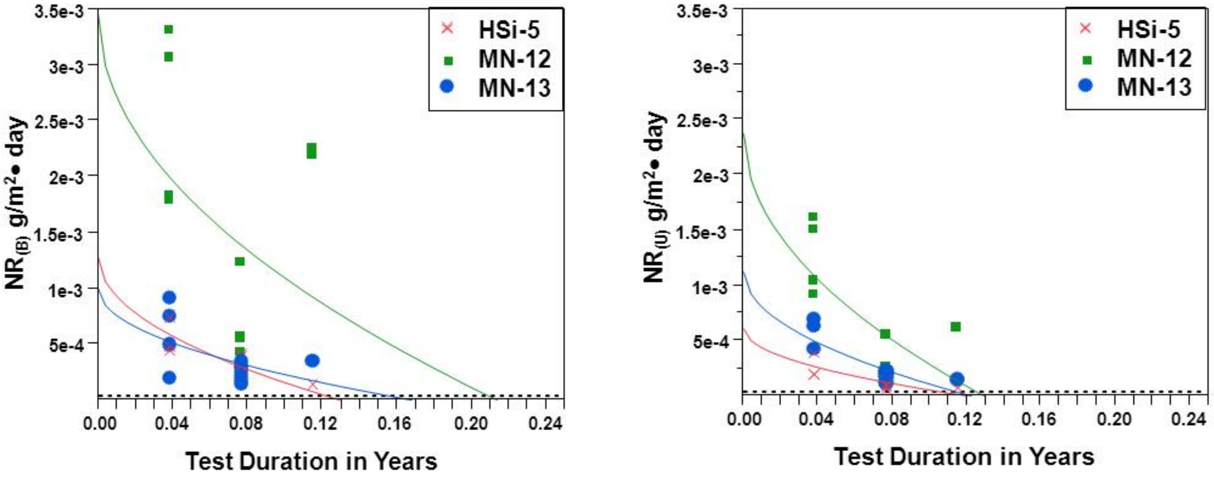
Figure 10. Relationship of the SA/V and time durations in the 25°C E-Area Groundwater Tests.

Solid lines are the square root correlation for each glass (HSi-5, MN-12 and MN-13) but the MN-12 and MN-13 lines overlap so the 95% error bars were shown for MN-13 as the dotted lines.

The data of Whited [23,24], using an approximate 75 kcal/mole activation energy for M-Area glass dissolution, states "if M-Area waste glass is of above average durability compared with the reference glasses, those from which the activation energy was derived, the allowable leach rate of NR_B = 2.7 E-05 g/m^2•day determined by performance assessment calculations should be met, and the performance objective (maximum uranium concentration of 20 µg/L in the groundwater) for trench disposal should be satisfied."

To graphically illustrate this by a different mathematical treatment, one can plot the NR_i as the ordinate in g/m^2•day versus test duration time (in cumulative days or years) as the abscissa and fit this to a square root dependency which demonstrates that the leaching is via diffusion (Figure 11). This is an intrinsic characteristic of a diffusion-controlled process rather than a mechanism of glass matrix dissolution via hydrolysis. The latter mechanism would show a constant leaching rate.

The point at which the square root dependency for diffusion crosses the ordinate axis at the value of NR_B or NR_U = 2.7 E-05 g/m^2•day is the length of time it will take for the glass to reach the desired long-term rate once exposed to the groundwater. After that time period the long-term rate will be less than the 2.7 E-05 g/m^2•day. The NR_i vs test duration time plots for NR_B and NR_U are shown in Figure 11 fit with a square root dependency. The dashed horizontal line in Figure 11 represents the SRS burial ground performance objective for the maximum concentration of uranium in groundwater. The normalized release (NR_i in g/m^2day) vs. cumulative time, which defines the final long term rate, decreases asymptotically to values <2.7 E-05 g/m^2•day in 44-80 days for B release (Figure 11a) and ~44 days for U release (Figure 11b). Since the M-Area glass is sealed in canisters, dissolution will not be uniform but will occur only as the canister degrades. In addition, there is a large uncertainty and a large amount of scatter in the E-area groundwater analyses since it has subsequently been determined that leaching in the 20°C range creates such minimal concentrations of species in solution, compared to leaching at 40°C and 90°C, that measurements are usually at the detection limit of the analytic instrument. This is why leaching analyses are normally performed at 40°C or above. [41]



(a) (b)

Figure 11. Plot of the 25°C E-Area Groundwater Testing Fit to A Square Root Dependency to verify that the B and U leach by diffusion.

The dashed horizontal line is the SRS E-Area trench performance objective for the maximum concentration of uranium in groundwater.

Table 5-5. M-Area PCT's at 25°C in E-Area Groundwater*,†

Sample ID	Size ID	Test Duration (Days)	Test Duration (Years)	pH	fi(B)	fi(Na)	fi(U)	B (ppm)	Na (ppm)	U (ppm)	Li (ppm)	Al (ppm)	Fe (ppm)	Si (ppm)	Mg (ppm)	Ca (ppm)	Zn (ppm)	SA/V (m^2/L)	SA/V*t (day/m^{-1})
HSi-5	A	14	0.04	9.29	0.037	0.1007	0.0287	0.261	6.533	0.079	0.004	0.027	0.003	2.840	0.355	2.432	0.179	1043	14602
HSi-5	A	14	0.04	9.25	0.037	0.1007	0.0287	0.239	6.503	0.082	0.004	0.027	0.003	2.683	0.349	2.421	0.080	1043	14602
MN-12	A	14	0.04	9.58	0.044	0.0504	0.0316	1.175	6.242	0.42	3.220	1.502	0.003	3.306	0.226	1.171	0.071	1043	14602
MN-12	A	14	0.04	9.60	0.044	0.0504	0.0316	1.149	6.209	0.48	3.228	1.411	0.003	3.324	0.227	1.148	0.171	1043	14602
MN-13	A	14	0.04	9.70	0.016	0.0584	0.0375	0.043	2.747	0.23	0.874	0.027	0.003	1.432	0.17	1.114	0.061	1043	14602
MN-13	A	14	0.04	9.65	0.016	0.0584	0.0375	0.112	5.582	0.23	1.699	0.264	0.013	3.087	0.337	2.231	0.175	1043	14602
HSi-5	B	14	0.04	8.79	0.037	0.1007	0.0287	0.414	7.728	0.16	0.047	0.027	0.003	3.049	0.345	2.117	0.172	1043	14602
HSi-5	B	14	0.04	8.85	0.037	0.1007	0.0287	0.397	7.642	0.16	0.033	0.027	0.003	3.024	0.339	2.087	0.130	1043	14602
MN-12	B	14	0.04	9.73	0.044	0.0504	0.0316	2.142	7.609	0.74	5.832	2.899	0.003	4.823	0.087	0.325	0.152	1043	14602
MN-12	B	14	0.04	9.71	0.044	0.0504	0.0316	1.982	7.765	0.69	6.016	2.334	0.003	3.869	0.115	0.402	0.191	1043	14602
MN-13	B	14	0.04	9.74	0.016	0.0584	0.0375	0.209	6.164	0.38	2.824	0.477	0.003	3.651	0.298	1.713	0.069	1043	14602
MN-13	B	14	0.04	9.71	0.016	0.0584	0.0375	0.173	6.072	0.34	2.817	0.375	0.003	3.852	0.286	1.700	0.113	1043	14602
HSi-5	E	28	0.08	7.38	0.037	0.1007	0.0287	0.319	6.824	0.09	0.030	0.027	0.003	2.942	0.342	2.426	0.108	2085	58380
HSi-5	E	28	0.08	7.4	0.037	0.1007	0.0287	0.316	6.954	0.08	0.026	0.027	0.038	3.003	0.352	2.512	0.091	2085	58380
MN-12	E	28	0.08	9.50	0.044	0.0504	0.0316	1.434	6.658	0.49	3.903	2.289	0.017	3.553	0.2203	1.025	0.099	2085	58380
MN-12	E	28	0.08	9.45	0.044	0.0504	0.0316	1.459	6.652	0.48	3.946	2.222	0.012	3.574	0.201	1.025	0.075	2085	58380
MN-13	E	28	0.08	9.28	0.016	0.0584	0.0375	0.145	5.645	0.25	1.952	0.561	0.018	3.324	0.322	2.233	0.085	2085	58380
MN-13	E	28	0.08	9.29	0.016	0.0584	0.0375	0.130	5.589	0.25	1.838	0.514	0.015	3.285	0.322	2.299	0.071	2085	58380
HSi-5	F	28	0.08	7.98	0.037	0.1007	0.0287	0.498	8.139	0.15	0.065	0.027	0.018	4.240	0.324	2.041	0.103	2082	58296
HSi-5	F	28	0.08	7.94	0.037	0.1007	0.0287	0.534	8.456	0.13	0.045	0.027	0.014	3.401	0.338	2.138	0.114	2082	58296
MN-12	F	28	0.08	9.80	0.044	0.0504	0.0316	3.145	8.889	1.01	7.558	6.062	0.018	6.358	0.047	0.209	0.075	2082	58296
MN-12	F	28	0.08	9.76	0.044	0.0504	0.0316	1.392	6.701	0.48	3.946	1.879	0.12	3.388	0.199	0.980	0.069	2082	58296
MN-13	F	28	0.08	9.58	0.016	0.0584	0.0375	0.227	6.369	0.48	3.240	0.908	0.009	3.915	0.278	1.732	0.068	2082	58296
MN-13	F	28	0.08	9.60	0.016	0.0584	0.0375	0.186	6.065	0.37	2.696	0.644	0.049	3.578	0.307	2.025	0.080	2082	58296
HSi-5	G	28	0.08	10.86	0.037	0.1007	0.0287	18.145	16.833	5.00	26.314	29.42	1.037	35.575	0.038	0.130	0.081	1750	49000
HSi-5	G	28	0.08	10.88	0.037	0.1007	0.0287	17.68	16.19	4.7	25.561	28.078	0.920	33.785	0.026	0.067	0.081	1750	49000
MN-12	G	28	0.08	8.83	0.044	0.0504	0.0316	0.920	3.488	0.2	0.062	0.951	0.010	2.413	0.010	0.64	0.074	1750	49000
MN-12	G	28	0.08	8.75	0.044	0.0504	0.0316	0.923	3.417	0.2	0.065	0.992	0.003	2.452	0.007	0.44	0.054	1750	49000
MN-13	G	28	0.08	9.63	0.016	0.0584	0.0375	0.260	6.172	0.41	2.994	0.945	0.057	4.182	0.290	1.865	0.068	1750	49000

Sample ID	Size ID	Test Duration (Days)	Test Duration (Years)	pH	fi(B)	fi(Na)	fi(U)	B (ppm)	Na (ppm)	U (ppm)	Li (ppm)	Al (ppm)	Fe (ppm)	Si (ppm)	Mg (ppm)	Ca (ppm)	Zn (ppm)	SA/V (m^2/L)	SA/V*t (day/m^{-1})
MN-13	G	28	0.08	9.67	0.016	0.0584	0.0375	0.220	6.071	0.39	2.751	0.914	0.025	4.084	0.295	2.016	0.069	1750	49000
HSi-5	H	28	0.08	8.72	0.037	0.1007	0.0287	1.488	5.731	0.38	0.105	1.167	0.035	3.425	0.017	0.119	0.084	3500	98000
HSi-5	H	28	0.08	8.72	0.037	0.1007	0.0287	1.408	5.418	0.36	0.104	1.086	0.011	3.136	0.014	0.084	0.066	3500	98000
MN-12	H	28	0.08	10.88	0.044	0.0504	0.0316	26.823	22.983	0.004	38.579	39.246	1.094	43.159	0.035	0.154	0.101	3500	98000
MN-12	H	28	0.08	10.86	0.044	0.0504	0.0316	18.611	17.033	0.004	27.004	29.254	0.999	35.964	0.022	0.065	0.087	3500	98000
MN-13	H	28	0.08	10.25	0.016	0.0584	0.0375	0.456	7.503	0.68	5.046	1.934	0.018	5.521	0.187	1.134	0.083	3500	98000
MN-13	H	28	0.08	10.30	0.016	0.0584	0.0375	1.262	5.871	1.6	5.921	7.685	0.144	14.145	0.014	0.053	0.077	3500	98000
HSi-5	I	42	0.12	8.59	0.037	0.1007	0.0287	1.027	11.949	0.43	0.131	0.418	0.025	3.832	0.226	1.024	0.082	4938	207396
HSi-5	I	42	0.12	8.62	0.037	0.1007	0.0287	0.995	11.726	0.43	0.123	0.461	0.018	3.735	0.218	0.974	0.112	4938	207396
MN-12	I	42	0.12	10.90	0.044	0.0504	0.0316	20.232	23.218	4.01	31.194	35.435	0.625	33.731	0.040	0.142	0.106	4938	207396
MN-12	I	42	0.12	10.88	0.044	0.0504	0.0316	20.557	23.486	4.01	31.400	35.535	0.680	34.151	0.063	0.222	0.127	4938	207396
MN-13	I	42	0.12	10.52	0.016	0.0584	0.0375	1.093	10.357	1.2	8.962	6.668	0.067	11.152	0.052	0.290	0.082	4938	207396
MN-13	I	42	0.12	10.55	0.016	0.0584	0.0375	1.100	10.469	1.1	9.081	6.866	0.056	11.327	0.051	0.292	0.085	4938	207396
HSi-5	J	42	0.12	8.81	0.037	0.1007	0.0287	0.559	8.226	0.16	0.117	0.188	0.017	3.476	0.334	2.20	0.078	9876	414792
HSi-5	J	42	0.12	8.55	0.037	0.1007	0.0287	1.998	16.558	0.85	0.214	0.995	0.048	4.772	0.048	0.176	0.091	9876	414792
MN-12**	J	42	0.12	10.00	0.044	0.0504	0.0316	5.387	10.995	1.7	10.962	11.736	0.116	11.421	0.018	0.106	0.030	9876	414792
MN-13**	J	42	0.12	10.33	0.016	0.0584	0.0375	0.84	9.159	1.1	7.968	4.607	0.035	8.607	0.078	0.457	0.081	9876	414792

*The data that is shaded was not used in the plots of durability in E-Area groundwater leaching as the values would be negative after blank correction to the composition of the E-Area groundwater

† sets C and D were cancelled due to funding issues

**no sample

Table 5-5. (Continued with NLi's)

Sample ID	Size ID	Test Duration (Days)	Test Duration (Years)	SA/V (m^2/L)	SA/V*t (day/m^{-1})	NLi(B) (g/m^2)	NLi(Na) (g/m^2)	NLi(U) (g/m^2)	NC(B) (g/L)	NC(Na) (g/L)	NC(U) (g/L)	NRi (B) (g/m^2●day)	NRi(Na) (g/m^2●day)	NRi(U) (g/m^2●day)
HSi-5	A	14	0.04	1043	14602	6.76E-03	1.54E-02	2.64E-03	7.05	16.09	2.75	4.83E-04	1.10E-03	1.89E-04
HSi-5	A	14	0.04	1043	14602	6.19E-03	1.51E-02	2.74E-03	6.46	15.79	2.86	4.42E-04	1.08E-03	1.96E-04
MN-12	A	14	0.04	1043	14602	2.55E-02	2.53E-02	1.27E-02	26.64	26.39	13.29	1.82E-03	1.81E-03	9.10E-04
MN-12	A	14	0.04	1043	14602	2.49E-02	2.47E-02	1.46E-02	25.96	25.79	15.19	1.78E-03	1.77E-03	1.04E-03
MN-13	A	14	0.04	1043	14602	2.61E-03	#	5.88E-03	2.72	#	6.13	1.86E-04	#	4.20E-04
MN-13	A	14	0.04	1043	14602	6.79E-03	1.10E-02	5.88E-03	7.09	11.47	6.13	4.85E-04	7.86E-04	4.20E-04
HSi-5	B	14	0.04	1043	14602	1.07E-02	2.68E-02	5.35E-03	11.19	28.00	5.57	7.66E-04	1.92E-03	3.82E-04
HSi-5	B	14	0.04	1043	14602	1.03E-02	2.60E-02	5.35E-03	10.73	27.11	5.57	7.35E-04	1.86E-03	3.82E-04
MN-12	B	14	0.04	1043	14602	4.63E-02	5.14E-02	2.25E-02	48.31	53.57	23.42	3.31E-03	3.67E-03	1.60E-03
MN-12	B	14	0.04	1043	14602	4.29E-02	5.44E-02	2.09E-02	44.70	56.75	21.84	3.06E-03	3.89E-03	1.50E-03
MN-13	B	14	0.04	1043	14602	1.27E-02	2.05E-02	9.72E-03	13.23	21.40	10.13	9.06E-04	1.47E-03	6.94E-04
MN-13	B	14	0.04	1043	14602	1.05E-02	1.90E-02	8.69E-03	10.95	19.86	9.07	7.50E-04	1.36E-03	6.21E-04
HSi-5	E	28	0.08	2085	58380	4.14E-03	9.10E-03	1.50E-03	8.62	18.97	3.14	1.48E-04	3.25E-04	5.37E-05
HSi-5	E	28	0.08	2085	58380	4.10E-03	9.72E-03	1.34E-03	8.54	20.26	2.79	1.46E-04	3.47E-04	4.77E-05
MN-12	E	28	0.08	2085	58380	1.55E-02	1.67E-02	7.44E-03	32.28	34.72	15.51	5.53E-04	5.95E-04	2.66E-04
MN-12	E	28	0.08	2085	58380	1.58E-02	1.66E-02	7.29E-03	32.96	34.52	15.19	5.65E-04	5.91E-04	2.60E-04
MN-13	E	28	0.08	2085	58380	4.55E-03	6.08E-03	3.20E-03	9.49	12.67	6.67	1.63E-04	2.17E-04	1.14E-04
MN-13	E	28	0.08	2085	58380	3.95E-03	5.58E-03	3.20E-03	8.23	11.64	6.67	1.41E-04	1.99E-04	1.14E-04
HSi-5	F	28	0.08	2082	58296	6.46E-03	1.54E-02	2.51E-03	13.46	32.08	5.23	2.31E-04	5.50E-04	8.97E-05
HSi-5	F	28	0.08	2082	58296	6.93E-03	1.69E-02	2.18E-03	14.43	35.25	4.53	2.48E-04	6.05E-04	7.77E-05
MN-12	F	28	0.08	2082	58296	3.42E-02	3.79E-02	1.54E-02	71.11	78.97	31.96	1.22E-03	1.35E-03	5.48E-04
MN-12	F	28	0.08	2082	58296	1.51E-02	1.71E-02	7.30E-03	31.38	35.52	15.19	5.38E-04	6.09E-04	2.61E-04
MN-13	F	28	0.08	2082	58296	6.99E-03	1.20E-02	6.15E-03	14.56	25.00	12.80	2.50E-04	4.29E-04	2.20E-04
MN-13	F	28	0.08	2082	58296	5.78E-03	9.54E-03	4.74E-03	12.03	19.86	9.87	2.06E-04	3.41E-04	1.69E-04
HSi-5	G	28	0.08	1750	49000	2.80E-01	6.75E-02	9.96E-02	490.54	118.07	174.22	1.00E-02	2.41E-03	3.56E-03
HSi-5	G	28	0.08	1750	49000	2.73E-01	6.41E-02	9.36E-02	477.84	112.12	163.76	9.75E-03	2.29E-03	3.34E-03
MN-12	G	28	0.08	1750	49000	1.19E-02	#	3.62E-03	20.77	#	6.33	4.24E-04	#	1.29E-04
MN-12	G	28	0.08	1750	49000	1.19E-02	#	3.62E-03	20.77	#	6.33	4.24E-04	#	1.29E-04
MN-13	G	28	0.08	1750	49000	9.40E-03	1.23E-02	6.25E-03	16.46	21.58	10.93	3.36E-04	4.40E-04	2.23E-04

Sample ID	Size ID	Test Duration (Days)	Test Duration (Years)	SA/V (m^2/L)	SA/V*t (day/m^{-1})	NLi(B) (g/m^2)	NLi(Na) (g/m^2)	NLi(U) (g/m^2)	NC(B) (g/L)	NC(Na) (g/L)	NC(U) (g/L)	NRi (B) (g/m^2●day)	NRi(Na) (g/m^2●day)	NRi(U) (g/m^2●day)
MN-13	G	28	0.08	1750	49000	7.96E-03	1.14E-02	5.94E-03	13.92	19.86	10.40	2.84E-04	4.05E-04	2.12E-04
HSi-5	H	28	0.08	3500	98000	1.15E-02	9.16E-03	3.78E-03	40.27	32.07	13.24	4.11E-04	3.27E-04	1.35E-04
HSi-5	H	28	0.08	3500	98000	1.09E-02	1.01E-02	3.58E-03	38.11	35.21	12.54	3.89E-04	3.59E-04	1.28E-04
MN-12	H	28	0.08	3500	98000	1.73E-01	1.02E-01	3.62E-05	604.97	356.94	0.13	6.17E-03	3.64E-03	1.29E-06
MN-12	H	28	0.08	3500	98000	1.20E-01	6.91E-02	3.62E-05	419.86	241.87	0.13	4.28E-03	2.47E-03	1.29E-06
MN-13	H	28	0.08	3500	98000	8.32E-03	1.27E-02	5.18E-03	29.11	44.52	18.13	2.97E-04	4.54E-04	1.85E-04
MN-13	H	28	0.08	3500	98000	2.28E-02	4.70E-03	1.22E-02	79.75	16.44	42.67	8.14E-04	1.68E-04	4.35E-04
HSi-5	I	42	0.12	4938	207396	5.62E-03	1.41E-02	3.03E-03	27.76	69.41	14.98	1.34E-04	3.35E-04	7.22E-05
HSi-5	I	42	0.12	4938	207396	5.45E-03	1.37E-02	3.03E-03	26.89	67.43	14.98	1.30E-04	3.25E-04	7.22E-05
MN-12	I	42	0.12	4938	207396	9.23E-02	7.35E-02	2.57E-02	455.98	362.90	126.90	2.20E-03	1.75E-03	6.12E-04
MN-12	I	42	0.12	4938	207396	9.42E-02	7.47E-02	2.57E-02	465.01	368.85	126.90	2.24E-03	1.78E-03	6.12E-04
MN-13	I	42	0.12	4938	207396	1.40E-02	1.90E-02	6.48E-03	68.99	94.01	32.00	3.33E-04	4.53E-04	1.54E-04
MN-13	I	42	0.12	4938	207396	1.41E-02	1.94E-02	5.94E-03	69.62	95.72	29.33	3.36E-04	4.62E-04	1.41E-04
HSi-5	J	42	0.12	9876	414792	1.53E-03	3.33E-03	5.64E-04	15.11	32.93	5.57	3.64E-05	7.94E-04	1.34E-05
HSi-5	J	42	0.12	9876	414792	5.47E-03	1.12E-02	3.00E-03	54.00	110.13	29.62	1.30E-04	2.66E-04	7.14E-05
MN-12	J	42	0.12	9876	414792	1.23E-02	1.22E-02	5.45E-03	121.60	120.73	53.80	2.93E-04	2.91E-04	1.30E-04
MN-13	J	42	0.12	9876	414792	5.39E-03	7.37E-03	2.97E-03	53.23	72.76	29.33	1.28E-04	1.75E-04	7.07E-05

6.0 CONCLUSIONS

The target composition envelope developed for the M-Area sludges were bracketed by making nominal, low SiO_2 and high SiO_2 blend mixtures of sludge tanks and the spent filter aid tank while spent filter aid was actively being added to the tank, i.e. the exact final volume of filter aid was an unknown. It is interesting to note that the final tank volumes, when measured in 1995, were most similar to the "low SiO_2" SRNL blend, i.e.; 385,000 gallons of plating line sludge and 228,000 gallons of Tank 10 filter aid or a Tank 8/Tank 10 volume ratio of 1.69.

The glass formulations from the M-Area study can be used to illustrate that high durability glasses can be made with high Al_2O_3 and high U_3O_8 sludges. The glass formulations and PCT results serve to illustrate the range of successful combinations of alkali and B_2O_3 can be used to target these high durability glasses. The details of the QA under which this task was performed is also documented in this report so that these glasses can be used in ComPro™ to facilitate glass formulations for high Al_2O_3 and U_3O_8 sludges. Specifically, examination of the Al_2O_3 solubility limit in these glasses, was used to define new compositional regions of technological importance for DWPF and WTP . The data indicates that the P_2O_5 limit of 2.25 wt% P_2O_5 (3 wt% PO_4) set for DWPF glass in 1987 may not apply for high alumina glasses, especially those with no Li_2O or minimal Li_2O in the frit. This is based on the data presented in this study for homogeneous and durable borosilicate glasses (SLS glasses were excluded) and the following:

- the DWPF P_2O_5 limit was set based on a simulated Stage 1 waste glass at 28 wt% waste loading: the glass contained only 4.01 wt% Al_2O_3
- the DWPF P_2O_5 limit was set using frit 165 at 72 wt% waste loading
- the simulated glass contained no U_3O_8 as did the glasses in this study (2.93-5.25 wt%).
- the 3 wt% PO_4 limit agreed with data in literature which cited solubility limits in silicate and borosilicate glasses between 3-4 wt% PO_4.

Therefore, combinations of low Li_2O and P_2O_5 appear to allow high Al_2O_3 glass loadings up to 25-26wt% without compromising glass durability. Since nominal DWPF sludges only contain ~0.22 (Purex HAW), 0.16 (Average), and 0.13 (HM HAW) wt% PO_4, which at 28 wt% waste loading in glass is only 0.05-0.08 wt% PO_4, small concentrations of P_2O_5 up to 1-2 wt% could be investigated as a mechanism to increase the Al_2O_3 loadings of HM sludges and allow the amount of Al-dissolution to be optimized. This data will have applicability to WTP as well.

The logarithm of the normalized release rates (NC_i) for 90°C PCT tests, where "i" equals Li, Na, and K, were compared to the logarithm of the normalized release rate of B to demonstrate that the alkali and boron releases are congruent for glasses that are not crystallized. It should be noted that the log NC_{Na} is a better linear fit of the data to the log NC_B than log NC_{Li} or log NC_K. The poor correlation between log NC_B and log NC_{Li} is attributed to the strong interactions between Li and P in these glasses which can cause lithium phosphate CPS to form. The poor correlation between log NC_B and log NC_K was attributed to the fact that B was measured by ICP-ES while K was measured by a less accurate AA method.

A stepwise regression of the mean uranium ppm values measured in the triplicate PCT's indicated that the Li_2O content of the glass was the single most important parameter in determining the release of uranium to the groundwater. Many of the glasses contained no Li_2O. However, for the glasses that contained >9 wt% Li_2O, the durability decreased as the Li_2O content increased above 9 wt%. This may be due to the interactions between Li_2O and PO_4 in these glasses.

The extrapolation made for the M-Area glass PA from 90°C PCT data to 25°C data are also confirmed in this report. In this extrapolation, the release of U was bounded by the release of B. It should be noted that log NC_U at 90°C is solubility limited and little correlation was found with soluble boron in this study. However, since log NC_U never rises above log = 0, the use of NC_B which does rise above log = 0, as an indication of the maximum radionuclide release is conservative.

This report documents the 25°C PCT release data in E-Area groundwater not previously published. For the set of three glasses used for the PA confirmation of the 90°C to 25°C extrapolation at varying SA/V, the impacts of glass formulation can be examined since Li_2O, Na_2O, SiO_2 and B_2O_3 were widely varied. Both the B release and the U release seem to be positively correlated with the Li/Si cation ratio, i.e. more Li or less Si makes the glass more durable. The durability of the glass in terms of the leach rate release of B and U is negatively correlated with the Na/Al cation ratio (Figure 8b and d), i.e. the most durable glasses are formed when the cation Na/Al is high.

Lastly, the M-Area 25°C data was fit to a cumulative release plot (NR_i in g/cm^2day vs. cumulative time in years) and the data fit was achieved as the square root of the cumulative time. The square root dependency demonstrates that the leaching is via diffusion. This is an intrinsic characteristic of a diffusion-controlled process rather than a mechanism of glass matrix dissolution via hydrolysis. The latter mechanism would show a constant leaching rate.

The point at which the square root dependency for diffusion crosses the ordinate axis at the value of NR_B or NR_U = 2.7 E-05 g/m^2•day is the length of time it will take for the glass to reach the desired long-term rate once exposed to the groundwater. After that time period, the long-term rate will be less than the 2.7 E-05 g/m^2•day. The NR_i vs test duration time plots for NR_B and NR_U decrease asymptotically to values <2.7 E-05 g/m^2•day in 44-80 days for B release and ~44 days for U release. Since the M-Area glass is sealed in canisters, dissolution will not be uniform but occur only as the canister degrades. In addition, there is a large uncertainty and a large amount of scatter in the E-area groundwater analyses since it was subsequently determined by researchers at Argonne National Laboratory (ANL) that leaching in the 20°C range creates such minimal concentrations of species in solution, compared to leaching at 40°C and 90°C, that measurements are usually at the detection limit of most analytic instruments.[41] This is why leaching analyses are normally performed at 40°C or above.

7.0 ACKNOWLEDGEMENTS

The authors would like to gratefully acknowledge the assistance of Patricia Toole-Simmons of SRNL in performing the durability experiments. This paper was prepared in connection with work done under Contract No. DE-AC09-96SR18500 with the U.S. Department of Energy (DOE).

APPENDIX A. DETAILS OF GLASS MELTS

Table A1. Nominal M-Area Glasses

GLASS ID	TYPE OF GLASS	TANK 10 (ML)	TANK 8 (ML)	NOMINAL SLUDGE (ML)	TOTAL WASTE LOADING (WT%)	ADDITIVE WASTE LOADING (WT%)	TYPE OF ADDITIVE	GLASS ADDITIVE (GMS)	ACTUAL MELT TEMP (°C)	DATE MELTED	OVEN ID	OVEN CALIB DATE	EASY TO POUR	COMMENTS
MN-1	BS	193	112	305	90	10	**H3BO3**	17.76	1400	9/14/1993	GT-1-227	4/30/1993	YES	
										9/14/1993	GT-1-227	4/30/1993	YES	
MN-2	BS	171	100	271	80	20	**H3BO3**	35.52	1260	8/10/1993	GT-1-097	7/29/1993	YES	
MN-3	BS	150	87	237	70	30	**H3BO3**	53.30	1150	8/1/1993	GT-1-097	7/29/1993	YES	
									1150	8/1/1993	GT-1-097	7/29/1993	YES	
MN-4	BS	193	112	305	90	10	**H3BO3**	12.43	1400	9/9/1993	GT-1-227	4/30/1993	YES	
							Na2CO3	5.13	1400	9/9/1993	GT-1-227	4/30/1993	YES	
MN-5	BS	171	100	271	80	20	**H3BO3**	24.87	1300	7/20/1993	GT-1-227	4/30/1993	YES	MN - NO VISIBLE AL
							Na2CO3	10.26	1300	7/20/1993	GT-1-227	4/30/1993	YES	MN-5 AL
									1300	7/20/1993	GT-1-227	4/30/1993	YES	MN-5 AL
MN-6	BS	150	87	237	70	30	**H3BO3**	37.30	1150	7/8/1993	GT-1-227	4/30/1993	YES	EXCELLENT GLASS
							Na2CO3	15.39						POPPED OUT OF CRUCIBLE
MN-7	BS	193	112	305	90	10	**H3BO3**	8.88	1400	9/21/1993	GT-1-227	4/30/1993	YES	GOOD GLASS
							Na2CO3	8.55						
MN-8	BS	171	100	271	80	20	**H3BO3**	17.76	1150	8/1/1993	GT-1-097	7/29/1993	YES	DID NOT FINE
							Na2CO3	17.10	1150	8/3/1993	GT-1-097	7/29/1993	YES	DID NOT FINE
MN-9	BS	150	87	237	70	30	**H3BO3**	26.64	1200	7/8/1993	GT-1-227	4/30/1993	YES	EXCELLENT GLASS
							Na2CO3	25.65	1200	7/11/1993	GT-1-227	4/30/1993	YES	POPPED OUT OF CRUCIBLE
														RATHER FLAKY
MN-10	BS	193	112	305	90	10	**H3BO3**	8.88	1200	8/7/1993	GT-1-097	7/29/1993	YES	
							Li2CO3	12.36	1200	9/13/1993	GT-1-227	4/30/1993	YES	

GLASS ID	TYPE OF GLASS	TANK 10 (ML)	TANK 8 (ML)	NOMINAL SLUDGE (ML)	TOTAL WASTE LOADING (WT%)	ADDITIVE WASTE LOADING (WT%)	TYPE OF ADDITIVE	GLASS ADDITIVE (GMS)	ACTUAL MELT TEMP (°C)	DATE MELTED	OVEN ID	OVEN CALIB DATE	EASY TO POUR	COMMENTS
MN-11	BS	171	100	271	80	20	**H_3BO_3**	17.76	1150	7/9/1993	GT-1-227	4/30/1993	YES	
							Li_2CO_3	24.73						
MN-12	BS	150	87	237	70	30	**H_3BO_3**	26.64	1150	7/9/1993	GT-1-227	4/30/1993	YES	
							Li_2CO_3	37.09						
MN-13	BS	182	106	288	85	15	**H_3BO_3**	7.99	1150	7/9/1993	GT-1-227	4/30/1993	YES	
							Li_2CO_3	25.96	1150	7/11/1993	GT-1-227	4/30/1993	YES	
MN-14	BS	161	94	255	75	25	**H_3BO_3**	13.99	1150	7/10/1993	GT-1-227	4/30/1993	YES	
							Li_2CO_3	43.27						
MN-15	BS	182	106	288	85	15	**H_3BO_3**	7.99	1200	8/8/1993	GT-1-097	7/29/1993	YES	
							Na_2CO_3	17.95						
MN-16	BS	161	94	255	75	25	**H_3BO_3**	13.32	1150	7/10/1993	GT-1-227	4/30/1993	YES	GOOD GLASS
							Na_2CO_3	29.92						
MN-17	SLS	193	112	305	90	10	**$CaCO_3$**	8.92	1350	9/10/1993	GT-1-227	4/30/1993	YES	NOT HOMOGENEOUS
							Na_2CO_3	8.55						
MN-18	SLS	171	100	271	80	20	**$CaCO_3$**	17.85	1150	8/3/1993	GT-1-097	7/29/1993	YES	GOOD GLASS
							Na_2CO_3	17.10	1150	8/3/1993	GT-1-097	7/29/1993	YES	
MN-19	SLS	150	87	237	70	30	**$CaCO_3$**	26.77	1150	7/10/1993	GT-1-227	4/30/1993	YES	GOOD GLASS-SOME
							Na_2CO_3	25.65	1150	7/12/1993	GT-1-227	4/30/1993	YES	CRYSTALS ON MELT SURF
MN-20	LLS	193	112	305	90	10	**$CaCO_3$**	8.92	1200	8/7/1993	GT-1-097	7/29/1993	YES	
							Li_2CO_3	12.36	1200	8/7/1993	GT-1-097	7/29/1993	YES	

GLASS ID	TYPE OF GLASS	TANK 10 (ML)	TANK 8 (ML)	NOMINAL SLUDGE (ML)	TOTAL WASTE LOADING (WT%)	ADDITIVE WASTE LOADING (WT%)	TYPE OF ADDITIVE	GLASS ADDITIVE (GMS)	ACTUAL MELT TEMP (°C)	DATE MELTED	OVEN ID	OVEN CALIB DATE	EASY TO POUR	COMMENTS
MN-21	LLS	171	100	271	80	20	**CaCO3**	17.85	1150	7/11/1993	GT-1-227	4/30/1993	YES	NOT A GOOD GLASS
							Li2CO3	24.73						
MN-22	LLS	150	87	237	70	30	**CaCO3**	26.77	1150	7/12/1993	GT-1-227	4/30/1993	YES	STUCK TO CRUCIBLE
							Li2CO3	37.09		7/15/1993	GT-1-227	4/30/1993	YES	BADLY
MN-23	SLS	193	112	305	90	10	**CaCO3**	17.85	1400	9/20/1993	GT-1-227	4/30/1993	YES	GOOD GLASS
MN-24	SLS	193	112	305	90	10	**CaCO3**	5.35	1400	9/20/1993	GT-1-227	4/30/1993	YES	GOOD GLASS
							Na2CO3	11.97						
MN-25	SLS	171	100	271	80	20	**CaCO3**	10.70	1150	8/4/1993	GT-1-097	7/29/1993	YES	
							Na2CO3	23.94						
MN-26	SLS	150	87	237	70	30	**CaCO3**	16.05	1150	7/12/1993	GT-1-227	4/30/1993	YES	
							Na2CO3	35.91						

Table A2. High SiO_2-Containing M-Area Glasses

GLASS ID	TYPE OF GLASS	TANK 10 (ML)	TANK 8 (ML)	NOMINAL SLUDGE (ML)	TOTAL WASTE LOADING (WT%)	ADDITIVE WASTE LOADING (WT%)	TYPE OF ADDITIVE	GLASS ADDITIVE (GMS)	ACTUAL MELT TEMP (°C)	DATE MELTED	OVEN ID	OVEN CALIB DATE	EASY TO POUR	COMMENTS
MHSI-1	BS	361	94	455	90	10	**H3BO3**	17.76	1400	9/16/1993	GT-1-227	4/30/1993	YES	GOOD GLASS -SOME
									1400	9/16/1993	GT-1-227	4/30/1993	YES	BUBBLES
MHSI-2	BS	321	83	404	80	20	**H3BO3**	35.52	1300	9/17/1993	GT-1-227	4/30/1993	YES	GOOD GLASS WITH AL
														CHUNKS
MHSI-3	BS	281	73	354	70	30	**H3BO3**	53.30	1150	8/30/1993	GT-1-097	7/29/1993	YES	GOOD GLASS WITH AL
									1150	8/30/1993	GT-1-097	7/29/1993	YES	CHUNKS
MHSI-4	BS	361	94	455	90	10	**H3BO3**	12.43	1400	9/20/1993	GT-1-227	4/30/1993	YES	GOOD GLASS-SOME
							Na2CO3	5.13		9/16/1993	GT-1-227	4/30/1993	YES	BUBBLES
MHSI-5	BS	321	83	404	80	20	**H3BO3**	24.87	1150	9/18/1993	GT-1-227	4/30/1993	YES	GOOD GLASS WITH AL
							Na2CO3	10.26	1150	9/18/1993	GT-1-227	4/30/1993	YES	CHUNKS
MHSI-6	BS	281	73	354	70	30	**H3BO3**	37.30	1200	9/15/1993	GT-1-227	4/30/1993	YES	
							Na2CO3	15.39	1200	9/15/1993	GT-1-227	4/30/1993	YES	
MHSI-7	BS	361	94	455	90	10	**H3BO3**	8.88	NOT MADE DUE TO SLUDGE VOLUME LIMITATIONS					
							Na2CO3	8.55						
MHSI-8	BS	321	83	404	80	20	**H3BO3**	17.76	NOT MADE DUE TO SLUDGE VOLUME LIMITATIONS					
							Na2CO3	17.10						
MHSI-9	BS	281	73	354	70	30	**H3BO3**	26.64	NOT MADE DUE TO SLUDGE VOLUME LIMITATIONS					
							Na2CO3	25.65						
MHSI-10	BS	361	94	455	90	10	**H3BO3**	8.88	NOT MADE DUE TO SLUDGE VOLUME LIMITATIONS					
							Li2CO3	12.36						
MHSI-11	BS	321	83	404	80	20	**H3BO3**	17.76	1200	9/15/1993	GT-1-227	4/30/1993	YES	GOOD GLASS-Ni PARTICLES
							Li2CO3	24.73						on wall

Table A3. Low SiO_2-Containing M-Area Glasses

GLASS ID	TYPE OF GLASS	TANK 10 (ML)	TANK 8 (ML)	NOMINAL SLUDGE (ML)	TOTAL WASTE LOADING (WT%)	ADDITIVE WASTE LOADING (WT%)	TYPE OF ADDITIVE	GLASS ADDITIVE (GMS)	ACTUAL MELT TEMP (°C)	DATE MELTED	OVEN ID	OVEN CALIB DATE	EASY TO POUR	COMMENTS
MLSI-1	BS	116	143	259	90	10	**H3BO3**	17.76	1350	9/10/1993	GT-1-227	4/30/1993	YES	
									1350	9/10/1993	GT-1-227	4/30/1993	YES	
MLSI-2	BS	103	127	230	80	20	**H3BO3**	35.52	1300	9/17/1993	GT-1-227	4/30/1993	YES	GOOD GLASS-FALLS FROM
										9/17/1993	GT-1-227	4/30/1993	YES	CRUCIBLE IN CHUNKS
MLSI-3	BS	90	111	201	70	30	**H3BO3**	53.30	1150	8/30/1993	GT-1-097	7/29/1993	YES	EXCELLENT GLASS
MLSI-4	BS	116	143	259	90	10	**H3BO3**	12.43	1400	9/9/1993	GT-1-227	4/30/1993	YES	
							Na2CO3	5.13		9/14/1993	GT-1-227	4/30/1993	YES	
MLSI-5	BS	103	127	230	80	20	**H3BO3**	24.87	1150	8/16/1993	GT-1-097	7/29/1993	YES	
							Na2CO3	5.13		8/17/1993	GT-1-097	7/29/1993	YES	
										8/18/1993	GT-1-097	7/29/1993	YES	
										8/19/1993	GT-1-097	7/29/1993	YES	
MLSI-6	BS	90	111	201	70	30	**H3BO3**	37.30	1150	8/27/1993	GT-1-097	7/29/1993	YES	
							Na2CO3	15.39						
MLSI-7	BS	116	143	259	90	10	**H3BO3**	8.88	1400	9/12/1993	GT-1-227	4/30/1993	YES	
							Na2CO3	8.55	1400	9/12/1993	GT-1-227	4/30/1993	YES	
									1400	9/12/1993	GT-1-227	4/30/1993	YES	
MLSI-8	BS	103	127	230	80	20	**H3BO3**	17.76	1150	8/27/1993	GT-1-097	7/29/1993	YES	
							Na2CO3	17.10	1150	8/27/1993	GT-1-097	7/29/1993	YES	
MLSI-9	BS	90	111	201	70	30	**H3BO3**	26.64	1150	9/18/1993	GT-1-227	4/30/1993	YES	GOOD GLASS
							Na2CO3	25.65		9/19/1993	GT-1-227	4/30/1993	YES	
MLSI-10	BS	116	143	259	90	10	**H3BO3**	8.88	1200	9/13/1993	GT-1-227	4/30/1993	YES	
							Li2CO3	12.36	1200	9/13/1993	GT-1-227	4/30/1993	YES	
MLSI-11	BS	103	127	230	80	20	**H3BO3**	17.76	1150	9/19/1993	GT-1-227	4/30/1993	YES	GOOD GLASS BUT STUCK TO
							Li2CO3	24.73						CRUCIBLE

APPENDIX B. DETAILS OF SLUDGE/FILTER AID BLENDS

TABLE B1. NOMINAL SLUDGE MIXTURE (TANKS 8 AND 10) ANALYSES IN WT%

	NOMINAL	**NOMINAL**	**NOMINAL**	**NOMINAL**
ANALYSIS #	300011340	300011341	**AVERAGE**	**STANDARD**
ANALYSIS DATE	7/6/1993	7/6/1993		**DEVIATION**
RECORDED	DPSTN 4695	DPSTN 4695		
Al (ICP)	8.786	8.867	8.827	0.057
Ca (ICP)	0.318	0.308	0.313	0.007
Fe (ICP)	0.711	0.719	0.715	0.006
Mg (ICP)	0.168	0.166	0.167	0.001
Mn (ICP)	0.025	0.022	0.024	0.002
Na (ICP)	6.529	5.738	6.134	0.559
Na (AA)	6.689	7.410	7.049	0.510
Li (ICP)	0.004	<0.001	<0.001	
Ni (ICP)	0.540	0.562	0.551	0.016
Ni (AA)	0.687	0.660	0.674	0.019
Si (ICP)	22.920	23.033	22.977	0.080
Si (AA)	*21.640*	*21.890*	21.765	0.177
Cr (ICP)	0.010	0.011	0.011	
B (ICP)	<0.004	<0.004	<0.004	
U (ICP-MS)	4.709	4.815	4.762	0.075
Sr (ICP)	0.002	0.002	0.002	0.000
Zr (ICP)	0.014	0.013	0.014	
Ti (ICP)	0.057	0.057	0.057	0.000
K (AA)	0.885	0.987	0.936	0.072
P (ICP)***	1.325	1.350	1.338	0.018
P (Calc IC)**	0.936	0.895	0.915	0.029
Ba (ICP)	0.011	0.010	0.011	
Pb (ICP)	0.035	0.037	0.036	
Mo (ICP)	0.004	0.004	0.004	
Zn (ICP)	0.418	0.408	0.413	0.007
Cu (ICP)	0.013	0.014	0.014	
F (ISE)	0.551	<0.101	0.551	0.000
Cl (ISE)	0.1175	0.1073	0.1124	
SO_4 (IC)	0.212	<0.101	0.212	
NO_3 (IC)	6.833	7.560	7.197	0.514
PO_4(IC)**	2.870	2.744	2.807	0.089
% SOLIDS (105°C)	26.220	26.150	26.185	0.049
% SOLIDS (90°C)	5.310	5.310	5.310	
Moles of Na	0.291	0.322	0.307	0.022
Moles of NO_3	0.110	0.122	0.116	0.008
Moles of Cl	0.000	0.000	0.000	0.000

N/A = Not Analyzed Insufficient Sample

*AA Silicon values in italics from HCl/HF dissolution; others from Na_2O_2 dissolution
all anions from Na_2O_2 fusion with H_2O uptake (see text)

water soluble phosphate only * acid soluble phosphate

TABLE B2. HIGH Si SLUDGE MIXTURE (TANKS 8 AND 10) ANALYSES IN WT%

	HIGH Si	**HIGH Si**	**HIGH Si**	**HIGH Si**
ANALYSIS #	300011342	300011343	**AVERAGE**	**STANDARD**
ANALYSIS DATE	7/6/1993	7/6/1993		**DEVIATION**
RECORDED	DPSTN 4695	DPSTN 4695		
Al (ICP)	9.040	9.253	9.147	0.151
Ca (ICP)	0.290	0.374	0.332	0.059
Fe (ICP)	0.967	0.736	0.852	0.163
Mg (ICP)	0.146	0.153	0.150	0.005
Mn (ICP)	0.030	0.028	0.029	0.001
Na (ICP)	5.714	5.890	5.802	0.124
Na (AA)	6.614	6.490	6.552	0.088
Li (ICP)	<0.001	<0.001	<0.001	
Ni (ICP)	0.393	0.425	0.409	0.023
Ni (AA)	0.505	0.503	0.504	
Si (ICP)	23.265	23.693	23.479	0.303
Si (AA)	*23.229*	*23.531*	23.380	0.214
Cr (ICP)	0.010	0.012	<0.004	
B (ICP)	<0.004	<0.004	<0.004	
U (ICP-MS)	3.561	3.486	3.524	0.053
Sr (ICP)	0.001	0.002	0.002	0.001
Zr (ICP)	0.015	0.012	<0.002	
Ti (ICP)	0.052	0.057	0.055	0.004
K (AA)	0.842	1.089	0.966	0.175
P (ICP)***	1.304	1.214	1.259	0.064
P (Calc IC)**	1.017	1.044	1.030	0.018
Ba (ICP)	0.011	0.011	0.011	
Pb (ICP)	0.033	0.037	0.035	
Mo (ICP)	0.005	0.004	0.005	
Zn (ICP)	0.492	0.164	0.328	0.232
Cu (ICP)	0.013	0.015	0.014	
F (ISE)	<0.084	<0.102	<0.093	
Cl (ISE)	0.0929	0.1077	0.1003	
SO_4 (IC)	0.133	<0.102	0.133	
NO_3 (IC)	7.010	6.410	6.710	0.424
PO_4(IC)**	3.120	3.200	3.160	0.057
% SOLIDS (105°C)	25.190	25.300	25.245	0.078
% SOLIDS (90°C)	6.530	6.530	6.530	
Moles of Na	0.288	0.282	0.285	0.004
Moles of NO_3	0.113	0.103	0.108	0.007
Moles of Cl	0.000	0.000	0.000	0.000

N/A = Not Analyzed Insufficient Sample

*AA Silicon values in italics from HCl/HF dissolution; others from Na_2O_2 dissolution
all anions from Na_2O_2 fusion with H_2O uptake (see text)

water soluble phosphate only * acid soluble phosphate

TABLE B3. LOW Si SLUDGE MIXTURE (TANKS 8 AND 10) ANALYSES IN WT%

	LOW Si	**LOW Si**	**LOW Si**	**LOW Si**
ANALYSIS #	300011344	300011345	**AVERAGE**	**STANDARD**
ANALYSIS DATE	7/6/1993	7/6/1993		**DEVIATION**
RECORDED	DPSTN 4695	DPSTN 4695		
Al (ICP)	9.143	9.268	9.206	0.088
Ca (ICP)	0.319	0.320	0.320	0.001
Fe (ICP)	0.606	0.714	0.660	0.076
Mg (ICP)	0.166	0.160	0.163	0.004
Mn (ICP)	0.017	0.019	0.018	0.001
Na (ICP)	6.848	7.208	7.028	0.255
Na (AA)	8.703	9.390	9.047	0.486
Li (ICP)	<0.001	<0.001	<0.001	
Ni (ICP)	0.675	0.665	0.670	0.007
Ni (AA)	0.776	0.793	0.785	
Si (ICP)	20.003	20.149	20.076	0.103
Si (AA)	*19.037*	*19.150*	19.093	0.080
Cr (ICP)	0.043	0.011	0.027	
B (ICP)	<0.004	<0.004	<0.004	
U (ICP-MS)	5.396	5.520	5.458	0.088
Sr (ICP)	0.003	0.001	0.002	0.001
Zr (ICP)	0.012	0.015	<0.002	
Ti (ICP)	0.052	0.059	0.056	0.005
K (AA)	0.656	0.717	0.687	0.043
P (ICP)***	1.188	1.170	1.179	0.013
P (Calc IC)**	1.053	1.109	1.081	0.039
Ba (ICP)	0.010	0.008	0.009	
Pb (ICP)	0.042	0.040	0.041	
Mo (ICP)	0.005	0.005	0.005	
Zn (ICP)	1.308	0.402	0.855	0.641
Cu (ICP)	0.019	0.013	0.016	
F (ISE)	<0.1055	<0.0987	<0.1021	0.000
Cl (ISE)	0.1129	0.1115	0.1122	
SO_4 (IC)	<0.1055	0.129	0.129	
NO_3 (IC)	9.979	10.659	10.319	0.481
PO_4(IC)**	3.230	3.400	3.315	0.120
% SOLIDS (105°C)	27.010	26.970	26.990	0.028
% SOLIDS (90°C)	7.120	7.120	7.120	
Moles of Na	0.379	0.408	0.394	0.021
Moles of NO_3	0.161	0.172	0.166	0.008
Moles of Cl				

N/A = Not Analyzed Insufficient Sample

*AA Silicon values in italics from HCl/HF dissolution; others from Na_2O_2 dissolution
all anions from Na_2O_2 fusion with H_2O uptake (see text)

water soluble phosphate only * acid soluble phosphate

APPENDIX C. GLASS VISCOSITY MEASUREMENTS

Sample ID	Temp (°C)	Log_{10}(Visc)	Visc (poise)
MN-2	1293.50	2.59	389.18
MN-2	1247.50	2.74	543.59
MN-2	1198.50	2.95	896.69
MN-2	1152.50	3.18	1526.83
MN-2	1095.00	3.50	3141.84
MN-3	1199.00	2.56	364.78
MN-3	1150.00	2.77	594.67
MN-3	1100.00	3.01	1027.27
MN-3	1050.00	3.28	1888.92
MN-3	996.00	3.59	3930.66
MN-5D	1249.50	2.80	625.72
MN-5D	1197.00	3.05	1121.64
MN-5D	1147.50	3.32	2068.55
MN-5D	1098.50	3.60	3981.01
MN-5D	1050.00	3.90	7974.78
MN-6	1289.00	1.75	56.30
MN-6	1250.00	1.87	74.36
MN-6	1200.00	2.04	110.53
MN-6	1149.00	2.24	172.35
MN-6	1100.00	2.45	279.82
MN-7	1301.50	3.22	1648.77
MN-7	1251.00	3.48	2992.64
MN-7	1200.00	3.76	5809.80
MN-10	1200.00	2.51	321.49
MN-10	1149.00	2.72	529.78
MN-10	1099.00	2.95	897.09
MN-10	1049.00	3.20	1595.28
MN-11	1200.50	1.25	17.91
MN-11	1151.50	1.39	24.55
MN-11	1100.00	1.56	36.06
MN-11	1050.00	1.73	54.31
MN-11	1000.00	1.93	85.78

Sample ID	Temp (°C)	Log_{10}(Visc)	Visc (poise)
MN-14	1200.00	0.68	4.82
MN-14	1151.00	0.81	6.44
MN-14	1100.00	0.95	8.93
MN-14	1050.00	1.11	12.90
MN-14	1000.00	1.29	19.33
MN-14	950.00	1.48	30.03
MH-Si-2	1290.00	3.04	1101.12
MH-Si-2	1250.00	3.23	1716.90
MH-Si-2	1200.00	3.50	3192.84
MH-Si-3	1200.00	2.95	893.80
MH-Si-3	1150.00	3.18	1527.48
MH-Si-3	1100.00	3.45	2823.38
MHSi-6	1255.50	2.39	246.65
MHSi-6	1199.00	2.62	420.44
MHSi-6	1151.00	2.84	686.81
MHSi-6	1099.50	3.09	1238.28
MHSi-6	1048.50	3.37	2327.40
MHSi-11A	1253.00	2.18	151.55
MHSi-11A	1198.50	2.40	252.53
MHSi-11A	1150.00	2.61	412.01
MHSi-11A	1097.50	2.86	728.75
MHSi-11A	1048.50	3.12	1325.60
MLSi-1	1299.50	2.67	471.05
MLSi-1	1249.00	2.91	811.74
MLSi-1	1199.00	3.16	1448.03
MLSi-1	1148.00	3.44	2745.67
MLSi-2	1288.00	2.22	165.51
MLSi-2	1250.00	2.37	236.65
MLSi-2	1200.00	2.59	391.65
MLSi-2	1150.00	2.83	683.35

Sample ID	**Temp (°C)**	**Log$_{10}$(Visc)**	**Visc (poise)**
MLSi-3B	1199.00	2.10	124.86
MLSi-3B	1150.00	2.29	194.44
MLSi-3B	1099.50	2.51	322.92
MLSi-3B	1049.50	2.75	561.50
MLSi-3B	999.50	3.03	1059.58
MLSi-5	1200.00	2.53	339.87
MLSi-5	1150.00	2.76	570.95
MLSi-5	1100.00	3.00	1009.54
MLSi-5	1050.00	3.28	1900.12
MLSi-5	1000.00	3.58	3835.91
MLSi-9	1200.00	1.70	49.92
MLSi-9	1149.50	1.88	75.06
MLSi-9	1099.00	2.07	117.00
MLSi-9	1050.00	2.27	186.98
MLSi-9	1001.00	2.50	317.18

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