

PREDICTING PHASE SEPARATION IN NUCLEAR WASTE GLASSES

C.M. Jantzen and K.G. Brown
Westinghouse Savannah River Company
Aiken, SC 29808

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

This report has been reproduced directly from the best available copy.

Available for sale to the public, in paper, from: U.S. Department of Commerce, National Technical Information Service, 5285 Port Royal Road, Springfield, VA 22161, phone: (800) 553-6847, fax: (703) 605-6900
email: orders@ntis.fedworld.gov
online ordering: <http://www.ntis.gov/ordering.htm>

Available electronically at <http://www.doe.gov/bridge>
Available for a processing fee to U.S. Department of Energy and its contractors, in paper, from: U.S. Department of Energy, Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831-0062, phone: (865) 576-8401, fax: (865) 576-5728
email: reports@adonis.osti.gov

ABSTRACT

Phase separation in nuclear waste glasses has an adverse effect on glass durability. Phase separation in glasses generally takes the form of two immiscible glass phases which differ in chemical composition, density, and surface tension. Usually one

phase is more soluble than the other. Phase separation complicates modeling of glass durability as a function of composition because the composition of the overall glass is known but the compositions of the two immiscible phases is not known: the performance of the overall glass is unpredictable and the long term durability of the glass can not be modeled. A discriminate analysis of 110 homogeneous and phase separated waste glasses allowed a “phase separation discriminate function” to be defined. The discriminate function is calculated based on glass oxide wt% and compositionally differentiates between immiscible phases of different density. The discriminate function is defined in 14 component composition space although >95% of the glass chemistry is dominated by seven major components (Na_2O - K_2O - Li_2O - SiO_2 - Al_2O_3 - B_2O_3 - Fe_2O_3). The compositionally dependent discriminator function is used to eliminate phase separated glasses from being processed in the Savannah River Site (SRS) Defense Waste Processing Facility (DWPF). All glasses produced are homogeneous and thus have predictable long term durability.

INTRODUCTION

High-level liquid nuclear waste (HLLW) at the Savannah River Site (SRS) is being immobilized by vitrification into borosilicate glass. The glass is produced and poured into stainless steel canisters in the Defense Waste Processing Facility (DWPF) for ultimate geologic disposal. The canistered borosilicate waste glass must comply with the Waste Acceptance Product Specifications (WAPS) established by the U.S. Department of Energy. WAPS Specification 1.3 relates to the ability of the vitrification process to consistently control the final waste form durability, i.e., the stability of the glass against attack by water.

The durability of the final DWPF glass is predicted by analysis of vitrified melter feed prior to transfer of the feed to the melter. The composition analysis is used to calculate a predicted durability for the DWPF production glass from a glass durability model. In order to be fed to the melter, each batch of melter feed must produce a glass whose predicted durability response is more durable (by at least two standard deviations) than the benchmark waste glass identified in the DWPF Environmental Assessment (EA) based on ASTM C1285, the Product Consistency Test (PCT).

In 1994 Tovená, et. al. [1] demonstrated that the Jantzen/Plodinec free energy model [2] as well as the Feng/Barkatt enthalpy model [3-4] and the Bray/Yun [5-6] structural durability models did not predict waste glass durability accurately when the composition of the waste glass contained >15% B₂O₃ with little or no Al₂O₃. For these glasses all the models underpredicted the glass durability significantly. Tovená, et. al. [6] attributed the underprediction to phase separation and complete dissolution of a borate rich phase in the glass when the Al₂O₃ content was insufficient.

Glass-in-glass also known as liquid-liquid phase separation is the growth of two or more non-crystalline glassy phases each of which has a different composition from the overall melt [7]. Phase separation in glasses generally takes the form of two immiscible glass phases which differ in chemical composition, density, and surface tension. Separation into two phases may have various causes but the final result is that the original homogeneous glass is separated into two or more non-crystalline phases of different density.

Phase separation, if it occurs on either a microscopic or macroscopic scale, has been shown to be detrimental to the stability and durability of nuclear waste glasses [1, 8-10]. Phase separation complicates modeling of glass durability as a function of composition because the composition of the overall glass is known but the compositions of the two individual phases composing the glass is not known: the leach rate from either of the immiscible phases is unpredictable as the composition of the phases is not known.

Phase separation is dependent on the volume fraction of phase separated glass that is present. The volume fraction is a function of the thermal history experienced by the glass. Since the thermal history of each waste glass canister is not identical and cannot be controlled during pouring, then glass compositions that have a tendency to phase separate must be avoided. Data generated using the 1995 revision of the Jantzen/Plodinec free energy model called the Thermodynamic Hydration Energy Reaction Model (THERMO™) [8], shows that the ASTM C1285 (PCT) response of phase separated glasses can vary widely as a function of composition (Figure 1).

The durability response of waste glasses must be predictable. Therefore, waste glasses must be homogeneous. Controlling the glass chemistry in compositional regions that avoid phase separation is the key to achieving waste glass durability control during processing. Moreover, durability modeling of only homogeneous glasses avoids confounding any model with different leaching responses.

Phase separated glasses are excluded from the THERMO™ process model used by the Defense Waste Processing Facility (DWPF) based upon a mathematically derived phase separation discriminator. The basis for this compositionally dependent discriminator, termed the homogeneity constraint, is described in this study.

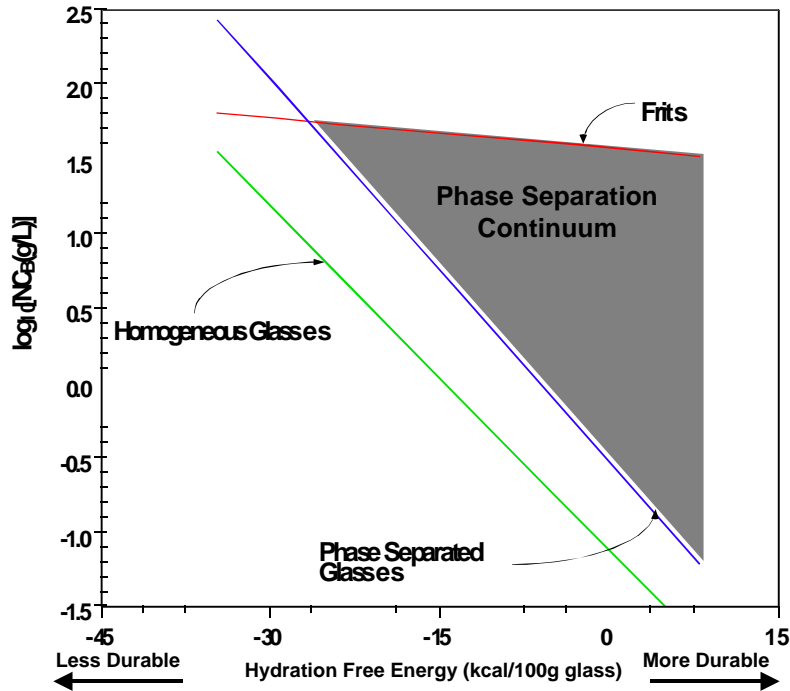


Figure 1. Example of glass durability response (log boron release from the ASTM C-1285 (PCT) test) versus glass composition (expressed as the Hydration Free Energy, THERMO™) based on the analysis of 88 homogeneous and 22 phase separated glasses [8]. A wide variety (possibly a continuum as indicated by the shading) of PCT response is noted for phase separated glasses depending on the type and scale of the phase separation [8,10], e.g. phase separated waste glasses and phase separated frits have a different PCT response.

MODELING AND EXPERIMENTAL APPROACH

A well analyzed and well characterized set of 110 glasses was used to determine the phase separation discriminator which is a mathematical expression of the composition boundary between phase separated and homogeneous glasses. The 110 glasses are designated as "Model Data" and are given by name and production mode in Table I. All glasses in "Model Data" were chemically analyzed by Corning Engineering Laboratory Services (CELS) or bias corrected to CELS standards. The number of replicate analyses performed varied from a minimum of 2 for production and crucible melt glasses to a maximum of 10 for glass standards such as the Environmental Assessment glass and the Waste Compliance Plan (WCP) glasses.

A "Validation Data" set was developed from production and crucible melt glasses not included in "Model Data" and from data taken from the literature. Many of the glass compositions are "as made" rather than "as analyzed." The validation set of glasses is given in Table II along with their production mode.

X-ray Diffraction (XRD) analysis was performed on all of the "Model Data" and "Validation Data" glasses studied. Scanning Electron Microscopy (SEM) analyses coupled with Energy Dispersive Analysis by X-ray (EDAX) were performed on many of the glasses to identify if crystalline species below the detection limit of XRD existed and to identify any large scale phase separation. The EA glass was examined by optical microscopy, SEM, and TEM in order to determine the homogeneity of the glass on a microscopic level. Additional glasses such as Pyrex, the Batch 1 study glasses, white frit 202, and the Hanford glasses were analyzed by Transmission Electron Microscopy (TEM) for phase separation.

COMPOSITIONAL NATURE OF PHASE SEPARATION

Phase separation in 15-20 component waste glasses is not well understood. However, many of the nuclear waste glass components are present in minor amounts and >95% of the glass chemistry is dominated by seven major components, $M_2O-SiO_2-Al_2O_3-B_2O_3-Fe_2O_3$, where $M = K + Na + Li$. Although the compositional dependency of phase separation in the individual $M_2O-SiO_2-B_2O_3$ systems [11] and in the $(M_2O+MO)-(SiO_2+Al_2O_3)-B_2O_3$ systems [11] where M_2O is any alkali oxide and MO is any alkaline earth oxide are known, phase separation in the $M_2O-SiO_2-Al_2O_3-B_2O_3-Fe_2O_3$ system has not previously been studied. Since high level waste glasses contain Fe_2O_3 as a significant

component, phase separation in the seven component system $\text{Na}_2\text{O-Li}_2\text{O-K}_2\text{O-SiO}_2\text{-Al}_2\text{O}_3\text{-B}_2\text{O}_3\text{-Fe}_2\text{O}_3$ needed to be examined.

In order to determine the compositional nature of the phase separation observed in the glasses in this study, it was necessary to examine the distribution of the oxide wt% concentrations of the homogeneous and phase separated glasses. Weight percent is used preferentially over mole percent or mole fraction because glass-in-glass phase separation is the separation of two immiscible phases that have different densities [18-20]. Indeed, the dependence of the reciprocal of the density of each phase on the glass composition in weight percent is linear [18].

Graphical histograms were used to compare the differences in the compositional distributions between the 88 homogeneous and 22 phase separated glasses comprising "Model Data." The histogram analysis of the glass chemistry in oxide wt% indicated that the phase separated glasses were significantly lower in Al_2O_3 while being somewhat higher in B_2O_3 (Figure 2) in agreement with the findings of Tovená, et. al. [1]. Significant differences in the concentrations of other glass oxide components were not observed.

Table I. Glasses Comprising “Model Data”

Glasses By Classification	No. of Glasses	Production History	Analytical Laboratory
Homogeneous Glasses			
Hg Campaign Glasses	9	IDMS Melter	SRTC/ETF
AH Algorithm Glasses	29	Crucible Melts	CELS
DWPF Startup Frit	1	Fritted	CELS
Waste Glass 202G and 202P Standards	2	Crucible melt	CELS
Waste Glass 200R	1	Crucible Melt	SRTC/ADS
Waste Glass 165 CELS Standard	1	Crucible Melt	CELS
ARM-1 Standard	1	Crucible Melt	PNNL/MCC
Environmental Assessment (EA) Glass Standard	1	Small Melter	CELS
Waste Glass 131 TDS	2	Crucible Melt	SRTC/ADS
Batch 1 Study 8,9,13,14,T	5	Crucible Melt	SRTC/ADS
WCP-Blend Standard	1	Crucible Melt	CELS
WCP-Batch-1 Standard	1	Crucible Melt	CELS
WCP-Batch-2 Standard	1	Crucible Melt	CELS
WCP-Batch-3 Standard	1	Crucible Melt	CELS
WCP-Batch-4 Standard	1	Crucible Melt	CELS
WCP-HM Standard	1	Crucible Melt	CELS
WCP-PX Standard	1	Crucible Melt	CELS
Blends-1	4	IDMS Melter	SRTC/ETF
Blends-2	5	IDMS Melter	SRTC/ETF
Blends-3	4	IDMS Melter	SRTC/ETF
HM-1	4	IDMS Melter	SRTC/ETF
HM-2	3	IDMS Melter	SRTC/ETF
HM-3	3	IDMS Melter	SRTC/ETF
PX-1	3	IDMS Melter	SRTC/ETF
PX-2	3	IDMS Melter	SRTC/ETF
Phase Separated Glasses			
PX-4	3	IDMS Melter	SRTC/ETF
PX-5	9	IDMS Melter	SRTC/ETF
PX-6	1	IDMS Melter	SRTC/ETF
PNNL Hanford (H) Glass	9	IDMS Melter	SRTC/ETF
Totals	110		

Table II. Glasses Comprising “Validation Data”

Sample ID	Type		Analytical Method	Production History
	Known	Predicted		
AH 168AL	ϕ Sep. ^t	ϕ Sep.	SEM	Crucible Melt
PYREX	ϕ Sep.	ϕ Sep.	SEM/TEM	Glass Rod
NBS SRM 623	ϕ Sep.	ϕ Sep.	TEM	Crucible Melt
MG-6	Homog.	Homog.	TEM	Crucible Melt
MG-7	ϕ Sep.	ϕ Sep.	TEM [12]	Crucible Melt
MG-9,18	Homog.	ϕ Sep.	SEM [12]	Crucible Melt
MG-10,23,30	Homog.	Homog.	SEM[12]	Crucible Melt
MG-17	Homog.	Homog.	SEM [12]	Crucible Melt
MG-8,16,20,22, 27,29,32,33	Homog.	Homog.	SEM [12]	Crucible Melt
Remaining 14 MG	Homog.	Homog.	SEM [12]	Crucible Melt
FRIT 131,165	ϕ Sep.	ϕ Sep.	SEM	Crucible Melt
FRIT 202	ϕ Sep.	ϕ Sep.	SEM/TEM	Crucible Melt
CAC Glass 15,20	Homog.	Homog.	TEM	Crucible Melt
CAC Glass 31	Homog.	Homog.	TEM	Crucible Melt
Batch 1 Study 10,15	ϕ Sep.	ϕ Sep.	TEM	Crucible Melt
PNL-77-268	ϕ Sep.	ϕ Sep.	TEM [13]	Crucible Melt
PNL-76-101	ϕ Sep.	ϕ Sep.	TEM [13]	Crucible Melt
PNL-77-269	ϕ Sep.	ϕ Sep.	TEM [13]	Crucible Melt
UK Glass M5 (189)	ϕ Sep.	ϕ Sep.	SANS [14]	Crucible Melt
PNL CVS-1-11	Homog.	Homog.	PNL SEM [9,15]	Crucible Melt
PNL CVS-2-30	Homog.	Homog.	PNL SEM [9,15]	Crucible Melt
PNL CVS-2-29	ϕ Sep.	ϕ Sep.	PNL SEM/TEM [9,15]	Crucible Melt
PNL CVS-2-31	ϕ Sep.	Homog.	PNL SEM/TEM [9,15]	Crucible Melt
Elmer Glass A,B	ϕ Sep.	ϕ Sep.	SEM [16]	Crucible Melt

Ventura Glass A,B	ϕ Sep.	ϕ Sep.	SEM [17]	Crucible Melt
----------------------	-------------	-------------	----------	---------------

^t ϕ Sep. indicates phase separated glasses.
 SANS = Small Angle Neutron Scattering; SEM = Scanning Electron Microscopy;
 TEM = Transmission Electron Microscopy

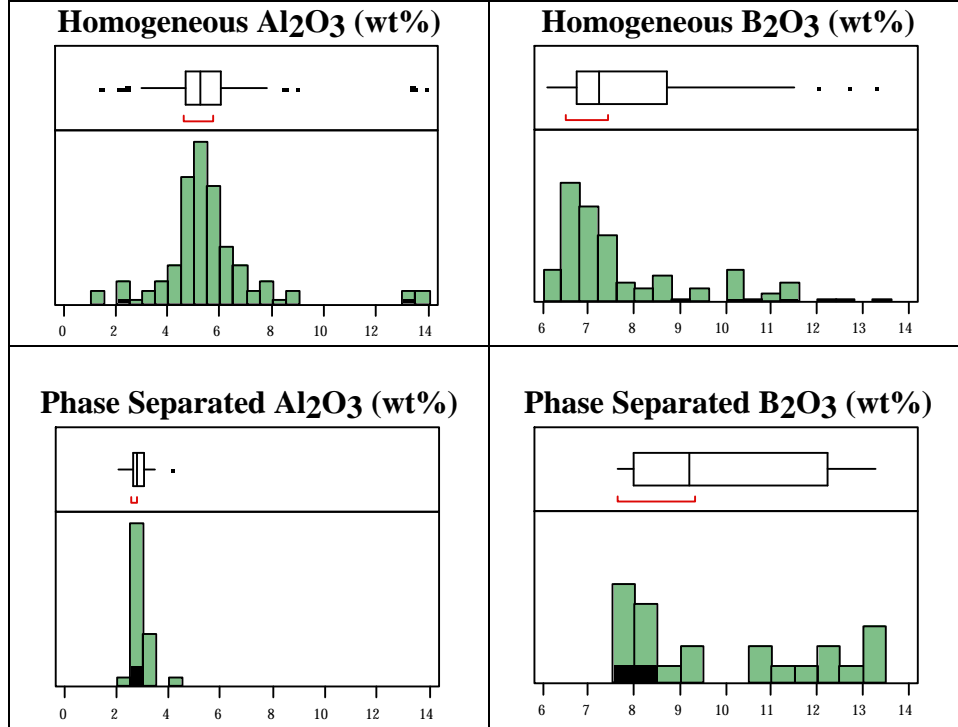


Figure 2. Histogram analysis of the compositional differences (in wt%) of the 110 phase separated and homogeneous “Model Data” glasses.

Visualization of the immiscibility region in the seven component $\text{Na}_2\text{O-Li}_2\text{O-K}_2\text{O-SiO}_2\text{-Al}_2\text{O}_3\text{-B}_2\text{O}_3\text{-Fe}_2\text{O}_3$ system is difficult. In order to simplify the graphical representation all of the alkali oxides can be represented as one corner in the pseudo-quaternary system. $\text{M}_2\text{O-(SiO}_2\text{+Al}_2\text{O}_3\text{)-B}_2\text{O}_3\text{-Fe}_2\text{O}_3$ system. Since the SiO_2 content of the 110 glasses are approximately constant (varying only between 40 and 65 wt%), the remaining $\text{M}_2\text{O-Al}_2\text{O}_3\text{-B}_2\text{O}_3\text{-Fe}_2\text{O}_3$ were re-normalized and plotted as a pseudo-quaternary diagram (Figure 3). The shaded region in Figure 3 sharply delineates a compositional difference in weight percent Al_2O_3 between the phase separated glasses and the homogeneous glasses: sharp phase boundaries in weight percent composition space are indicative of immiscibility boundaries.

Figures 2 and 3 indicate that the phase separated glasses are highly dependent on the Al_2O_3 content of the waste glasses. This is in agreement with the widely known effects of increased Al_2O_3 to stabilize glasses against phase separation [11]. It is also in agreement with the natural analog quaternary system $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{Fe}_2\text{O}_3-\text{SiO}_2$ for basaltic magmas shown in Figure 4. Figure 4 depicts a region of phase separation in alkali iron silicates with less than ~ 4 wt% Al_2O_3 [21]. In addition, glasses in the $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system are known to phase separate when the glasses contain less than ~ 3 wt% Al_2O_3 [22-23].

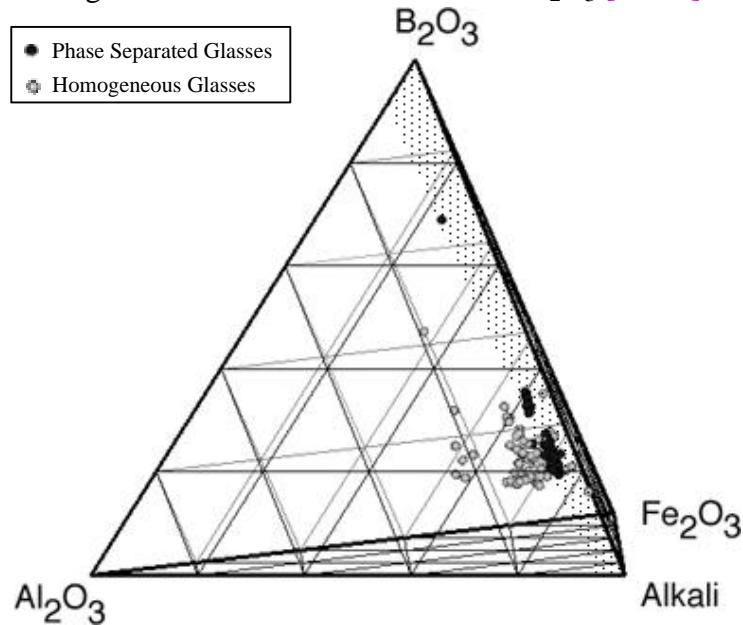


Figure 3. Compositions of the glasses in “Model Data” plotted in $\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3-\Sigma\text{M}_2\text{O}-\text{Fe}_2\text{O}_3$ composition space indicate that the phase separated glasses (shaded region of solid circles) are low in Al_2O_3 content relative to the homogeneous glasses.

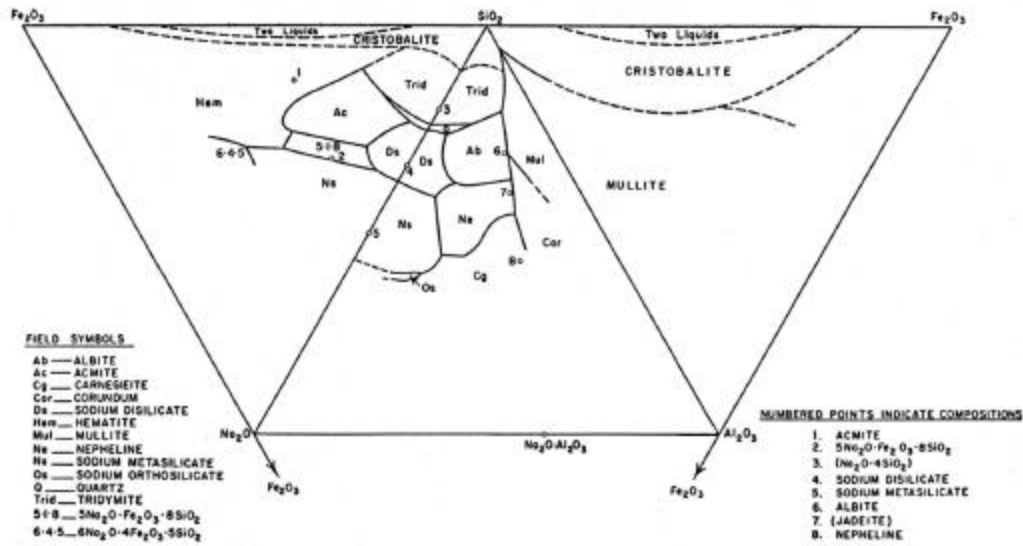


Figure 4. Natural analog system $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{Fe}_2\text{O}_3-\text{SiO}_2$ of geologic significance which shows a region of liquid-liquid immiscibility in the $\text{Fe}_2\text{O}_3-\text{Al}_2\text{O}_3-\text{SiO}_2$ subsystem sub-system below ~ 4 wt% Al_2O_3 .

DEVELOPMENT OF THE PHASE SEPARATION DISCRIMINATOR

Compositionally, good discrimination between the homogeneous and phase separated glasses was achieved by plotting the sum of the lighter density alkali borosilicate (primarily frit) components vs. the denser sludge components, e.g. Al_2O_3 plus all of the iron present as Fe_2O_3 (Figure 5). Calcium oxide, MoO_3 , and the rare earth oxides (i.e., Nd_2O_3 , Ce_2O_3 , La_2O_3 , and Y_2O_3) were included as heavier density components to properly account for the contributions from significant heavier sludge components.[†] Since the compositions of the glasses in this study were not statistically designed, certain minor sludge components (e.g., NiO , MnO , MgO , SrO , and ZrO_2) were found to be insignificant to the discrimination and were thus omitted from the definition of the heavier density component.^{††}

[†] In this study, the MoO_3 and rare earth oxides only occurred in the Hanford glasses including the ARM-1 reference glass although these species are also anticipated in DWPF glasses. Calcium oxide was included since it was present in most of the glasses, including significant amounts in ARM-1, 200R, and the CGW 165 STD. Furthermore, CaO was included because it can play a role in phase separation in borosilicate glasses[11].

^{††} Many of these elements are highly correlated (colinear) with the major sludge oxides, e.g., Al_2O_3 and Fe_2O_3 , and their inclusion tends to add considerable noise into the discrimination with minimal improvement.

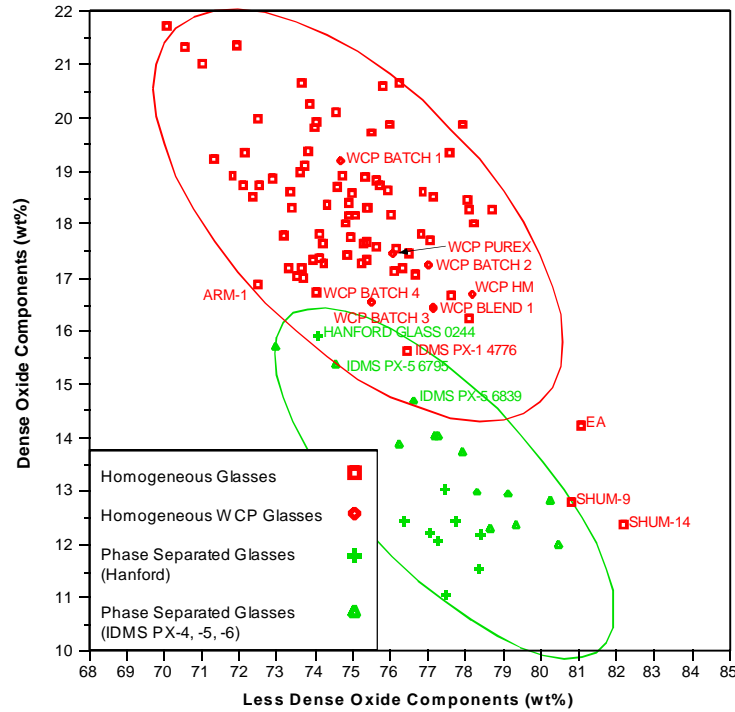


Figure 5. Compositional distinction between homogeneous and phase separated glasses. 95% confidence ellipsoids are indicated for the 110 “Model Data” homogeneous and phase separated glasses.

A discriminant analysis was performed in 14 component oxide wt% space based upon work by Mahalanobis and Hotelling and is described in the JMP® Users Guide [24]. Equation 1 [8] represents the compositional differences in 14 component space that discriminates between homogeneous and phase separated glasses. Glasses will be homogeneous if the following criterion is satisfied:

$$-1.6035 x - 5.6478 y + 210.9203 < 0 \quad (1)$$

where y = Dense Oxide Components = $\text{Al}_2\text{O}_3 + (\text{Fe}_2\text{O}_3 + \text{FeO calculated as } \text{Fe}_2\text{O}_3) + \text{Nd}_2\text{O}_3 + \text{Ce}_2\text{O}_3 + \text{La}_2\text{O}_3 + \text{Y}_2\text{O}_3 + \text{CaO} + \text{MoO}_3$ (wt%)

x = Less Dense Oxide Components = $\text{Na}_2\text{O} + \text{Li}_2\text{O} + \text{K}_2\text{O} + \text{Cs}_2\text{O} + \text{SiO}_2 + \text{B}_2\text{O}_3$ (wt%)

This analysis assumes that the homogeneous and phase separated populations in Table I have multivariate normal distributions with the same covariance matrix. Assuming that an unknown glass also has the same covariance matrix allows the posterior probability of that glass being homogeneous to be calculated. For an unknown glass to be considered homogeneous, the Mahalanobis distance from the new observation to the centroid of the homogeneous group of glass compositions must be less than that to the centroid of the phase separated group of glass compositions.

STATISTICAL VALIDATION OF THE PHASE SEPARATION DISCRIMINATOR

Applying Equation 1 to the 53 validation glasses described in Table II, 95% were correctly classified by Equation 1. Thirty four glasses were determined analytically (SEM, TEM, or SANS) to be homogeneous and 19 phase separated. Thirty two of the 34 known homogeneous glasses (94%) were correctly classified by Equation 1. Eighteen of the 19 known phase separated glasses (95%) were correctly classified. Note that it is more conservative to predict a glass to be phase separated when it is homogeneous rather than to predict that a glass is homogeneous when it is phase separated. Overall, the discriminator was found to be 95% accurate when applied to the "Validation Data." It should be noted that many of the glasses in "Validation Data" represented glasses well outside the composition range of the glasses from which the discriminator was developed. This demonstrates the robust nature of the phase separation discriminator.

CONCLUSIONS

Based on a discriminant analysis of 110 waste glasses in 14 component composition space, a compositionally dependent phase separation discriminator function has been defined (Equation 1). The discriminator function is defined in oxide wt% since the two phases separating represent different melt densities. This constraint, when used to eliminate phase separated glasses from waste glass durability studies or databases, ensures that only homogeneous waste glass durability is modeled. This prevents mixed mechanism durability modeling which would otherwise allow phase separated waste glasses to be produced and waste glass durability to be incorrectly underpredicted.

ACKNOWLEDGEMENT

This paper was prepared in connection with work done under Contract No. DE-AC09-96SR18500 with the U.S. Department of Energy.

REFERENCES

1. I. Tovená, T. Advocat, D. Ghaleb, E. Vernaz and F. Larche, **“Thermodynamic and Structural Models Compared with the Initial Dissolution Rates of SON Glass Samples,”** Sci. Basis for Nucl. Waste Mgt., XVII, A. Barkatt and R.A. Van Konynenburg (Eds.), Mat. Res. Soc., Pittsburgh, PA, 595-602 (1994).
2. C.M. Jantzen, **“Thermodynamic Approach to Glass Corrosion,”** Corrosion of Glass, Ceramics, and Ceramic Superconductors, D.E. Clark and B.K. Zoitos, Noyes Publications, Park Ridge, NJ, 153-215 (1992).
3. X. Feng, **Composition Effects on Chemical Durability and Viscosity of Nuclear Waste Glasses-Systematic Studies and Structural Thermodynamic Models**, Catholic University of America, PhD Thesis (1988).
4. X. Feng and A. Barkatt, **“Structural Thermodynamic Model for the Durability and Viscosity of Nuclear Waste Glasses,”** Sci. Basis for Nucl. Waste Mgt., XI, M.J. Apted and R.E. Westerman (Eds.), Mat. Res. Soc., Pittsburgh, PA, 543-554 (1987).
5. W.J. Dell and P.J. Bray, **“¹¹B NMR Studies and Structural Modeling of Na₂O-B₂O₃-SiO₂ Glass of High Soda Content”**, J. Non-Crystalline Solids, **58**, 1-16 (1983).
6. Y.H. Yun and P.J. Bray, **“Nuclear Magnetic Resonance Studies of the Glasses in the System Na₂O-B₂O₃-SiO₂,”** J. Non-Crystalline Solids, **27**, 363-380 (1978).
7. A Paul, **“Chemistry of Glasses,”** Chapman & Hall, London, 293pp. (1982)
8. C.M. Jantzen, J.B. Pickett, K.G. Brown, T.B. Edwards, U.S. Patent #5,846,278, **“Method of Determining Glass Durability (THERMO™)”** (December 8, 1998).
9. P.R. Hirma, D.K. Peeler, et.al, **“Property/Composition Relationships for Hanford High-Level Waste Glass Melting at 1150°C,”** U.S. DOE Report PNL-10359, Pacific Northwest Laboratory (December, 1994).
10. A.D. Cozzi and C.M. Jantzen, **“Glass Durability Along the Compositional Continuum Between a Phase Separated Frit and a Homogeneous Glass,”** this proceedings
11. M.B. Volf, **“Chemical Approach to Glass,”** Glass Science and Technology, V. 7, Elsevier Science Publishing Co., Inc, New York, 594 pp (1984).

12. W.G. Ramsey, **"Glass Dissolution Chemistry of the System $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2-\text{Al}_2\text{O}_3-\text{Fe}_2\text{O}_3-\text{CaO}$,"** PhD Thesis, Clemson University, 202p (1995).
13. M. Tomozawa, G.M. Singer, Y. Oka, and J.T. Warden, **"Phase Separation in Nuclear Waste Glasses,"** *Ceramics in Nuclear Waste Management*, T.D. Chikalla and J.E. Mende. (Eds.), U.S. Dept. of Energy, Technical Information Center, Springfield, VA, CONF-790420, 193-196 (1979).
14. R.N. Sinclair, J.A. Erwin Desa, and A.D. Wright, **"Neutron Scattering Studies of Vitrified Radioactive Waste,"** *J. Am. Ceram. Soc.*, 66[1], 72-77 (1983).
15. D.K. Peeler and P. Hrma, **"Compositional Range of Durable Borosilicate Simulated Waste Glasses,"** *Emerging Technologies in Hazardous Waste Management*, V. VI, D.W. Tedder and F.G. Pohand, pp.323-338, *American Academy of Environmental Engineers* (1996).
16. T.H. Elmer, M.E. Nordberg, G.B. Carrier, and E.J. Korda, **"Phase Separation in Borosilicate Glasses as Seen by Electron Microscopy and Scanning Electron Microscopy,"** *J. Am. Ceram. Soc.*, 53[4], 171-175 (1970).
17. P.C.S. Ventura, **"High Content Silicate Porous Glasses Used for Radioactive Wastes Storage: Preparation and Characterization of the Spinodal Decomposition,"** *Energy Research Abstracts*, 19[9], 282 (1995).
18. O.V. Mazurin and E.A. Porai-Koshits, **"Phase Separation in Glass,"** North Holland Publishing Co., Amsterdam, 369p. (1984).
19. C.M. Jantzen, D. Schwahn, J. Schelten, and H. Herman, **"The $\text{SiO}_2-\text{Al}_2\text{O}_3$ System, I. Later Stage of Spinodal Decomposition and Metastable Immiscibility,"** *Physics and Chemistry of Glasses*, 22[5], 122-137(1981).
20. C.M. Jantzen, D. Schwahn, J. Schelten, and H. Herman, **"The $\text{SiO}_2-\text{Al}_2\text{O}_3$ System, II. The Glass Structure and Decomposition Model,"** *Physics and Chemistry of Glasses*, 22[5], 138-144 (1981).
21. D.K. Bailey and J.F. Schairer, **"The System $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{Fe}_2\text{O}_3-\text{SiO}_2$ at 1 Atmosphere, and the Petrogenesis of Alkaline Rocks,"** *Journal of Petrology*, 7[1], 114-170 (1966).
22. I. Hager, M. Hahnert, and W. Hinz, **"Beitrag zur Phasentrennung in Glasern der Systemme $\text{Na}_2\text{O}-\text{SiO}_2-\text{B}_2\text{O}_3$ and $\text{Na}_2\text{O}-\text{SiO}_2-\text{Al}_2\text{O}_3$,"** *Silikatechnik*, 18 [11], 360 (1967).
23. J.A. Topping and M.K. Murthy, **"Effect of Small Additions of Al_2O_3 and Ga_2O_3 on the Immiscibility Temperature of $\text{Na}_2\text{O}-\text{SiO}_2$ Glasses,"** *J. Am. Ceram. Soc.*, 56 [5], 270-275 (1973).
24. JMP® User's Guide: Version 3 of JMP, SAS Institute, Cary, NC (1994).