

Date Received for Clearance Process (MM/DD/YYYY) 04/09/2013		INFORMATION CLEARANCE FORM	
A. Information Category ☐ Abstract ☐ Journal Article ☐ Summary ☐ Internet ☐ Visual Aid ☐ Software ☐ Full Paper ☐ Report ☒ Other Poster		B. Document Number ORP-54939 Revision 0 C. Title Compositional threshold for nuclear waste glass durability	
		D. Proposed Internet Address _____	
E. Required Information (MANDATORY) 1. Is document potentially Classified? ☒ No ☐ Yes Harp, Ben j Approved via IDMS data file _____ Manager Required (Print and Sign) _____ If Yes _____ ADC Required (Print and Sign) ☐ No ☐ Yes Classified _____ 2. Official Use Only ☒ No ☐ Yes Exemption No. _____ 3. Export Controlled Information ☒ No ☐ Yes OUO Exemption No. 3 4. UCNi ☒ No ☐ Yes 5. Applied Technology ☒ No ☐ Yes OUO Exemption No. 5 6. Other (Specify) _____		7. Does Information Contain the Following: a. New or Novel (Patentable) Subject Matter? ☒ No ☐ Yes If "Yes", OUO Exemption No. 3 If "Yes", Disclosure No.: _____ b. Commercial Proprietary Information Received in Confidence, Such as Proprietary and/or Inventions? ☒ No ☐ Yes If "Yes", OUO Exemption No. 4 c. Corporate Privileged Information? ☒ No ☐ Yes If "Yes", OUO Exemption No. 4 d. Government Privileged Information? ☒ No ☐ Yes If "Yes", Exemption No. 5 e. Copyrights? ☒ No ☐ Yes If "Yes", Attach Permission. f. Trademarks? ☒ No ☐ Yes If "Yes", Identify in Document. 8. Is Information requiring submission to OSTI? ☒ No ☐ Yes 9. Release Level? ☒ Public ☐ Limited	
F. Complete for a Journal Article 1. Title of Journal Transactions of the Korean Radioactive Waste Society Spring Meeting			
G. Complete for a Presentation 1. Title for Conference or Meeting 2013 Korean Radioactive Waste Society Spring Meeting 2. Group Sponsoring Korean Nuclear Society 3. Date of Conference 9-10 May 2013 4. City/State DAEGU, Korea 5. Will Information be Published in Proceedings? ☐ No ☒ Yes 6. Will Material be Handed Out? ☒ No ☐ Yes			
H. Information Owner/Author/Requestor Kruger, Albert A Approved via IDMS data file _____ (Print and Sign) Approval by Direct Report to President (Speech/Articles Only) _____ (Print and Sign)		Responsible Manager Harp, Ben j Approved via IDMS data file _____ (Print and Sign)	
I. Reviewers	Yes	Print	Signature
General Counsel	☒	Neff, William J	Approved via IDMS data file
Office of External Affairs	☒	Meyer, Carrie C	Approved via IDMS data file
DOE	☐	_____	_____
Clearance	☐	_____	_____
Other	☐	_____	_____
Other	☐	_____	_____
			Public Y/N (If N, complete J)
			Y / N
			Y / N
			Y / N
			Y / N
			Y / N
			Y / N
J. Comments Information Clearance Approval Approved for Public Release; Further Dissemination Unlimited APPROVED By Shauna Adams at 12:47 pm, Apr 24, 2013			

Compositional threshold for nuclear waste glass durability

Rahmatullah Farooqi^{a*}, Pavel Hrma^{a,b}

^a Division of Advanced Nuclear Engineering, Pohang University of Science and Technology (POSTECH), Pohang, South Korea

^b Pacific Northwest National Laboratory, Richland, Washington, United States

*Corresponding author: rufarooqi@postech.ac.kr

1. Introduction

High level waste (HLW) management requires the waste form safety to be convincingly demonstrated. This includes an understanding of the key phenomena controlling the source term, i.e., the flux of radionuclides released from the waste form. The issue of major concern with the waste form, such as glass, is its chemical durability, i.e., the resistance to corrosion by aqueous media.

A number of standard durability tests have been established for waste glasses, among which the product consistency test (PCT) [1] was selected as a criterion of HLW glass acceptability for the repository. Subsequently, a large PCT database has been collected containing over 1000 glasses [2]. Such a database allows the development of models that relate PCT releases to glass composition. Because chemical durability of glass is a strong function of composition, these models are used to formulate acceptable glasses in which the waste loading is maximized.

Within the composition space of glasses, a distinct threshold appears to exist that separates “good” glasses, i.e., those which are sufficiently durable, from “bad” glasses of a low durability. According to Piepel *et al.* [3], transition region between durable and less durable glasses lies around 2 g m^{-2} as determined by the 7-day PCT normalized B release.

The objective of our research is to clarify the origin of this threshold by exploring the relationship between glass composition, glass structure and chemical durability around the threshold region.

2. Method

We used as the baseline the International Simple Glass ISG3 with added 5% Na_2O as baseline (Table 1). As follows from the cut-off model by Piepel *et al.* [3], changing the $\text{Al}_2\text{O}_3/\text{B}_2\text{O}_3$ ratio can shift the glass from one side of the durability threshold to another—see also [5]. We have varied this ratio from 0 to 0.53 in a series of test glasses. In another series, we varied $\text{Na}_2\text{O}/\text{CaO}$ ratio.

Table 1. Baseline glass composition.

Oxide	Na_2O	B_2O_3	SiO_2	Al_2O_3	CaO
Mass fr.	0.1785	0.1629	0.5616	0.0389	0.0581

The glasses were batched from analytical grade chemicals (Na_2CO_3 , H_3BO_3 , SiO_2 , Al_2O_3 and CaCO_3)

and melted for 1 h at 1400°C . The 7-day PCT was performed following the ASTM procedure [1]. The glasses were ground, sieved, ultrasonically cleaned, and dried to produce powder of $75\text{--}150 \mu\text{m}$. Then 1.5-g glass was mixed with 15-ml deionized water in a Teflon vessel and kept in the oven at $90(\pm 2)^\circ\text{C}$ for 7 days.

3. Results

Piepel *et al.* [3] found it necessary to develop different property-composition models (the cut-off model) for glasses located above and below the durability threshold mentioned above. This strongly indicates that below this threshold, glasses interact with water differently than above it. As Fig. 1 demonstrates, one of the striking features of glasses with the normalized B release of $>2 \text{ g m}^{-2}$ is that B exhibits a tendency to be released from these glasses faster than Na, whereas glasses with the normalized B release of $<2 \text{ g m}^{-2}$ dissolve more or less congruently. As Fig. 2 shows, the cut-off model [3] predicts such behavior for our $\text{Al}_2\text{O}_3/\text{B}_2\text{O}_3$ series.

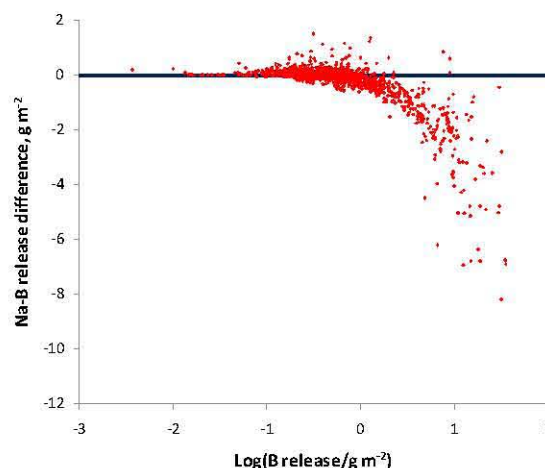


Fig. 1. Difference between normalized Na and B releases versus logarithm of normalized B release.

Table 2 lists the measured data. The measured differences between normalized Na and B releases are plotted in Fig. 2. These differences are negative for all glasses, even though the value for the glass with $\text{Al}_2\text{O}_3/\text{B}_2\text{O}_3 = 0.53$ is close to zero. However, the measured data follow a different trend than the cut-off model suggests. This could be caused by a relatively high model uncertainty of glass durability models in general and the difference between many-component waste glasses and our simple in particular.

Table 2. Releases of B and Na by 7-day PCT for composition variations (defined by $\text{Al}_2\text{O}_3/\text{B}_2\text{O}_3$ ratio) of the baseline glass (Table 1).

$\text{Al}_2\text{O}_3/\text{B}_2\text{O}_3$	0.24	0.05	0.17	0.33	0.53
$r_B, \text{g m}^{-2}$	2.43	3.16	2.25	1.45	0.69
$r_{\text{Na}}, \text{g m}^{-2}$	2.07	2.97	2.03	1.25	0.68

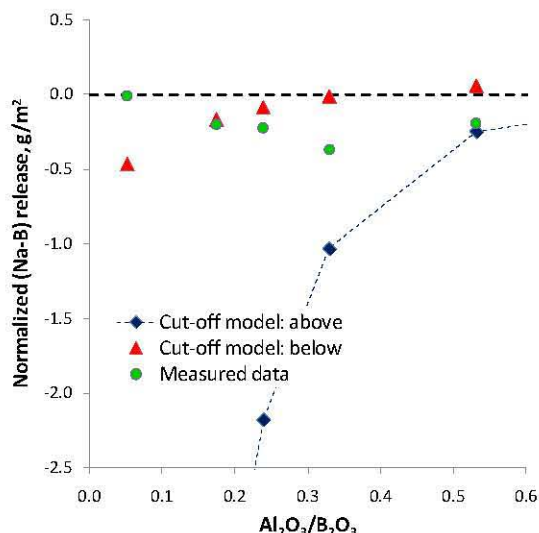


Fig. 2. Difference between normalized Na and B releases, both measured and estimated by cut-off model, as a function of $\text{Al}_2\text{O}_3/\text{B}_2\text{O}_3$ ratio. The cut-off model predicts the difference differently for glasses with normalized B release $>2 \text{ g m}^{-2}$ (above) than for $<2 \text{ g m}^{-2}$ (below).

4. Discussion

We have presented preliminary results of a larger study that will identify the compositional neighborhood of the durable-nondurable threshold. Because the residual rate of corrosion, typically achieved after 1000 days in static conditions, is considered a predictor of the glass endurance in the repository [4], we will test the glasses for long-term behavior using the PCT B method [1]. To elucidate the change of the glasses over the durability threshold, we will investigate the glasses using nuclear magnetic resonance (NMR) spectroscopy, Raman spectroscopy, and transmission electron microscopy (TEM). For a deeper characterization of corrosion layers, including its passivating properties, we will employ secondary ion mass spectrometry (SIMS) and x-ray reflectivity (XRR) analysis.

3. Conclusions

Our study is focused on the corrosion behavior of $\text{SiO}_2 - \text{B}_2\text{O}_3 - \text{Na}_2\text{O} - \text{Al}_2\text{O}_3 - \text{CaO}$ glass composition region. In particular, we try to identify the durability threshold separating durable from nondurable glasses in

the composition space. So far we have explored the elemental releases of Na and B measured with the 7-day PCT.

Acknowledgement

The authors gratefully acknowledge the support by the World Class University program through the National Research Foundation of Korea funded by the Min. of Education, Science and Technology (R31-3005). The authors thank to Stéphane Gin for helpful suggestions and R.U. Farooqi thanks to his mentors Prof. Jong Heo and Dr. Xu Kai for training.

REFERENCES

- [1] ASTM, Standard Test Methods for Determining Chemical Durability of Nuclear, Hazardous, and Mixed Waste Glasses and Multiphase Glass Ceramics: The Product Consistency Test (PCT), 2008.
- [2] J. D. Vienna, A. Fluegel, D. S. Kim, P. Hrma, Glass Property Data and Models for Estimating High-Level Waste Glass Volume, PNNL-18501, Pacific Northwest Laboratory, Richland, Washington, 2009.
- [3] G. F. Piepel, S. K. Cooley, I. Muller, H. Gan, I. Joseph, I. L. Pegg, ILAW PCT, VHT, Viscosity, and Electrical Conductivity Model Development, VSL-07R1230-1, Vitreous State Laboratory, The Catholic University of America, Washington, DC 20064, 2007.
- [4] S. Gin, X. Beaudoux, F. Angéli, C. Jégou, N. Godon, Effect of composition on the short-term and long-term dissolution rates of ten borosilicate glasses of increasing complexity from 3 to 30 oxides, Journal of Non-Crystalline Solids 358, 2559–2570, 2012.
- [5] E. M. Pierce, L. R. Reed, W. J. Shaw, B. P. McGrail, J. P. Icenhower, C. F. Windisch, E. A. Cordova, and J. Broady, Experimental determination of the effect of the ratio of B/Al on glass dissolution along the nepheline ($\text{NaAlSi}_3\text{O}_8$)–malinkoite (NaBSi_3O_8) join, Geochimica et Cosmochimica Acta, Vol. 74, pp. 2634–2654, 2010.