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Transactions of the Korean Radioactive Waste Society Spring Meeting
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Compositional threshold for nuclear waste glass durability

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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 Al_2O_3/B_2O_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 Na_2O/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 75–150 µm Then 1.5-g glass was mixed with 15-ml deionized water in a Teflon vessel and kept in the oven at 90(±2)°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 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 g m^{-2} dissolve more or less congruently. As Fig. 2 shows, the cut-off model [3] predicts such behavior for our Al_2O_3/B_2O_3 series.

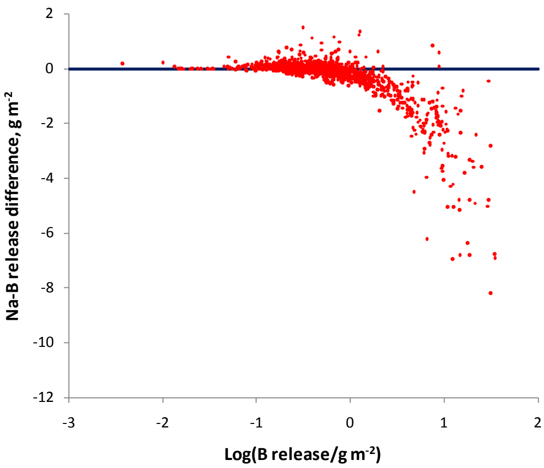

Fig. 1. Difference between normalized Na and B releases versus logarithm of normalized B release.

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 Al_2O_3/B_2O_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 Al_2O_3/B_2O_3 ratio) of the baseline glass (Table 1).

Al_2O_3/B_2O_3	0.24	0.05	0.17	0.33	0.53
r_B, g m^{-2}	2.43	3.16	2.25	1.45	0.69
r_{Na}, g m^{-2}	2.07	2.97	2.03	1.25	0.68

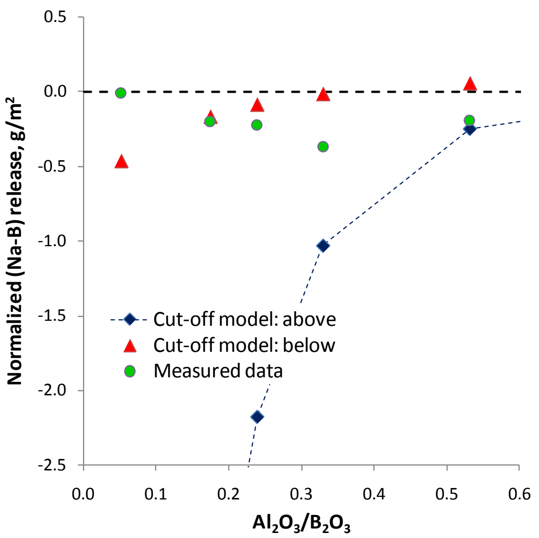

Fig. 2. Difference between normalized Na and B releases, both measured and estimated by cut-off model, as a function of Al_2O_3/B_2O_3 ratio. The cut-off model predicts the difference differently for glasses with normalized B release >2 g m^{-2} (above) than for <2 g m^{-2} (below).

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 $SiO_2 - B_2O_3 - Na_2O - Al_2O_3 - CaO$ 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.

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