Long-Term Durability of High-Level Waste Borosilicate Glass

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1. Introduction

Borosilicate glass is considered as the most feasible candidate for high level waste glasses. Major concern for disposal of the waste glasses into a deep geological formation is intrusion of groundwater into a disposed waste glasses and a subsequent release of the radionuclides from altered glasses into the biosphere. It is very important, therefore, to formulate borosilicate glass compositions which show an excellent durability.

Although there have been many researches to predict the durability of glasses based on leaching rates of borosilicate glasses, the longest test period is only 8 years [1]. However, because it requires at least 10^3 years to isolate the radionuclides in the glasses from the biosphere, the predictions based on the leaching rates can hardly give a reliable evaluation on the long-term durability of the waste glasses.

In this study, a new approach has been tried, which is based on the time needed for crystallization of glass, the final stage of glass alteration, to evaluate the long-term durability of borosilicate glasses.

2. Experimental

2.1 Glass Preparation

The chemical reagents were weighted based on each one of the selected 58 compositions, and mixed in a platinum crucible. The mixtures, preliminarily heated at about 850℃, were melted at 1200℃ about for 1 hour. The melt quenched in deionized water. In order to ensure compositional homogeneity of the glass, each glass was pulverized and re-melted at 1200℃ for about 1 hour and quenched. For 14 glass compositions of those selected, it was impossible to obtain glass due to their high silica contents. Table 1 lists the formulated 44 glass compositions which were analyzed by Electron Probe Micro Analysis (EPMA). It is noted that the Li_2O contents in Table 1 were calculated from the weighed amount of Li_2CO_3 reagent because EPMA cannot detect lithium.

2.2 Hydrothermal Treatment

For each glass composition, 7 glass powder samples of identical weight were prepared, each of which was sealed in a gold capsule together with excess deionized water. The samples were then treated in an autoclave at 200℃ under vapor pressure of 15.4 MPa. The reason to use a temperature of 200℃ was to accelerate alteration of glasses. Each one of the samples was taken out from the autoclave sequentially after 1, 3, 7, 14, 28, 56 and 168 days. The product taken out of the capsule was air-dried at room temperature.

2.3 XRD Examination

Each one of the 7 products obtained for each glass composition was examined by X-ray Diffraction (XRD) to determine starting day (SDC) and completion day (CDC) of crystallization: SDC refers to a running day when peaks of formed crystalline material(s) first appear, and CDC designates a running day when the

Table 1: Glass Compositions Tested (mol %) and Starting Day (SDC) and Completion Day (CDC) of Crystallization

Glass Comp. / Oxides	A1	A2	A3	A4	B4	C1	C2	C4	D1	D2	D3	D4	D6	E1	E2	E3	E4	E5	E6	F1	F2	F3
SiO_2	63.47	48.31	65.38	45.52	44.85	65.74	50.37	47.24	69.13	61.65	73.57	68.24	72.13	51.45	48.23	63.10	59.86	69.07	44.19	68.87	59.78	72.93
B_2O_3	24.60	24.24	17.91	14.20	12.99	21.90	21.43	12.09	26.25	27.52	19.14	16.22	5.94	29.83	21.02	15.71	14.17	7.12	4.81	24.32	26.32	17.37
Al_2O_3														3.84	2.73	3.10	3.13	2.78	2.37			
FeO																	19.92					
L_2O	10.96	26.68	15.89	39.64	39.72	10.48	26.46	39.20						9.94	25.46	15.21	0.00	18.49	46.50			
Na_2O									3.66	10.06	6.51	15.11	21.84							3.58	10.68	6.62
Cs_2O	0.97	0.77	0.83	0.64		0.46	0.40	0.25	0.96	0.77	0.79	0.42	0.09									
SrO					2.45	1.42	1.33	1.23					0.00	4.94	2.55	2.89	2.93	2.55	2.14	3.23	3.22	3.08
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
SDC	28	1	7	1	1	1	7	1	168	7	3	1	1	1	1	3	1	1	1	1	3	14
CDS	168	28	28	7	3	168	28	3	-	56	56	3	56	-	3	14	14	28	1	168	56	28

Glass Comp. / Oxides	F4	F6	G1	G2	G3	G4	G5	H1	I1	J1	K1	L1	M1	N1	O1	P1	P2	P3	P4	Q1	R1	S1
SiO_2	69.24	69.85	72.14	67.44	77.46	70.74	76.83	57.57	58.03	57.83	55.45	56.51	57.73	59.62	59.44	59.00	62.30	59.58	61.55	59.43	58.84	58.93
B_2O_3	14.41	6.74	25.13	25.02	17.22	17.11	5.44	11.62	11.90	11.88	12.18	11.43	12.82	13.65	13.38	13.90	11.28	14.02	11.75	12.81	11.46	11.28
Al_2O_3								3.43	3.46	3.42	3.68	3.89	3.81	4.27	4.22	4.21	4.18	4.21	4.37	4.34	4.20	4.21
FeO																				6.28	6.35	6.31
L_2O								6.74	0.00	3.32	6.91	0.00	3.37									
Na_2O	12.72	19.99						10.68	10.75	10.71	11.52	11.55	11.75		13.38	13.58	8.10	13.05	10.09	8.17		6.09
K_2O			2.02	6.79	4.39	11.63	17.17	0.00	6.01	2.97	0.00	6.32	0.01	13.76	0.91	0.00	0.00	0.00	0.00	0.00	10.19	
Cs_2O			0.71	0.76	0.93	0.52	0.56	1.44	1.40	1.40	1.34	1.26	1.39			0.64	5.05	0.37	3.34	0.00	0.00	4.38
MgO											3.70	3.70	3.77									
CaO								3.69	3.57	3.58				2.98	3.06	3.05	3.25	3.10	3.19	3.18	3.20	3.25
SrO	3.62	3.42						4.83	4.89	4.90	5.23	5.33	5.35	5.71	5.60	5.62	5.83	5.66	5.71	5.77	5.77	5.56
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
SDC	1	1	168	56	1	7	1	3	1	3	3	3	3	7	28	14	14	7	14	56	168	14
CDS	7	168	168	56	28	7	3	3	14	7	28	7	3	-	28	14	14	7	14	168	168	56

background of XRD pattern of remaining amorphous material (glass) was completely disappeared. The SDC and CDC for each glass are listed in the first and second rows from the bottom of Table, respectively. The SDC and CDC are used as a criterion of glass durability in the models below.

3. Results and Discussions

3.1 Thermodynamic Model

In this model, SDC or CDC is predicted in terms of hydration Gibbs free energy or formation enthalpy, which is an additive function of glass components' hydration Gibbs free energies or formation enthalpies, weighted according to their molar fraction, with the equation being given as follows (for more details, refer to [2] and [3]);

$$\Delta Y_{E,glass} = \sum_i x_i \Delta Y_{E,i} \qquad (1)$$

where

$\Delta Y_{E,glass}$: hydration Gibbs free energy or formation enthalpy of component *i*
x_i : molar fraction of component *i*
$\Delta Y_{E,i}$: hydration Gibbs free energy or formation enthalpy of component *i*

Fig. 1 shows the dependence of a square root of CDC on the calculated hydration Gibbs free energy and the calculated formation enthalpy of glass, respectively. From this, it can be seen that the bigger the hydration Gibbs free energy or the smaller formation enthalpy of glass, the longer $CDC^{0.5}$, namely, a better durability. Although not shown here, a similar but less dependence was observed with $SDC^{0.5}$.

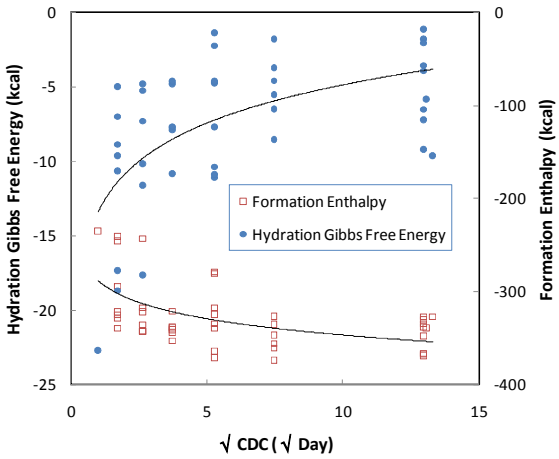

Fig. 1. Dependency of CDC on hydration Gibbs free energy or formation enthalpy of glasses

3.2 Structural Model

The durability of glass can be affected by structural factors, such as Non-Bridging Oxygen (NBO). NBO refers to oxygen whose bonds do not all participate in forming tetrahedral SiO_4 network of glass. Therefore, glass with higher NBO ratio can be more vulnerable to aqueous attack. NBO ratio can be calculated as follows (for more details, refer to [3]):

$$NBO = \frac{2[\sum_i (M_2O)_i + \sum_j (MO)_j - \sum_k (M_2O_3)_k - N4B_2O_3]}{Molar\ sum\ of\ all\ oxides} \qquad (2)$$

where

M_2O, MO, M_2O_3 : molar fraction of mono-, di- and tri-valent metal oxide except for boron
$N4B_2O_3$: molar fraction of 4-coordinate boron oxide

From Fig. 2 which shows the relationship between a square root of CDC and NBO, it can be seen that a glass with higher NBO ratio has a smaller $CDC^{0.5}$, that is, a poorer durability. Although not shown here, a similar but weak relationship was observed with $SDC^{0.5}$.

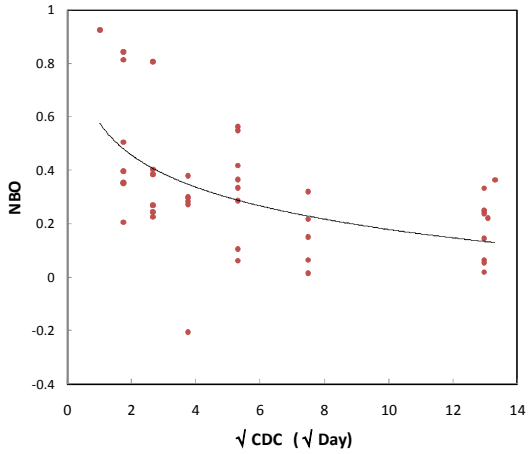

Fig.2. Relationship between CDC and NBO of glasses

4. Conclusions

In this study, the long-term durability of borosilicate glasses with various compositions was evaluated in terms of thermodynamic and structural models, employing crystallization of glass as a criterion for the durability of waste glass. The model results implied that the glass crystallization could be employed as a valuable criterion of glass durability, though not fully satisfactory. However, since only the crystallization of glass can give a reliable evaluation for the long-term durability of waste glasses, further research is needed.

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