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Prepared for the U.S. Department of Energy
Assistant Secretary for Environmental Management

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EMPIRICAL MODEL FOR FORMULATION OF CRYSTAL-TOLERANT HLW GLASSES

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ABSTRACT

Historically, high-level waste (HLW) glasses have been formulated with a low liquidus temperature (T_L), or temperature at which the equilibrium fraction of spinel crystals in the melt is below 1 vol % ($T_{0.01}$), nominally below 1050°C. These constraints cannot prevent the accumulation of large spinel crystals in considerably cooler regions (~ 850°C) of the glass discharge riser during melter idling and significantly limit the waste loading, which is reflected in a high volume of waste glass, and would result in high capital, production, and disposal costs. A developed empirical model predicts crystal accumulation in the riser of the melter as a function of concentration of spinel-forming components in glass, and thereby provides guidance in formulating crystal-tolerant glasses that would allow high waste loadings by keeping the spinel crystals small and therefore suspended in the glass.

INTRODUCTION

The high-level radioactive waste (HLW) from the Hanford and Savannah River Sites is being vitrified in stable borosilicate glass for long-term storage and disposal. This process is time consuming and expensive because it is highly dependent on loading of HLW in glass and on the rate of HLW glass production. The current HLW melters are projected to operate in an inefficient manner as they are subjected to artificial constraints that limit waste loading to far below its intrinsic level.[1] These constraints, such as liquidus temperature (T_L) of glass or the temperature at which the equilibrium fraction of spinel crystals in the melt is below 1 vol % ($T_{0.01}$), nominally below 1050°C, were imposed to prevent clogging of the melter with spinel crystals that can accumulate at the bottom and in the glass discharge riser based upon operational experience with static melters (i.e., non-bubbled).[2]

To protect the melter from detrimental accumulation of spinel crystals, attention has been focused on studying the settling of spinel crystals in molten glasses[3-6] as well as transparent liquids[7,8]. Lamont and Hrma[4] observed the parabolic shape of the settling front indicating that the settling crystals generated a convective cell within the melt. Klouzek et al.[5] determined that the measured settling distances between the glass level and the uppermost crystals in the centerline of the crucible were less than 10% smaller than the distances calculated with the modified Stoke's law. Matyas et al.[3] determined the accumulation rate of crystals as a function of spinel forming components and noble metals, and revealed a beneficial effect of suppressing the crystal size and accumulation rate through additions of Fe and noble metals. Matlack et al. reported that the high-crystal content glasses of up to 4.2 vol% at 950°C have been successfully discharged from the DuraMelter® DM-100 after about 8 days of melter idling at 950 °C.[6]

The goal of this work was to develop an empirical linear model of spinel settling that can predict crystal accumulation in the riser as a function of glass composition and therefore provide the guidance to formulate crystal-tolerant glasses for higher waste loading. By keeping the spinel

crystals small and therefore limiting spinel deposition in the melter, these glasses will allow high waste loading without decreasing melter lifetime.

EXPERIMENTAL

Glass Matrix Design and Fabrication

Glass matrix of twelve compositions was developed by changing concentrations of Cr_2O_3, NiO, Fe_2O_3, ZnO, MnO, Al_2O_3, and noble metals (Rh_2O_3 and RuO_2) one or two components-at-a-time from the baseline glass composition (BL) while proportionally decreasing the concentration of all other components. The concentration of these components was varied to encompass their variation in Hanford HLW, see Table I. Table II shows the composition of designed glasses, including the baseline glass.

Table I. Concentration Variation of Noble Metals, Cr, Ni, Fe, Zn, Mn, and Al in Hanford HLW in Mass Fraction of Oxides.

Component	Minimum	Maximum
Rh_2O_3	1.1E-08	0.0004
RuO_2	2.8E-06	0.0024
Cr_2O_3	0.0027	0.0584
NiO	0.0012	0.0351
Fe_2O_3	0.0140	0.5244
ZnO	0.0005	0.0181
MnO	0.0018	0.0668
Al_2O_3	0.0704	0.7350

Glass batches were prepared from AZ-101 simulant and additives (H_3BO_3, Li_2CO_3, Na_2CO_3, and SiO_2). Extra Cr, Ni, Fe, Zn, Mn, and Al were added as Cr_2O_3, NiO, Fe_2O_3, ZnO, MnO, Al_2O_3, and Rh_2O_3. Ruthenium was added in the form of ruthenium nitrosyl nitrate solution drop by drop to 100 g of SiO_2 that was dispersed on a Petri dish. The SiO_2 cake was dried in oven at 105°C for 1 hour, quenched, and hand-mixed in the plastic bag with the rest of the glass batch. Then, the glass batch was milled in an agate mill for 5 min to ensure homogeneity.

Glasses were produced in Pt-10%Rh crucibles following a two-step melting process: 1) melting of homogenized glass batches and 2) melting of produced glasses after quenching and grinding. The melting temperature for Ni1.5/Al12 and Fe20/Ni1.5 glasses was 1250°C and 1300°C, respectively. The other glasses were melted at1200°C.

Table II. Composition of Designed Glasses in Mass Fraction of Oxides and Halogens.

Component	BL	Cr0.6	Cr1.2	Ni1.07	Ni1.5	Ni1.5/nm[a]	Fe20	Fe20/Ni1.5	Mn1	Mn2.5	Zn0.6	Ni1.5/Al12
Al_2O_3	0.0821	0.0817	0.0813	0.0817	0.0814	0.0814	0.0768	0.0760	0.0816	0.0803	0.0816	**0.1200**
B_2O_3	0.0799	0.0796	0.0791	0.0796	0.0792	0.0792	0.0748	0.0739	0.0794	0.0782	0.0794	0.0758
BaO	0.0009	0.0009	0.0009	0.0009	0.0009	0.0009	0.0008	0.0008	0.0009	0.0009	0.0009	0.0009
CaO	0.0057	0.0057	0.0056	0.0057	0.0057	0.0056	0.0053	0.0053	0.0057	0.0056	0.0057	0.0054
CdO	0.0065	0.0065	0.0064	0.0065	0.0064	0.0064	0.0061	0.0060	0.0065	0.0064	0.0065	0.0062
Cr_2O_3	0.0017	**0.0060**	**0.0120**	0.0017	0.0017	0.0017	0.0016	0.0016	0.0017	0.0017	0.0017	0.0016
F	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001
Fe_2O_3	0.1451	0.1445	0.1436	0.1445	0.1438	0.1438	**0.2000**	**0.2000**	0.1442	0.1420	0.1443	0.1377
K_2O	0.0034	0.0034	0.0034	0.0034	0.0034	0.0034	0.0032	0.0031	0.0034	0.0033	0.0034	0.0032
Li_2O	0.0199	0.0198	0.0197	0.0198	0.0197	0.0197	0.0186	0.0184	0.0198	0.0195	0.0198	0.0189
MgO	0.0013	0.0013	0.0013	0.0013	0.0013	0.0013	0.0012	0.0012	0.0013	0.0013	0.0013	0.0012
MnO	0.0035	0.0035	0.0035	0.0035	0.0035	0.0035	0.0033	0.0032	**0.0100**	**0.0250**	0.0035	0.0033
Na_2O	0.1866	0.1858	0.1847	0.1858	0.1850	0.1849	0.1746	0.1726	0.1854	0.1826	0.1855	0.1771
NiO	0.0064	0.0064	0.0063	**0.0107**	**0.0150**	**0.0150**	0.0060	**0.0150**	0.0064	0.0063	0.0064	**0.0150**
P_2O_5	0.0032	0.0032	0.0032	0.0032	0.0032	0.0032	0.0030	0.0030	0.0032	0.0031	0.0032	0.0030
SiO_2	0.4031	0.4014	0.3989	0.4014	0.3996	0.3995	0.3772	0.3729	0.4005	0.3944	0.4008	0.3825
SO_3	0.0008	0.0008	0.0008	0.0008	0.0008	0.0008	0.0007	0.0007	0.0008	0.0008	0.0008	0.0008
TiO_2	0.0003	0.0003	0.0003	0.0003	0.0003	0.0003	0.0003	0.0003	0.0003	0.0003	0.0003	0.0003
ZnO	0.0002	0.0002	0.0002	0.0002	0.0002	0.0002	0.0002	0.0002	0.0002	0.0002	**0.0060**	0.0002
ZrO_2	0.0416	0.0414	0.0412	0.0414	0.0412	0.0412	0.0389	0.0385	0.0413	0.0407	0.0414	0.0395
Cl	0.0002	0.0002	0.0002	0.0002	0.0002	0.0002	0.0002	0.0002	0.0002	0.0002	0.0002	0.0002
Ce_2O_3	0.0020	0.0020	0.0020	0.0020	0.0020	0.0020	0.0019	0.0019	0.0020	0.0020	0.0020	0.0019
CoO	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001
CuO	0.0004	0.0004	0.0004	0.0004	0.0004	0.0004	0.0004	0.0004	0.0004	0.0004	0.0004	0.0004
La_2O_3	0.0022	0.0022	0.0022	0.0022	0.0022	0.0022	0.0021	0.0020	0.0022	0.0022	0.0022	0.0021
Nd_2O_3	0.0018	0.0018	0.0018	0.0018	0.0018	0.0018	0.0017	0.0017	0.0018	0.0018	0.0018	0.0017
SnO_2	0.0010	0.0010	0.0010	0.0010	0.0010	0.0010	0.0009	0.0009	0.0010	0.0010	0.0010	0.0009
Total	1.0000	1.0000	1.0000	1.0000	1.0000	0.9997	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000

[a] Added 0.0003 Rh_2O_3 and 2.9E-5 RuO_2

Settling experiments

The double crucible test was used to study the accumulation of spinel crystals.[3,8] The alumina crucible was nested in the big silica crucible, hold in place with the core-drilled silica crucible, and covered with molten glass to eliminate the Marangoni convection in the meniscus and bubble generation at the bottom of silica crucibles. First, glass powders were melted in Pt-10%Rh crucible at 1200°C for 1 h to dissolve spinel crystals that might formed during the quenching of the glass. Then, the crucible was removed from the melting furnace and molten glass was poured into three double crucibles that were rested inside the furnace at 850°C, mimicking the temperature in the glass discharge riser. The crucibles were removed at various times and cross-sectioned. The rectangular pieces 3 cm wide and 5 cm long were cut out from the bottom of the crucibles, thin-sectioned, and analyzed with scanning electron microscopy-

electron dispersive spectroscopy (SEM-EDS) and Clemex image analysis to determine the thickness of the spinel sludge layer.

Empirical Model of Spinel Crystal Settling

Three stages were identified during the settling experiments in the double crucibles: 1) latency period with no settling, 2) settling period with constant settling rate of spinel, and 3) end of settling period with a low and gradually decreasing settling rate of spinel due to a smaller and smaller number of settling crystals. Only the sludge layer thickness data for glasses that were collected during the constant settling rate period were used to build an experimental model predicting crystal accumulation in the glass discharge riser as a function of seven major components (Al_2O_3, Cr_2O_3, Fe_2O_3, ZnO, MnO, NiO, and Others). The constant settling rate allowed us to use a general linear model in the form:

$$h = \sum_{i=1}^{7} h_i x_i + t \sum_{i=1}^{7} s_i x_i \qquad (1)$$

where h_i is a compositional dependent intercept coefficient (μm), x_i is the i-th component mass fraction, t is the settling time (h), and s_i is a compositional dependent velocity coefficient (μm/h).

RESULTS AND DISCUSSION

Table III shows the calculated coefficients h_i and s_i, R^2 (expresses the fraction of the variability accounted for by the model), and R^2_{adj} (adjust R^2 for the number of parameters used in fitting the model). Negative coefficients s_i for Al_2O_3 and Fe_2O_3 suggest that these components decrease the settling rate of crystals. In contrast, additions of MnO, ZnO, Cr_2O_3, and NiO to the baseline glass increase the settling rate. Nickel oxide stands out as the most troublesome component with a more than six times faster settling rate than, e.g., Cr-rich glass. The detrimental effect of this component on the settling rate can be significantly suppressed by introducing the noble metals or Fe_2O_3 to the glass. The negative coefficients h_i for MnO, ZnO, Cr_2O_3, and NiO only indicate, but do not predict, the length of the latency period. This period is dependent on the initial growth rate of crystals to the size at which crystals start to settle.

Table III. Component Coefficients Calculated with PNNL Model

Components	h_i (μm)	s_i (μm/h)
Al_2O_3	8816.97	-350.41
Fe_2O_3	4304.182	-49.9117
MnO	-7498.52	259.3812
ZnO	-12257.6	313.0436
Cr_2O_3	-40257.3	443.5807
NiO	-197477	2672.734
Others	-366.91	27.00287
R^2	0.985	
R^2 adj	0.975	

Figure 1 shows the predictive versus measured thicknesses of a spinel sludge layer for tested glasses. The linear empirical model with coefficients h_i and s_i expressed as a linear function of mass fractions of seven major components fits the 35 data points reasonably well, R^2=0.985, and can become an efficient tool to formulate the crystal-tolerant glasses that would ultimately allow a substantial increase in the waste loading.

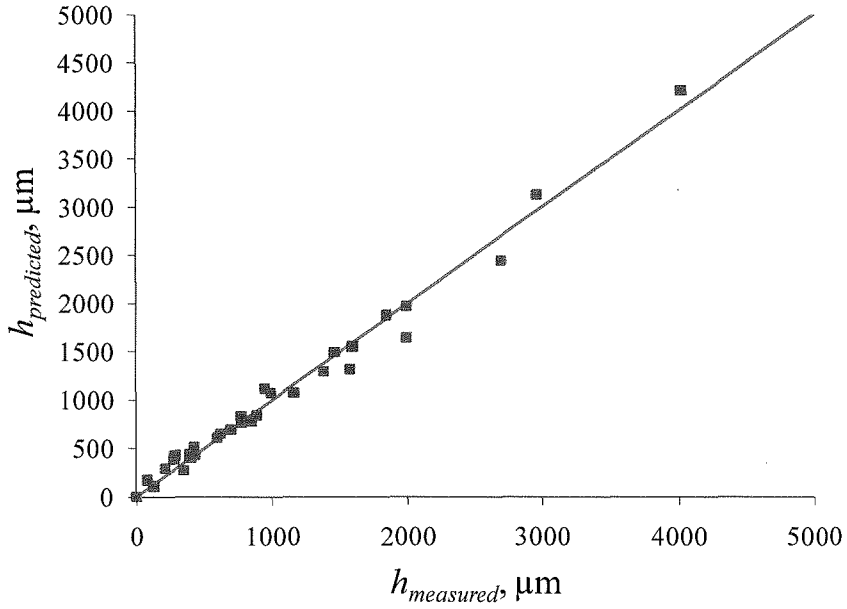

Figure 1. Predicted vs. Measured Spinel Layer Thickness.

CONCLUSION

The developed 7-component model can predict very well the crystal accumulation in the riser as a function of glass composition and therefore allows higher waste loadings, and at the same time protects the HLW glass melter from detrimental accumulation of spinel in the glass discharge riser during melter idling. In the future work, we plan to expand the compositional region covered by our model, and thereby improve its predictive performance. We will also elucidate the accumulation rate of spinel crystals at temperatures above 850°C because the temperature in the glass discharge riser varies and can exceed 950°C during melter idling. Additionally, we will investigate the impact of different components on agglomeration of particles and on the shape, size, and concentration of crystals.

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