Crystal-Tolerant HLW Glasses:

A Novel Pathway to High Waste Loading in the Borosilicate Glasses

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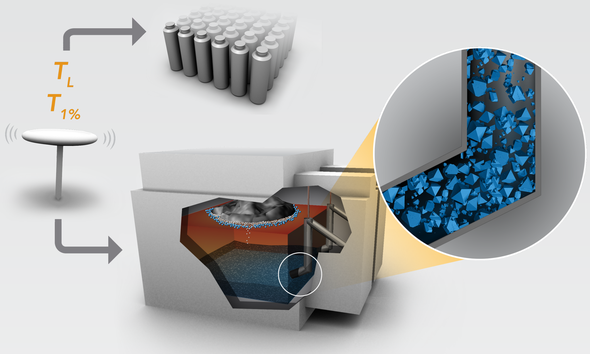
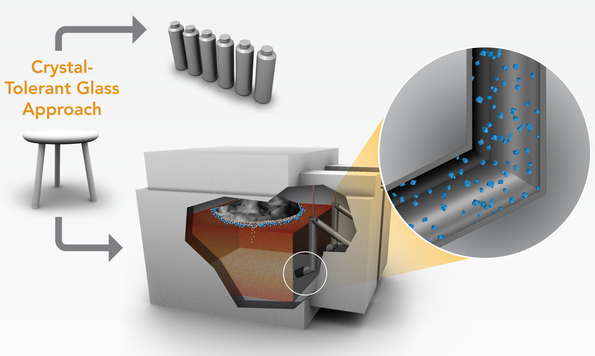
PROBLEM

For more than two decades, the loading of high-level waste (HLW) in borosilicate glasses has been limited by the minimum liquidus temperature (T_L) or the maximum equilibrium fraction of crystallinity at a given temperature. These constraints were imposed to prevent clogging the glass discharge riser of the Joule-heated ceramic melter with crystals of spinel during idling.



SOLUTION

Crystal-tolerant HLW glasses for higher waste loading are being developed at PNNL through the use of an empirical model that can calculate the crystal accumulation in the riser as a function of glass composition. These high waste-containing glasses prevent accumulation of crystals and allow a significant decrease in the volume of waste glass, and thus result in substantial reduction of production and disposal costs.



BACKGROUND

The Joule-heated ceramic melter is the technology of choice for vitrification of HLW from the Hanford and Savannah River Sites in stable borosilicate glass for long-term storage and disposal. However, a worry that crystals of spinel [(Fe, Ni, Mn, Sn, Zn)(Fe, Cr)$_2$O$_4$] may accumulate and eventually clog the 76 mm-diameter glass discharge riser of the melter during frequent and periodic idling conflicts with an effort to maximize the waste content in the glass (waste loading). Traditionally, artificial constraints, such as T_L of glass (100°C below the nominal melter operating temperature) or the temperature $T_{1\%}$ at which the equilibrium fraction of spinel crystals in the melt is 1 vol% (nominally below 950°C), were placed on the glass formulation to avoid the risk of crystal accumulation. However, these constraints are overly conservative (a large fraction of crystals can be safely removed from the melter with the glass melt as it is cast into canisters) and limit waste loading too far below its intrinsic level. As a result, current melters are projected to operate in an inefficient manner.

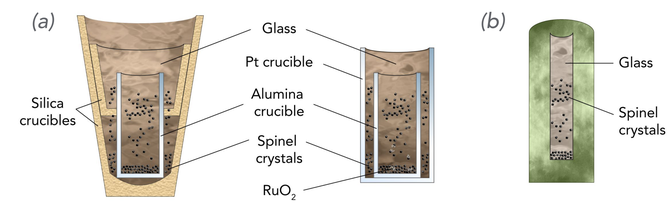
APPROACH

I *Formulation and preparation of HLW glasses*

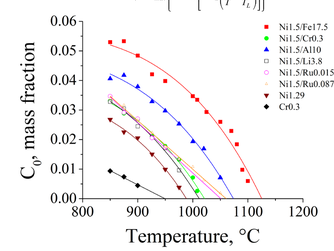
Component	BL	Ni1.29	Cr0.3	Ni1.5/Al10	Ni1.5/Fe17.5	Ni1.5/Li3.8	Ni1.5/Cr0.3
Al_2O_3	0.0821	0.0816	0.0820	0.1000	0.0784	0.0799	0.0813
B_2O_3	0.0799	0.0794	0.0798	0.0776	0.0763	0.0777	0.0791
BaO	0.0009	0.0009	0.0009	0.0009	0.0009	0.0009	0.0009
CaO	0.0057	0.0057	0.0057	0.0055	0.0054	0.0055	0.0056
CdO	0.0065	0.0065	0.0065	0.0063	0.0062	0.0063	0.0064
Cr_2O_3	0.0017	0.0017	0.0030	0.0017	0.0016	0.0017	0.0030
F	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001
Fe_2O_3	0.1451	0.1441	0.1448	0.1408	0.1750	0.1410	0.1436
K_2O	0.0034	0.0034	0.0034	0.0033	0.0032	0.0033	0.0034
Li_2O	0.0199	0.0198	0.0199	0.0193	0.0190	0.0380	0.0197
MgO	0.0013	0.0013	0.0013	0.0013	0.0012	0.0013	0.0013
MnO	0.0035	0.0035	0.0035	0.0034	0.0033	0.0034	0.0035
Na_2O	0.1866	0.1853	0.1864	0.1812	0.1781	0.1814	0.1847
NiO	0.0064	0.0129	0.0064	0.0150	0.0150	0.0150	0.0150
P_2O_5	0.0032	0.0032	0.0032	0.0031	0.0031	0.0031	0.0032
SiO_2	0.4031	0.4003	0.4025	0.3913	0.3847	0.3920	0.3989
SO_3	0.0008	0.0008	0.0008	0.0008	0.0008	0.0008	0.0008
TiO_2	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
ZrO_2	0.0416	0.0413	0.0415	0.0404	0.0397	0.0405	0.0412
Cl	0.0002	0.0002	0.0002	0.0002	0.0002	0.0002	0.0002
Ce_2O_3	0.0020	0.0020	0.0020	0.0019	0.0019	0.0019	0.0020
CoO	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
La_2O_3	0.0022	0.0022	0.0022	0.0021	0.0021	0.0021	0.0022
Nd_2O_3	0.0018	0.0018	0.0018	0.0017	0.0017	0.0018	0.0018
SnO_2	0.0010	0.0010	0.0010	0.0010	0.0010	0.0010	0.0010
Total	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000

Composition of glasses expressed in mass fraction of oxides and halogens

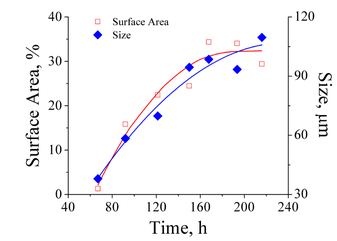
II *Lab-scale testing of crystal accumulation with double crucible assemblies (a) and high-chromia crucibles (b)*



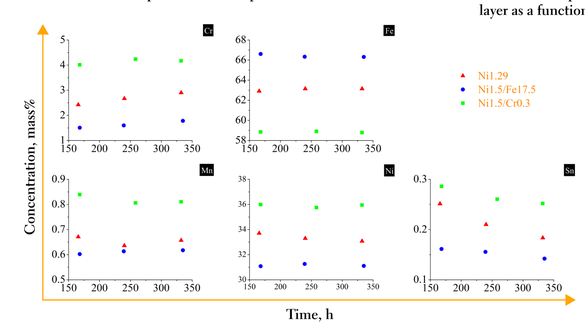
$$C_0 = C_{max}\left\{1 - \exp\left[-B_T\left(\frac{1}{T} - \frac{1}{T_L}\right)\right]\right\}$$



Effect of composition and temperature

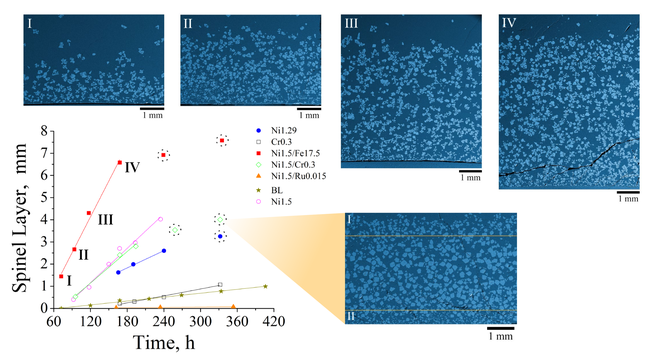


Surface area and size of spinel in accumulated layer as a function of time

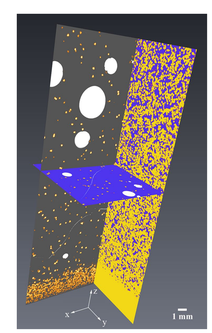


Composition of spinel in accumulated layer as a function of time

III *Analysis of samples for the size, shape, concentration, and composition of crystals and thickness of accumulated layers with XRD, SEM-EDS, image analysis, X-ray tomography, and chemical analysis*



Thickness of deposited spinel layer as a function of time. The lines were fitted with linear equation y = Ax + B. The circled points represent the post-settling period.



X-ray microtomography cross-sections (Ni1.5/Fe17.5 glass, 850°C - 96 h); glass is blue and gray, spinel crystals are yellow, cracks and air voids are white. All the crystals are projected onto y-z plane.

IV *Development of empirical model of crystal accumulation*

Coefficients expressed as linear functions of the mass fractions of seven major components in glass Al_2O_3, Cr_2O_3, Fe_2O_3, ZnO, MnO, NiO, and others.

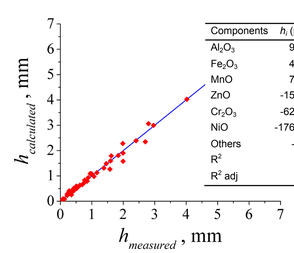
$$h = \sum_{i=1}^{7} h_i x_i + t \sum_{i=1}^{7} s_i x_i$$

h_i – composition-dependent intercept coefficient (μm)

x_i – i-th component mass fraction in the glass

t – settling time (h)

s_i – composition-dependent velocity coefficient (μm/h)



Components	h_i (μm)	s_i (μm/h)
Al_2O_3	9206	-339
Fe_2O_3	4895	-52
MnO	7734	189
ZnO	-15287	342
Cr_2O_3	-62253	520
NiO	-176907	2498
Others	-768	28
R^2	0.981	
R^2 adj	0.968	

V *Validation of the model with research-scale melter tests*

VI *Using a model to formulate crystal-tolerant glasses for high waste loadings with minimal crystal accumulation*

CONCLUSION

- Empirical model of crystal accumulation shows a good agreement between calculated and observed thicknesses of deposited layers.
- Additional glass compositions have to be formulated and tested for the accumulation rate of crystals, and validated in the research-scale melter, to make the model more robust and to better evaluate the impact of spinel-forming components, noble metals (e.g. Ru, Rh), Al, Li, Na, B, and crystal agglomeration on crystal accumulation.
- Preliminary estimates show a significant improvement in waste loading and concurrently a reduction in the risk of melter failure.

Recent Publications

J. Matyáš, A. Huckleberry, C. A. Rodriguez, J. D. Vienna and A. A. Kruger, 'Empirical Model for Formulation of Crystal-Tolerant HLW Glasses'; pp. 121–129 in Vol. 236, *Proceedings of the Ceramic Transactions: Advances in Materials Science for Environmental and Energy Technologies:113th Annual Meeting of ACerS*: held in Columbus, Ohio, USA, October 16-20, 2011. Edited by T. Ohji, M. Singh, E. Hoffman, M. Seabaugh and Z. G. Yang. John Wiley & Sons, Inc., Hoboken, NJ, USA. doi: 10.1002/9781118511435.ch13, 2012.

J. Matyáš, A. R. Huckleberry, C. P. Rodriguez, J. B. Lang, A. T. Owen, and A. A. Kruger, *HLW Glass Studies: Development of Crystal-Tolerant HLW Glasses*, PNNL-21308, 2012.

J. Matyáš, A. R. Huckleberry, C. P. Rodriguez, J. B. Lang, A. T. Owen, and A. A. Kruger, 'Crystal-tolerant glass approach for mitigation of crystal accumulation in continuous melters processing radioactive waste', *International Journal of Applied Glass Science*, 2013, submitted.

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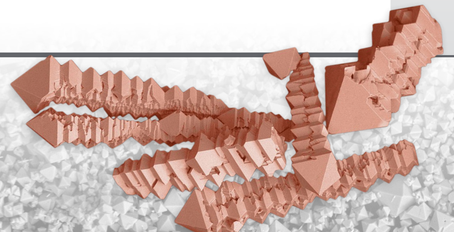

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