Modeling of Spinel Settling in Waste Glass Melter

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Dr. Pavel Hrma, Pacific Northwest National Laboratory

Petr Schill, Glass Service, Ltd.
Lubomir Nemec, Institute of Inorganic Chemistry
Jaroslav Klouzek, Institute of Chemical Technology
Martin Mika, Institute of Chemical Technology

Research Objective

Determine the fraction of spinel in molten HLW glass that is compatible with low-risk melter operation. To this end, investigate spinel behavior in HLW glass and obtain data to be used in a mathematical model for spinel settling in a HLW glass melter. Modify the current glass-furnace model to incorporate spinel settling.

Research Progress and Implications

We have studied the following aspects of spinel behavior in HLW glass:

- spinel formation during the initial melting stages
- the rates of dissolution and crystallization of spinel as a function of temperature
- the equilibrium concentration of spinel crystals as a function of temperature, oxygen partial pressure, and glass composition
- the composition of spinel as a function of temperature
- the effect of temperature history and minor components on the number density and the size of spinel crystals
- the rate and mode of spinel settling
- the rheological properties of spinel sludge in molten glass
- the physical characteristics of the spinel-glass system

Additionally, we have developed

- a mathematical model describing the electric, temperature, and velocity fields in an HLW melter
- a mathematical model of spinel settling in a limited volume of melt
- a physical model to verify the results of the mathematical model.

These results have been reported in the form of publications in conference proceedings and peer-review journals (see the list below). Some major achievements are described below.

Spinel crystals form during the initial melting stages, precipitating from the nitrate melt within the bed of reacting melter feed. Spinel formation starts at temperatures above 400ºC and peaks at 650ºC, the temperature at which the nitrate decomposition is nearly complete and the glass-forming melt is established. Though these crystals usually dissolve in the glass-forming melt during the final stages of conversion, spinel forms again when the temperature of molten glass drops below the liquidus temperature.

As the melter model shows, the temperature history of the melt in the HLW glass melter is rather wild. A spinel crystal may undergo several cycles of partial dissolution and growth before reaching its final destination either in the glass canister or at the melter bottom. The number density of spinel crystals depends on the concentration of some minor waste components, such as RuO_2 and Ag_2O, and may vary from 1 to 10^4 crystals per mm^3. As a result, spinel crystal size varies from 1 to 100 µm.

Laboratory studies of spinel formation must consider that spinel crystallization is a strong function of the temperature history and that surface crystallization may affect crystallization kinetics in powdered glass.

The rates of crystal growth and dissolution depend on melt temperature and on the crystal number density, which in turn is determined by the presence of heterogeneous nuclei provided by some minor waste components. The rate of spinel growth and dissolution has been measured under conditions similar to those in the melter. At low viscosity, when crystals move within the melt by buoyancy, the rate of dissolution of spinel is constant at constant temperature and exhibits a non-Arrhenius dependence on temperature. Measurements of crystal growth at low melt viscosity indicate that the growth rate does not drop to zero as temperature approaches liquidus. This is contrary to what has been reported in the literature. (See for example, H. Scholze, Glass, Springer, New York, 1991.) At higher viscosity, when waste glass is in the canister, the kinetics of spinel crystallization follows the Avrami equation with Avrami exponent 0.8. This is a low value, attributable to the impinging of concentration layers.

The concentration of spinel in the melt depends on melt temperature, composition, and redox. These functions were expressed in the form of constitutive equations to be used not only in melter models, but also in models for glass formulation, waste retrieval, blending, and pretreatment. These results have a potentially significant impact on Hanford HLW vitrification schedule and cost.

Planned Activities

- measure spinel response to a typical temperature history computed for a HLW glass melter
- study spinel settling under laboratory conditions as a function of temperature
- develop models for predicting the fraction of spinel that settles during HLW glass processing
- study the effect of spinel sludge aging on its rheological behavior

Information Access

The following papers have been published, are in print, or in final stages of preparation:

1. M. W. Stachnik, P. Hrma, and H. Li, "Effects of High-level Waste Glass Composition on Spinel Precipitation," *Ceram. Trans*. 107 (1999).
2. M. Mika, J. V. Crum, and P. Hrma, "Spinel Precipitation in High-Level Waste Glass," *Proceedings of the 5th ESG Conference,* Prague, Czech Republic 1999.
3. M. Mika, P. Hrma, and M. J. Schweiger, "Rheology of Spinel Sludge in Molten Glass," *Ceramics-Silikaty* (accepted).
4. P. Hrma :Modeling of Spinel Settling in Waste Glass Melter." *In Science to Support DOE Site Cleanup*, Pacific Northwest National Laboratory, PNNL-12208 UC-2000 (1999).
5. P. Izak, P. Hrma, M.J. Schweiger, "Nonisothermal crystallization of spinel from a high-level waste feed," submitted to ACS proceedings.
6. P. Schill and P. Vlcek, "Mathematical Model of Radioactive Waste Glass Melter, 5th International Seminar on Mathematical Simulation in Glass Melting," Horni Becva, Czech Republic, June 17-18,1999, Proceedings, p.112-118
7. P. Schill, A. Franek, M. Trochta, P. Viktorin, and P. Vlcek, "Integrated Glass Furnace Model, 5th International Seminar on Mathematical Simulation in Glass Melting," Horni Becva, Czech Republic, June 17-18,1999, Proceedings, p.125-137.
8. P. Hrma, J. D. Vienna, J. V. Crum, G. F. Piepel, and M. Mika, "Liquidus Temperature of High-Level Waste Borosilicate Glasses with Spinel Primary Phase," *Mat. Res. Soc. Proc.* (2000).
9. J. Alton, T. J. Plaisted, and P. Hrma, "Crucible Study of Spinel Settling in High-Level Waste Glass," Ceramic Transactions (to be submitted).
10. P. Izak, J. Klouzek, and P. Hrma, "Evolution of crystalline Phases during High-Level Waste Feed-to-Glass Conversion," Ceramic Transactions (to be submitted).
11. T. J. Plaisted, J. Alton, P. Hrma, and B. Wilson, "Spinel Nucleation and Growth in High-Level Waste Glass," Ceramic Transactions (to be submitted).
12. P. Izak, P. Hrma, J. D. Vienna, and B. Wilson, "Effect of Oxygen Partial Pressure on Liquidus Temperature with Spinel Primary Phase," Ceramic Transactions (to be submitted).
13. T.J. Plaisted, F. Mo, B. Wilson, and P. Hrma, Surface Crystallization of Spinel and Acmite in High-Level Waste Glass," Ceramic Transactions (to be submitted).