Mathematical Modeling of Conversion Kinetics during Vitrification of Nuclear Waste

Richard Pokorný [a], David A. Pierce[b], Jaehun Chun[b], Pavel Hrma,[b,c*]
[a]*Dept. of Chem.-Engineering, Institute of Chemical Technology Prague, Technická 5, 16628, Prague 6, Czech Republic*
[b]*Pacific Northwest National Laboratory, Richland, WA 99352, USA*
[c]*Division of Advanced Nuclear Engineering, Pohang University of Science and Technology, Pohang, Republic of Korea*
**Corresponding author: pavelhrma@postech.ac.kr*

1. Introduction

The last part of the high-level waste (HLW) glass melter that has not yet been fully understood, not to mention mathematically modeled, is the cold cap [1, 2]. Cold cap is a layer of dry melter feed, a mixture of the HLW with glass forming and modifying additives. It floats on the pool of molten glass from which it receives the heat necessary for melting. Mathematical modeling of the cold cap solves differential equations that express the mass and energy balances for the feed-to-glass conversion within the cold cap.

The feed-to-glass conversion consists of multiple chemical reactions and phase transitions. Reaction enthalpies and mass losses to gases evolved provide an important input for the cold cap modeling. In this study, we measured the kinetics of cold cap reactions using the non-isothermal thermo-gravimetric analysis (TGA) and differential scanning calorimetry (DSC). These thermoanalytical techniques show multiple overlapping peaks, necessitating the development of a deconvolution method for the determination of the kinetics of major reactions needed for cold cap modeling.

Assuming that the cold cap reactions are independent, we expressed the overall rate as a sum of rates of individual reactions that we treat as Arrhenius-type processes with a power-law based kinetics. Accordingly, we fitted to experimental data the following equation:

$$\frac{\mathrm{d}x}{\mathrm{d}T} = \frac{1}{\Phi}\sum_{i}^{N} w_i A_i (1-x_i)^{n_i} \exp\left(-\frac{B_i}{T}\right) \qquad (1)$$

where x is the fraction of material reacted, T is temperature, Φ is the heating rate, w_i the weight of the i^{th} reaction (the fraction of the total mass loss caused by the i^{th} reaction), A_i is the i^{th} reaction pre-exponential factor, B_i is the i^{th} reaction activation energy, and n_i is the i^{th} reaction (apparent) reaction order.

Because HLW melter feeds contain a large number of constituents, such as oxides, acids, hydroxides, oxyhydrates, and ionic salts, the number of cold cap reactions is very large indeed. For example, hydroxides, oxyhydrates, boric acid, and various crystalline forms release chemically bonded water, and reactions of nitrates with organics and molten salts with solid silica release copious amounts of NO_x, CO_x, and O_2. Because it is formidable to identify the chemistry of reactions associated with individual peaks, we focused on obtaining the kinetic parameters needed for cold cap modeling.

The number of kinetic parameters in Equation (1) is rather large. Therefore, in our recent study [3], we fitted TGA data using solely a first-order reaction kinetics, i.e., $n_i = 1$, for each reaction peak. In this study, we present an improved model in which the reaction order is a variable parameter.

2. Methods and Results

As in our previous studies [1, 2], the melter feed was formulated to produce a glass designed for vitrifying a high-alumina HLW. For TGA and DSC, melter-feed samples of 10–60 mg were placed into a platinum crucible and heated from ambient temperature (~25°C) to 1200°C. The results were expressed as the rate of mass loss (TGA) and the heat flow (DSC).

Fig. 1 displays the TGA and DSC based reaction rates for the melter feed heated at various rates. Unlike the TGA analysis, the DSC analysis requires to calculate the experimental reaction rates by integrating the heat flows, based on the following equation:

$$\frac{\mathrm{d}x}{\mathrm{d}T} = \left(\frac{dQ}{dt}\right)\Bigg|_T \left[\int_{T_{\min}}^{T_{\max}} \left(\frac{dQ}{dt}\right) dT\right]^{-1} \qquad (2)$$

where dQ/dt is the heat flow, and $T_{\max}$ and $T_{\min}$ are the maximum and minimum temperatures for the DSC analysis. It is noteworthy that the curves from DSC, compared to simple mass changes for TGA, are more complicated and vary with different heating rates more significantly, which gives rise to more challenges in the kinetic analysis with DSC.

To avoid the problem with the compensation effect between A_i and B_i values that impede optimization, we applied the Kissinger's method [4] to directly estimate B_is from the shifts of peak maximum temperatures with the rate of heating. We estimated peak maximum temperatures as maxima and shoulders on the dx/dT versus T curve. Then we obtained the values of the remaining parameters using least-squares analysis.

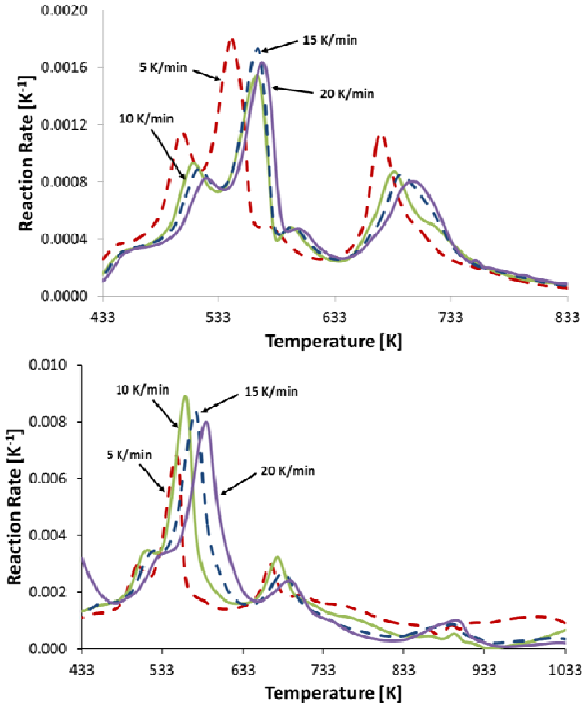


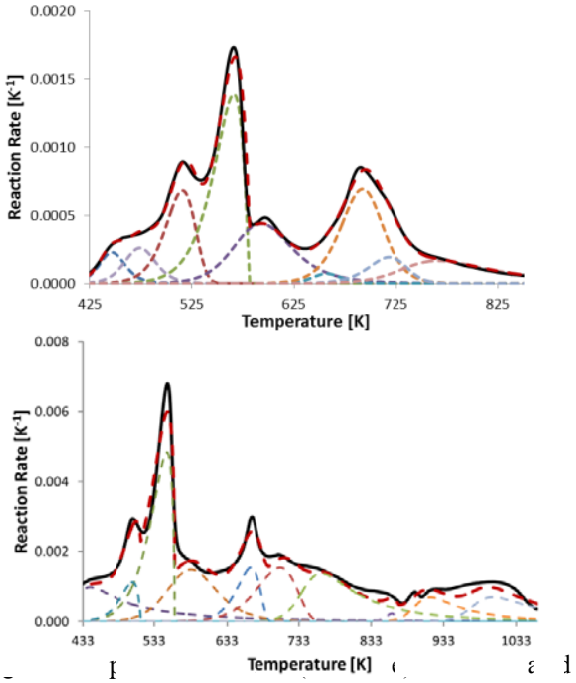
Fig.1. Measured TGA (top) and DSC (bottom) curves for melter feed heated at various rates.

The least-squares analysis showed that A_i values are virtually independent of Φ. Relatively larger standard deviations of n_is indicated variability in the shapes of the peaks, but no trends could be discerned from the values. Only w_i for some peaks showed a slight tendency to vary with Φ, but it was not clear whether the effect is real or a result of feed homogeneity fluctuations caused by the smallness of samples as compared with the size of component particles. On the other hand, consecutive reactions may be influenced by preceding ones, i.e., reactions that run at a lower temperature may affect the reactions that follow them, especially when the heating rate is low. However, this effect may not be significant for the rates within the interval of 5 to 20 K/min that exist in the melter cold cap.

As Fig. 2 illustrates, the agreement between measured and calculated kinetic curves appears to be reasonable and the mathematical representation of the conversion kinetics is acceptable for cold cap modeling.

3. Conclusions

Using TGA and DSC analyses, the kinetics of melter feed reactions was successfully simulated by the model based on the power-law kinetics. The model can be used for cold cap modeling as a key building block in modeling of the waste-glass melter.



F I ε l
(dashed line) TGA – 15 K/min (top) and DSC – 5 K/min (bottom) curves and deconvolution peaks.

Acknowledgements

The authors are grateful to the U.S. Department of Energy Federal Project Office Engineering Division for the Hanford Tank Waste Treatment and Immobilization Plant for financial support. This research was also supported by WCU (World Class University) program through the National Research Foundation of Korea funded by the Ministry of Education, Science and Technology (R31 - 30005).. Richard Pokorny is pleased to acknowledge support from Specific University Research (MSMT No. 21/2012)

References

[1] Hrma P, Schweiger MJ, Humrickhouse CJ, Moody JA, Tate RM, Rainsdon TT, TeGrotenhuis NE, Arrigoni BM, Marcial J, Rodriguez CP, Tincher BH. Effect of glass-batch makeup on the melting process. Ceram.-Silik., 54, 193-211, 2010.

[2] Schweiger MJ, Hrma P, Humrickhouse CJ, Marcial J, Riley BJ, TeGrotenhuis NE. Cluster formation of silica particles in glass batches during melting. J Non-Cryst Solids, 356, 1359–1367, 2010.

[3] Hrma P, Pierce DA, Pokorny R. Thermal Analysis of Waste Glass Melter Feeds. In: Proceedings of the International Symposium on Radiation Safety Management, p. 217-222, Gyeongju, Republic of Korea, November 2-4, 2011.

[4] Kissinger HE. Reaction Kinetics in Differential Thermal Analysis. Anal Chem., 29, 1702-1706, 1957.