Available online at www.sciencedirect.com

ScienceDirect

Procedia Materials Science 7 (2014) 148 – 155

Procedia Materials Science

www.elsevier.com/locate/procedia

2nd International Summer School on Nuclear Glass Wasteform: Structure, Properties and Long-Term Behavior, SumGLASS 2013

Compositional Models of Glass/Melt Properties and their Use for Glass Formulation

John D. Vienna*

Pacific Northwest National Laboratory, Richland, WA 99352, USA

Abstract

Nuclear waste glasses must simultaneously meet a number of criteria related to their processability, product quality, and cost factors. The properties that must be controlled in glass formulation and waste vitrification plant operation tend to vary smoothly with composition allowing for glass property-composition models to be developed and used. Models have been fit to the key glass properties. The properties are transformed so that simple functions of composition (e.g., linear, polynomial, or component ratios) can be used as model forms. The model forms are fit to experimental data designed statistically to efficiently cover the composition space of interest. Examples of these models are found in literature. The glass property-composition models, their uncertainty definitions, property constraints, and optimality criteria are combined to formulate optimal glass compositions, control composition in vitrification plants, and to qualify waste glasses for disposal. An overview of current glass property-composition modeling techniques is summarized in this paper along with an example of how those models are applied to glass formulation and product qualification at the planned Hanford high-level waste vitrification plant.

Selection and peer-review under responsibility of the scientific committee of SumGLASS 2013

Keywords: Glass; Nuclear Waste; Property; Borosilicate; Melt; Formulation; Model

1. Background

A nuclear waste glass must simultaneously meet a number of property constraints aimed at ensuring the processability of the waste glass melt and the quality of the ultimate glassy waste form. Glass compositions are

* Corresponding author. Tel.: +1(509) 372-6201; fax: +1(509) 372-5997.
E-mail address: john.vienna@pnnl.gov

Selection and peer-review under responsibility of the scientific committee of SumGLASS 2013
doi:10.1016/j.mspro.2014.10.020

formulated to meet all of the property constraints for a given waste. In the case of U.S. nuclear waste vitrification, variation in the composition of the waste make it is practically impossible to formulate an optimized waste glass for each waste composition on a purely experimental basis. Mathematical, statistical, and optimization methods are extremely useful in developing glass compositions that simultaneously meet the all of the glass property constraints for the full range of expected waste composition. An indispensable element of such a framework is a set of models to predict the melt and glass properties as functions of composition. Luckily, most glass properties of interest vary smoothly with composition and, therefore, can be readily modeled. For example, there is a roughly linear effect of alkali metal concentration on the logarithm of silicate melt viscosity as shown in Figure 1.

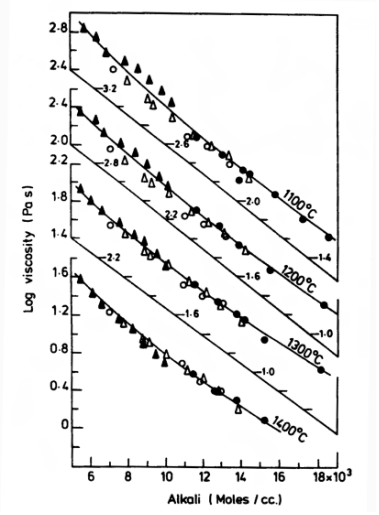

Figure 1. Variation of Logarithm of Silicate Melt Viscosity with Alkali Mole Fraction (Fig. 31 in (Rawson 1980)).

2. Property Model Equations

2.1 General Equations

Property-composition models are constitutive equations of the form:

$$p_\alpha = \mathrm{f}_\alpha(\mathbf{x}) \tag{1}$$

where p_α is the α-th property, $\mathbf{x}$ is the composition vector, and f_α denotes the functional form of the model. The composition is defined as $\mathbf{x} = (x_1, x_2, \ldots, x_{N-1})$, where x_i is the i-th component mass or mole fraction, and N is the number of components. Only N-1 components are independent because the mass and mole fractions must sum to 1:

$$\sum_{i=1}^{N} x_i = 1 \tag{2}$$

Typically, the functional form f_α involves parameters or coefficients that are independent of state variables, such as $\mathbf{x}$. Values of these coefficients must be determined by measurement. Models in which all coefficients are estimated from data are called *empirical models*. Models in which some coefficients are derived from fundamental principles of physics and chemistry, while other coefficients are estimated from data, are called *semi-empirical models*. Models that are developed from the fundamental laws of physics (e.g., quantum and statistical mechanics), without the use of any experimental data are called *first-principle models*. First-principle models are currently not

applicable for predicting multi-component waste-glass properties because they have only been successfully applied to systems with a small number of components while it is known that many components impact the properties of typical waste glasses. However, *first-principle models* may be useful in understanding fundamental relationships that guide model development.

2.2 Polynomial Functions

A simple but very useful property-composition model form is a *first-order* model (Cornell 2002):

$$t_\alpha(p_\alpha) = \sum_{i=1}^{N} b_{\alpha i} x_i \tag{3}$$

where $b_{\alpha i}$ is the i-th component coefficient for α-th property, and t_α is the transform of property p_α. Note that the mathematical transformation, t_α, could be the identity transformation (i.e., no transformation). The most commonly applied transformation is the logarithm. For example, in Figure 1, the logarithm of viscosity at a given temperature varies with alkali content.

If individual components in waste glasses are confined to sufficiently narrow ranges of concentrations, non-linear functions of composition may be approximated as linear with acceptable error. As components vary over wider ranges, linear functions of composition may not adequately approximate the underlying nonlinear relationship. In such cases, nonlinear approximating functions may be required. In polynomial models (which can be thought of as polynomial expansions of the properties in composition), the *second-order* model form includes quadratic and cross-products terms, such as:

$$t_\alpha(p_\alpha) = \sum_{i=1}^{N} b_{\alpha i} x_i + \text{Selected}\left\{ \sum_{i=1}^{N} b_{\alpha ii} (x_i)^2 + \sum_{i}^{N-1} \sum_{<j}^{N} b_{\alpha ij} x_i x_j \right\} \tag{4}$$

where $b_{\sigma ii}$ is the coefficient for the i-th component squared for α-th property, and $b_{\sigma ij}$ is the coefficient for the cross-product of the i-th and j-th components for α-th property. Piepel et al. (2002) discuss models of the form (4), referred to as partial quadratic mixture (PQM) models. Scheffé quadradic mixture models do not allow the use of squared terms ($b_{\sigma ii} x_i^2$) (Scheffe 1958). However, it is permissible to use them as long as all cross-product terms are not used and has been found to be very useful in mixture model development (Darroch and Waller 1985; Piepel et al. 2002). Squared terms have been used in a number of waste glass property models to great effect.

In addition to polynomial functions, glass property models often take the form of ratios of different components. For example Li (1997) define the composition region susceptible to nepheline formation as:

$$ND = \frac{g_{SiO_2}}{g_{SiO_2} + g_{Al_2O_3} + g_{Na_2O}} \tag{5}$$

where ND stands for nepheline discriminator and g_i is the mass fraction of i-th component.

2.3. Property Models in Composition and Temperature

Some glass properties, such as viscosity (η) and electrical conductivity (ε), are functions of temperature (T) as well as composition. For a given waste glass, the temperature dependence of a property, such as viscosity, is often approximated by the Vogel-Fulcher-Tammann (VFT) equation(†)

(†) See H. Vogel, *Phys. Z.* **22,** 645-646 (1921), G. S. Fulcher, *J. Am. Ceram. Soc*. **8**, 339-366 (1925), G. S. Fulcher, *J. Am. Ceram. Soc*. **8**, 789-794 (1925), and G. Tammann and W. Hesse, *Z. Anorg. Allg. Chem*., **156**, 245-257 (1926).

$$\eta = \exp(A + \frac{B}{T - T_0}) \tag{6}$$

or, in a narrow temperature interval, by the Arrhenius equation

$$\eta = \exp(E + \frac{F}{T}) \tag{7}$$

where A, B, E, F, and T_0 are temperature-independent coefficients.

In any of these equations, the parameters A, B, T_0, E, and F can be expressed as functions of composition to also capture the dependence of the property on composition. Expanding the parameters in Equations (6) and (7) as linear functions of composition (i.e., linear mixture models), yields:

$$\ln(\eta) = \sum_{i=1}^{N} A_i x_i + \frac{\sum_{i=1}^{N} B_i x_i}{T - \sum_{i=1}^{N} T_{0,i} x_i} \tag{8}$$

and

$$\ln(\eta) = \sum_{i=1}^{N} E_i x_i + \frac{\sum_{i=1}^{N} F_i x_i}{T} \tag{9}$$

The E coefficient of the Arrhenius equation is only moderately composition dependent. Hrma (2008) successfully modelled waste glass viscosity assuming E to be a composition-independent variable. When fitting models of the forms (8) and (9) to data, care must be taken to use the correct regression methods. Vienna et al. (1996) found that regressing Equation (8) directly to data as functions of T and x_i resulted in non-physically meaningful predictions of T_0. Much more reasonable results were obtained by first fit the parameters A, B, and T_0 to each glass then fit those values to composition in a two-step process.

Alternatively, the ln[η] (or ln[ε]) can be measured or estimated at fixed temperatures using Equation (6). The ln[η] can be expanded in composition using Equations (3) or (4). The viscosity (or conductivity) of the melt can then be estimated at any temperature by predicting the viscosities at the fixed temperatures and interpolating using Equation (6) or (7) (see for example (Vienna et al. 2009)). Finally, the temperature at a fixed viscosity (or conductivity) value can be modelled as a function of composition (see for example (Vienna et al. 1996)).

3. Model Fitting

As waste glass models are empirical or semi-empirical (mechanistic), their parameters are fit to experimental data. Because of the large number of independent compositional variables that are known to impact nuclear waste glass properties of interest, it is generally the case that statistical experimental design methods are used to minimize the number of glasses that need to be tested to sufficiently cover a composition space of interest. These statistical design methods, for mixture experiments, are commonly described in literature and available in commercial software (see for example (Chick and Piepel 1983; Cooley and Piepel 2003a; Cooley and Piepel 2003b; Cornell 2002; Hrma et al. 1994; Piepel et al. 1993; Piepel and Cornell 1994)). The data are compiled and screened for outliers and used to fit the empirical parameters of the property model. A data set or subset of the modelling data is used to independently validate the models and quantify the prediction uncertainties. The "goodness" of models is at least partially judged by model fit and validation statistics. The most commonly applied descriptive statistics are: R^2 (an estimate of the fraction of the variability in the property data accounted for by the fitted model), R^2_{Adj} (adjusts R^2 to the number of terms in the model and the number of data points used to fit the model), R^2_{Press} (a measure of R^2 where each data point is left out of the fit in evaluating how well the model predicts that data point), R^2_{Val} (the R^2

calculated using a validation data set not used to fit the model), and *RMSE* (the model root-mean-square-error).

Model fitting routines generally minimize the error (*RMSE*) and maximize the R^2 values for the model fit data. The ability of models to predict data not used in their development is the primary measure of the value of the model and is judged by the R^2_{Val} and $RMSE_{Val}$. A complete description of these parameters, how they are obtained, and their interpretation is published elsewhere (see for example (Cornell 2002; Hrma et al. 1994; Piepel et al. 2008; Piepel et al. 2007; Vienna et al. 2009)).

4. Waste Glass Property Models

Nuclear waste glass property models have been fit to a wide range of properties and a target waste glass composition regions. Summarized here are only a few examples of property models that are used for nuclear waste vitrification in the U.S. The properties generally modeled include:

- natural logarithm of melt viscosity as a function of temperature (η-T) and at fixed temperature(s) (η_T)
- natural logarithm of melt electrical conductivity as a function of temperature (ε-T) and at fixed temperature(s) (ε_T)
- liquidus temperature (T_L) typically within only a single primary phase field (most commonly within the spinel, $[Fe,Mn,Zn,Ni][Fe,Cr]_2O_4$, primary phase field)
- natural logarithm of product consistency test (PCT) method A, normalized silicon, boron, sodium, or lithium release (r_{Si}, r_B, r_{Na}, r_{Li})
- specific or molar volume (V) (used to estimate density)
- glass transition temperature (T_g)
- natural logarithm of vapor hydration test (VHT) response at 200°C
- natural logarithm of toxicity characteristic leaching procedure (TCLP)
- temperature at one volume percent crystal in equilibrium with the melt ($T_{1\%}$)
- fraction of crystal phase at a temperature C_T

Table 1. Overview of Commonly Used U.S. Waste Glass Property Models

Citation	Wastes Targeted	Modeled Properties
Chick et al. (1984)	West Valley	η_T, ε_T, C_T, MCC-1, Soxhlet[(a)]
Pegg et al. (1989)	West Valley	r_{Si}, r_B, η_T
Jantzen (1991)	Savannah River	η-T, ε-T, T_L, r_{Si}
Hrma et al. (1994)	Hanford HLW	η-T, ε-T, T_L, T_g, r_{Si}, r_B, r_{Na}, r_{Li}, MCC-1, immiscibility
Feng and Pegg (1994)	West Valley	r_{Si}, r_B, r_{Na}, r_{Li}
Vienna et al. (1996c)	Hanford HLW	η-T, ε-T, T_L, r_B, r_{Na}, r_{Li}
Jantzen et al. (1995)	Savannah River	r_{Si}, r_B, r_{Na}, r_{Li}, immiscibility
Vienna et al. (1996b)	Hanford HLW	r_B, r_{Na}, r_{Li}
Vienna et al. (1996a)	Hanford HLW	η-T, ε-T, T_L, C_T
Li et al. (1997)	Hanford HLW	nepheline formation
Vienna et al. (2002)	Hanford HLW & LAW	η-T, ε-T, T_L, r_B, r_{Na}, r_{Li}, TCLP
Hrma and Vienna (2003)	Hanford HLW	C_T, T_L
Jantzen and Brown (2007)	Savannah River	T_L
Piepel et al. (2007)	Hanford LAW	r_B, r_{Na}, VHT, η-T, ε-T
Piepel et al. (2008)	Hanford HLW	r_B, r_{Na}, r_{Li}, η-T, ε-T, $T_{1\%}$, TCLP
Vienna et al. (2009)	Hanford HLW	r_B, r_{Na}, r_{Li}, η-T, ε-T, $T_{1\%}$, T_L, TCLP
Vienna et al. (2013)	Hanford HLW & LAW	r_B, r_{Na}, r_{Li}, $T_{1\%}$, T_L, sulfate solubility, nepheline formation

(a) MCC-1 and Soxhlet are glass corrosion tests.

A number of additional models were developed by researchers outside of the U.S.; both for the properties listed above and additional properties and for composition regions of interest to the vitrification processes targeted by those researchers. No attempt is made here to develop a comprehensive list of those models.

A convenient way to visualize the effect of composition change on waste glass/melt properties as predicted by the models is using a so-called spider plot. Figure 2 shows the impact of changing individual glass components on the $\ln[\eta_{1150°C}, P]$. This shows the predicted nearly linear effect of all components on viscosity generally expands the impacts of composition on logarithm viscosity shown for binary alkali-silicate glasses shown in Figure 1 to multi-component waste glasses. Alkali ion concentration impacts on the viscosity of binary silicate glasses were found to be independent of which alkali is added as shown in Figure 1. For multicomponent waste glasses, different alkalis have a different impact on the viscosity (on either mole or mass fraction basis).

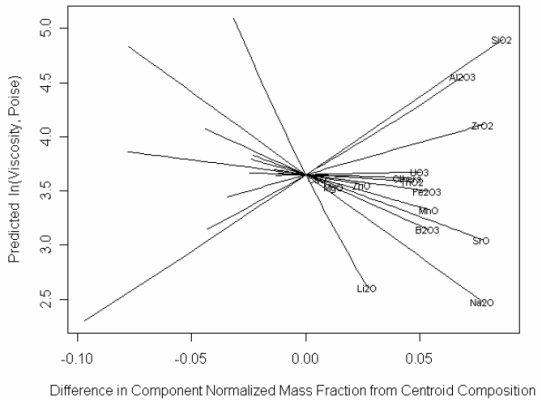

Figure 2. Effect of Individual Component Concentration Change on the $\ln[\eta_{1150°C}, P]$ (from Piepel et al. (2008))

5. Application of Models to Glass Formulation and Process/Product Control

Glass/melt property-composition models described above are applied to numerically optimize waste glass composition and for process and product control. The process of formulating a glass based on glass property-composition models is one of constrained numerical optimization. For example, to maximize the waste loading in a glass (i.e., minimize the amount of glass per unit waste vitrified), the fractions of waste and each chemical additive are systematically varied until the waste fraction is the highest while simultaneously meeting all property constraints (Hrma and Robertus 1993). This process is simple in concept, but, quickly becomes complicated in practice when process and prediction uncertainties are accounted for and multi-attribute optimization is needed to define the optimal glass.

Glass property models are applied to control the nuclear waste glass process and product in the U.S. (Drobot and Mahoney 1993; Edwards et al. 2006; Kim and Vienna 2012; Postles and Brown 1991; Vienna and Kim 2008). In this application, the variation in estimated glass composition is along with uncertainties in product quality predictions are combined to ensure that the final glass will meet product quality related constraints with sufficient confidence. The basic formats of the constraints are:

$$L_{\alpha}^{L} \le p_{\alpha}^{pred} - U_{\alpha}^{pred} - U_{\alpha}^{comp} \text{ and } L_{\alpha}^{U} \ge p_{\alpha}^{pred} + U_{\alpha}^{pred} + U_{\alpha}^{comp} \quad (10)$$

where L_{α}^{L} and L_{α}^{U} and the lower and upper limits on property p_{α}, U_{α}^{pred} is the uncertainty in prediction of the property p_{α}, and U_{α}^{comp} is the expression of composition uncertainty expressed in units of p_{α}. Prediction uncertainties typically take the form of a confidence interval that are functions of composition as described elsewhere (Kim and Vienna 2012; Vienna and Kim 2008). Composition uncertainties are handled differently

depending on the plant. At the WTP, all uncertain values in the glass composition mass balance equation are assigned probability distributions. A Monte Carlo calculation is then performed to calculate a number of glass composition estimates (or realizations). For each estimate, the glass properties are estimated. The resulting distribution of glass properties are then analyzed and the distribution half width associated with the desired confidence level is used as U_{α}^{comp}. Other processes, such as the DWPF, have fewer sources of composition uncertainty and use a composition variance-covariance matrix to determine U_{α}^{comp}.

Figure 3 shows a schematic diagram of the glass formulation method applied to Hanford HLW. The ternary diagram on the left is meant to represent the multidimensional composition region made up by a particular waste batch at the top of the diagram; the concentrations of each of the ten potential glass forming additives are expressed across the bottom. The property constraints (calculated using glass property models) limit the portion of composition region within which glass can be formulated as shown by the solid black lines for different properties. Model prediction uncertainties further narrow the composition space within which glass can be formulated as shown by the dotted black lines. A glass can be formulated anywhere within the region defined by the property limits with associated uncertainties. The composition of the glass isn't precisely known. So, various sources of composition uncertainties must be accounted for as shown by the tan circle. The final glass formulation region is the region surrounded by the dotted lines (representing property limits with prediction uncertainty) that an uncertain composition (represented by the tan circle) can fit. As shown in this simple diagram, there is most often a range of potential compositions that can be processed. In other words, there are excess degrees of freedom in glass formulation. A multi-attribute optimization routine is used to define an optimal glass within this region. Nine optimality criteria are each considered. The concentrations of B_2O_3, Na_2O, Li_2O, ZnO, and SiO_2 are targeted close to the center of the WTP HLW compositional region. Predicted $T_{1\%}$ and r_B are minimized, the $\eta_{1150°C}$ is targeted to 50 P, and the waste loading is targeted to be in a position between the maximum possible and the minimum acceptable by the WTP Contract. As the attribute values vary from their optimal point, a penalty is assigned. A penalty function increases the penalty the further the value varies from its optimal point. An optimization is performed to reduce the total penalty for a given glass composition.

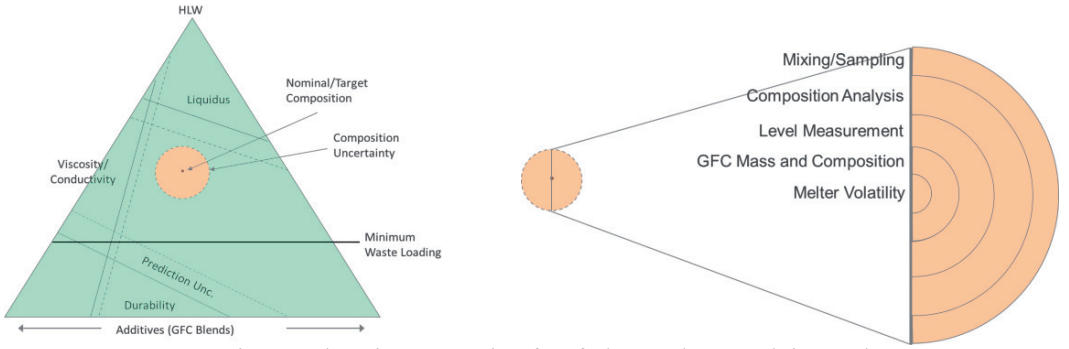

Figure 3. Schematic Representation of Hanford HLW Glass Formulation Envelope

Applying glass property-composition models, uncertainty definitions, and a multi-attribute optimization routine, optimal glass compositions are formulated for Hanford HLW. The details of this process are described in more detail by Vienna and Kim (2008).

6. References

Chick, L.A., W.M. Bowen, R.O. Lokken, J.W. Wald, L.R. Bunnell, and D.M. Strachan. 1984. *West Valley High-Level Nuclear Waste Glass Development: A Statistically Designed Mixture Study*, PNL-4992, Pacific Northwest Laboratory, Richland, WA.

Chick, L.A. and G.F. Piepel. 1983. "Nuclear-Waste-Glass Development by Statistically Designed Mixture Studies," *American Ceramic Society Bulletin*, **62**(8):880-880.

Cooley, S.K. and G.F. Piepel. 2003a. "A Two-Stage Layered Mixture Experiment Design for a Nuclear Waste Glass Application-Part 2," *Proceedings of the American Statistical Association*, 1044-1051. American Statistical Association.

Cooley, S.K. and G.F. Piepel. 2003b. "A Two-Stage Layered Mixture Experiment Design for a Nuclear Waste Glass Application—Part 1," *Proceedings of American Statistical Association*, 1036-1043. American Statistical Association.

Cornell, J.A. 2002. *Experiments with Mixtures*. Third ed., John Wiley and Sons, New York, NY.

Darroch, J.N. and J. Waller. 1985. "Additivity and Interaction in Three-Component Experiments with Mixtures," *Biometrika* **72**:153-163.

Drobot, A. and J.L. Mahoney. 1993. "Statistical Acceptance of West Valley HLW Glass," *Waste Management 1993*, 993-998.

Edwards, T.B., K.G. Brown, and R.L. Postles. 2006. *SME Acceptability Determination for DWPF Process Control (U)*, WSRC-TR-95-00364, Rev. 5, Savannah River National Laboratory, Aiken, SC.

Feng, X. and I.L. Pegg. 1994. "A Glass Dissolution Model for the Effects of S/V on Leachate pH," *Journal of Non-Crystalline Solids*, **175** (2-3):281-293. DOI: 10.1016/0022-3093(94)90022-1.

Hrma, P. 2008. "Arrhenius Model for High-Temperature Glass-Viscosity with a Constant Pre-Exponential Factor," *Journal of Non-Crystalline Solids*, **354**(18):1962-1968. DOI 10.1016/j.jnoncrysol.2007.11.016.

Hrma, P., G.F. Piepel, M.J. Schweiger, D.E. Smith, D.S. Kim, P.E. Redgate, J.D. Vienna, C.A. Lopresti, D.B. Simpson, D.K. Peeler, and M.H. Langowski. 1994. *Property/Composition Relationships for Hanford High-Level Waste Glasses Melting at 1150°C*, PNL-10359, Pacific Northwest Laboratory, Richland, WA.

Hrma , P. and P.J. Robertus. 1993. "Waste Glass Design Based on Property Composition Functions," *Ceram. Eng. Sci. Proc*., Vol. 14, 187-203.

Hrma, P. and J.D. Vienna. 2003. "Relationship between Liquidus Temperature and Solubility," *Environmental Issues and Waste Management Technologies in the Ceramic and Nuclear Industries VIII*, Vol. 143, 159-167. American Ceramic Society.

Jantzen, C.M. 1991. "First-Principle Process Product Models for Vitrification of Nuclear Waste: Relationship of Glass Composition to Glass Viscosity, Resistivity, Liquidus Temperature, and Durability," *Ceramics Transactions*, Vol. 23, 37-51. American Ceramic Society, Westerville, OH.

Jantzen, C.M. and K.G. Brown. 2007. "Predicting the Spinel-Nepheline Liquidus for Application to Nuclear Waste Glass Processing. Part II: Quasicrystalline Freezing Point Depression Model," *Journal of the American Ceramic Society*, **90** (6):1880-1891.

Jantzen, C.M., J.B. Pickett, K.G. Brown, T.B. Edwards, and D.C. Beam. 1995. *Process/Product Models for the Defense Waste Processing Facility (DWPF): Part I. Predicting Glass Durability from Composition Using a Thermodynamic Hydration Energy Reaction Model (Thermo)*, WSRC-TR-93-0672, Westinghouse Savannah River Company, Aiken, SC.

Kim, D.S. and J.D. Vienna. 2012. *Preliminary ILAW Formulation Algorithm Description*, 24590-LAW-RPT-RT-04-0003, Rev. 1, River Protection Project, Hanford Tank Waste Treatment and Immobilization Plant, Richland, WA.

Li, H., J.D. Vienna, P. Hrma, D.E. Smith, and M.J. Schweiger. 1997. "Nepheline Precipitation in High-Level Waste Glasses: Compositional Effects and Impact on the Waste Form Acceptability," *Scientific Basis for Nuclear Waste Management XX*, Vol. 465, 261-268. Materials Research Society, Pittsburgh, PA.

Pegg, I.L., E.E. Saad, X. Feng, R.B. Adiga, W.P. Freeborn, and P.B. Macedo. 1989. "Product Models for the Vitrification of West Valley High-Level Wastes," *Scientific Basis for Nuclear Waste Management XII*, Vol. 127, 215-221. Materials Research Society.

Piepel, G.F., C.M. Anderson, and P.E. Redgate. 1993. "Response Surface Designs for Irregularly-Shaped Regions (Parts 1, 2, and 3)," Physical and Engineering Sciences, 205-227. American Statistical Association, Alexandria, VA.

Piepel, G.F., S.K. Cooley, A. Heredia-Langner, S.M. Landmesser, W.K. Kot, H. Gan, and I.L. Pegg. 2008. *IHLW PCT, Spinel T1%, Electrical Conductivity, and Viscosity Model Development*, VSL-07R1240-4, Rev. 0, Vitreous State Laboratory, The Catholic University of America, Washington, D.C.

Piepel, G.F., S.K. Cooley, I.S. Muller, H. Gan, I. Joseph, and I.L. Pegg. 2007. *ILAW PCT, VHT, Viscosity, and Electrical Conductivity Model Development*, VSL-07R1240-4, Rev. 0, Vitreous State Laboratory, The Catholic University of America, Washington, D.C.

Piepel, G.F. and J.A. Cornell. 1994. "Mixture Experiment Approaches - Examples, Discussion, and Recommendations," *Journal of Quality Technology*, **26**(3):177-196.

Piepel, G.F., J.M. Szychowski, and J.L. Loeppky. 2002. "Augmenting Scheffe Linear Mixture Models with Squared and/or Crossproduct Terms," *Journal of Quality Technology*, **34**(3):297-314.

Postles, R.L. and K.G. Brown. 1991. "The DWPF Product Composition Control System (Pccs) at Savannah River: Statistical Process Control Algorithm," *Ceramic Transactions*, Vol. 23, 37-51. American Ceramic Society, Columbus, OH.

Rawson, H. 1980. *Properties and Applications of Glass*. Elsevier Scientific, New York, NY.

Scheffe, H. 1958. "Experiments with Mixtures," *Journal of the Royal Statistical Society B*, **20**:344-360.

Vienna, J.D., A. Fluegel, D.S. Kim, and P. Hrma. 2009. *Glass Property Data and Models for Estimating High-Level Waste Glass Volume*, PNNL-18501, Pacific Northwest National Laboratory, Richland, WA.

Vienna, J.D., P. Hrma , D.S. Kim, M.J. Schweiger, and D.E. Smith. 1996a. "Compositional Dependence of Viscosity, Electrical Conductivity, and Liquidus Temperature of Multicomponent Borosilicate Waste Glasses," *Ceramic Transactions*, Vol. 72, 427-436. American Ceramic Society, Westerville, OH.

Vienna, J.D., P. Hrma, M.J. Schweiger, and M.H. Langowski. 1996b. "Compositional Dependence of Elemental Release from HLW Glasses by the Product Consistency Test: A One Component-at-a-Time Study," *Ceramic Transactions*, Vol. 72, 307-316. American Ceramic Society, Westerville, OH.

Vienna, J.D., P. Hrma, M.J. Schweiger, M.H. Langowski, P.E. Redgate, D.S. Kim, G.F. Peipel, D.E. Smith, C.Y. Chang, D.E. Rinehart, S.E. Palmer, and H. Li. 1996c. *Effect of Composition and Temperature on the Properties of High-Level Waste (HLW) Glass Melting above 1200°C*, PNNL-10987, Pacific Northwest National Laboratory, Richland, WA.

Vienna, J.D. and D.S. Kim. 2008. *Preliminary IHLW Formulation Algorithm Description*, 24590-HLW-RPT-RT-05-001, Rev 0, River Protection Project, Hanford Tank Waste Treatment and Immobilization Plant, Richland, WA.

Vienna, J.D., D.S. Kim, and P. Hrma. 2002. *Database and Interim Glass Property Models for Hanford HLW and LAW Glasses*, PNNL-14060, Pacific Northwest National Laboratory, Richland, WA.

Vienna, J.D., D.S. Kim, D.C. Skorski, and J. Matyas. 2013. *Glass Property Models and Constraints for Estimating the Glass to Be Produced at Hanford by Implementing Current Advanced Glass Formulation Efforts*, PNNL-22631, Pacific Northwest National Laboratory, Richland, WA.