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Database and Interim Glass Property Models for Hanford HLW Glasses

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July 2001



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Abstract

This report discusses a methodology for increasing the efficiency and decreasing the cost of vitrifying high-level waste (HLW) by optimizing HLW glass formulation. This methodology involves collecting and generating a property-composition database (for glass properties that determine HLW glass processability and acceptability) and relating these properties to glass composition. The report explains how the property-composition models are developed, fitted to data, used for glass formulation optimization, and continuously updated in response to changes in HLW composition estimates and changes in glass processing technology. Further, the report describes a waste-glass property-composition database compiled from literature sources, and presents the results from a critical evaluation and screening of the data for applicability to Hanford. Finally the report provides interim property-composition models for melt viscosity, liquidus temperature (with spinel and zircon primary crystalline phases), and Product Consistency Test normalized releases of B, Na, and Li. Models were fitted to a subset of the database deemed most relevant for the current Hanford HLW composition region.

Summary

Efforts are being made to increase the efficiency and decrease the cost of vitrifying radioactive waste stored in tanks at U.S. Department of Energy waste sites. The composition of acceptable and processable high-level waste (HLW) glass needs to be optimized to minimize the waste-form volume and hence to save cost. A database of properties and associated compositions for simulated waste glasses was collected at Pacific Northwest National Laboratory (PNNL) for developing property-composition models. The database includes waste-glass compositions and properties, such as Product Consistency Test (PCT) response, viscosity, Toxicity Characteristic Leach Procedure (TCLP) response, and liquidus temperature (T_L), that are important for processability and product performance. Data from PNNL, West Valley Demonstration Project (WVDP), Savannah River Technology Center (SRTC), Catholic University of America (CUA), Idaho National Engineering and Environmental Laboratory (INEEL), and several other institutions were reviewed and compiled into a single, easy-to-use database. This database, although not complete, represents a large fraction of data on waste-glass compositions and properties that were available at the time of this report. Unfortunately, waste-glass property-composition data from the River Protection Project—Waste Treatment Plant (RPP-WTP) Project were not available at the time the database was compiled and hence could not be included in this report. Because of the size of the database, two versions of the report were printed, one version with the database attached as Appendix A and one version without the database attached.

First-order empirical models of several glass properties were fit to subsets of the database. Models were generated for normalized boron, sodium, and lithium release by PCT (r_B , r_{Na} , and r_{Li} , respectively); T_L in the spinel ($[\text{Fe,Ni,Mn}][\text{Fe,Cr}]_2\text{O}_4$) and zircon (ZrSiO_4) primary phase fields; and Arrhenius viscosity coefficients (A and B). These models and the composition regions of their validity are summarized in Tables S1 through S4.

These models were developed from available data in a limited period of time to meet a client need date. Selected statistical model development and evaluation methodologies were applied, but there was not time for complete evaluation and validation. Ordinary “good practices” quality assurance (QA) practices were followed, but the QA was not compliant with NQA-1 or QARD requirements. Future updates of models could be developed to tighter QA requirements when required.

In summary, the models in this report should be considered for interim use in calculating properties of Hanford HLW glasses. The models represent updates of the models generated by Hrma et al. (1994) and appear to perform as well or better than those models (they cover broader composition regions with comparable or higher R^2 values). However, the models should be updated when the database is updated to include RPP-WTP Project data and other relevant data. At that time, a more complete evaluation of the database for outlying and influential data points can be performed, and more time can be spent developing, evaluating, and validating the resulting models.

**Table S1. Partial Molar Coefficients and Validity Ranges for
Normalized B, Li, and Na Releases by PCT**

| Component (<i>j</i>) | Partial Molar $\ln(r_{ij}, \text{g/m}^2)^{(a)}$ | | | Validity Range, Mol Fraction | |
|--------------------------------|---|---------|---------|------------------------------|---------|
| | B | Li | Na | Minimum | Maximum |
| Al ₂ O ₃ | -33.419 | -29.999 | -32.668 | 0.00169 | 0.12748 |
| B ₂ O ₃ | 13.403 | 11.238 | 9.558 | 0.04141 | 0.19857 |
| CaO | -9.183 | -6.144 | -3.488 | 0.00000 | 0.12081 |
| Fe ₂ O ₃ | -11.947 | -13.028 | -10.357 | 0.00000 | 0.08363 |
| K ₂ O | -1.547 | -0.814 | 2.363 | 0.00000 | 0.05766 |
| Li ₂ O | 9.382 | 9.279 | 7.434 | 0.00000 | 0.18267 |
| MgO | 3.513 | 1.719 | 3.549 | 0.00000 | 0.13673 |
| MnO _x | -21.220 | -15.880 | -16.419 | 0.00000 | 0.03515 |
| Na ₂ O | 17.013 | 13.404 | 18.794 | 0.04660 | 0.24543 |
| P ₂ O ₅ | -41.830 | -31.893 | -39.952 | 0.00000 | 0.01280 |
| SiO ₂ | -4.106 | -3.431 | -4.243 | 0.36444 | 0.68148 |
| ZrO ₂ | -14.458 | -12.906 | -16.091 | 0.00000 | 0.07216 |
| Sum ^(b) | | | | 0.9452 | 1.0000 |
| Input | Normalized Mol Fraction of Oxide | | | | |
| # data points | 391 | 380 | 390 | | |
| R ² | 0.814 | 0.797 | 0.824 | | |
| R ² (adjusted) | 0.808 | 0.791 | 0.819 | | |
| R ² (predicted) | 0.798 | 0.779 | 0.809 | | |
| s (RMSE) | 0.531 | 0.468 | 0.475 | | |

(a) Normalized B, Li, and Na releases by PCT are calculated using the formula:

$$r_i = \exp\left(\sum_{j=1}^N b_{ij} x_j\right) \quad (\text{S.1})$$

where $i = \text{B, Li, Na}$ is the element released, j stands for the oxide component, N is the number of components, x_j is j -th component mol fraction where $\sum_{j=1}^N x_j = 1$, and b_{ij} is the coefficient listed in Table S1 ($b_{ij} = \ln r_{ij}$).

(b) This is the sum of the original component mol fractions before normalizing to the 12 components listed.

Table S2. Partial Molar Coefficients and Validity Ranges for Viscosity

| Component (j) | Viscosity Coefficients ^(a) | | Validity Range, Mol Fraction | |
|--------------------------------|---------------------------------------|-----------------|------------------------------|---------|
| | $A_j, \ln(\text{Pa}\cdot\text{s})$ | B_j, K | Minimum | Maximum |
| Al ₂ O ₃ | -2.860 | 27599 | 0.00169 | 0.12721 |
| B ₂ O ₃ | -13.594 | 8765 | 0.02834 | 0.19807 |
| CaO | -25.804 | 27511 | 0.00000 | 0.12052 |
| F | -83.850 | 108852 | 0.00000 | 0.01980 |
| Fe ₂ O ₃ | -3.490 | -835 | 0.00000 | 0.07754 |
| K ₂ O | -16.589 | 14436 | 0.00000 | 0.07504 |
| Li ₂ O | -7.100 | -10377 | 0.00000 | 0.19534 |
| Ln ₂ O ₃ | 43.460 | -78677 | 0.00000 | 0.02395 |
| MgO | -19.102 | 25120 | 0.00000 | 0.13404 |
| Na ₂ O | -9.974 | 632 | 0.04599 | 0.23582 |
| SiO ₂ | -10.136 | 26427 | 0.36356 | 0.66436 |
| ZrO ₂ | -55.621 | 95153 | 0.00000 | 0.08029 |
| Sum ^(b) | | | 0.95418 | 1.0000 |
| Input | Normalized Mol Fraction of Oxide | | | |
| # data points | 1574 | | | |
| R ² | 0.979 | | | |
| R ² (adjusted) | 0.979 | | | |
| R ² (predicted) | 0.978 | | | |
| s (RMSE) | 0.167 | | | |

(a) Melt viscosity is calculated using the formula:

$$\eta = \exp \sum_{j=1}^N [(A_j + B_j / T)x_j] \quad (\text{S.2})$$

where j stands for the oxide component, N is the number of components, x_j is j -th component mol fraction

where $\sum_{j=1}^N x_j = 1$, and A_j and B_j are coefficients listed in Table S2.

(b) This is the sum of the original component mol fractions before normalizing to the 12 components listed.

**Table S3. Partial Molar Coefficients and Validity Ranges for
Liquidus Temperature with Spinel Primary Phase**

| | Spinel | Validity Range, Mol Fraction | |
|---------------------------|-------------------------------------|------------------------------|---------|
| Component (<i>j</i>) | <i>T_j</i> , °C | Minimum | Maximum |
| Al | 3,063.7 | 0.00551 | 0.15316 |
| B | 548.5 | 0.00000 | 0.17000 |
| Ca | 1,651.0 | 0.00000 | 0.04000 |
| Cr | 31,857.3 | 0.00000 | 0.00770 |
| Fe | 3,737.5 | 0.02701 | 0.14689 |
| K | -687.7 | 0.00000 | 0.04000 |
| Li | 156.9 | 0.00000 | 0.18700 |
| Mg | 3,224.8 | 0.00000 | 0.03200 |
| Mn | 32.4 | 0.00000 | 0.02772 |
| Na | -263.8 | 0.08767 | 0.30000 |
| Ni | 13,842.6 | 0.00000 | 0.01969 |
| Si | 986.9 | 0.32000 | 0.48000 |
| Ti | 2,316.1 | 0.00000 | 0.02900 |
| U | 2,919.4 | 0.00000 | 0.01060 |
| Zr | 4,073.2 | 0.00000 | 0.02409 |
| Input | Normalized Mol Fraction of Elements | | |
| # data points | 158 | | |
| R ² | 0.93 | | |
| R ² (adjusted) | 0.93 | | |
| s (RMSE) | 29.65 | | |

Note: Liquidus temperature is calculated using the formula:

$$T_L = \sum_{j=1}^N T_j y_j \quad (\text{S.3})$$

where *j* stands for the element component, *N* is the number of components, *y_j* is *j*-th element mol fraction

where $\sum_{j=1}^N y_j = 1$, and *T_j* is the coefficient listed in Table S3.

Table S4. Partial Molar Coefficients and Validity Ranges for Liquidus Temperature with Zircon Primary Phase

| | Zircon | Validity Range, Mol Fraction | |
|--------------------------------|----------------------------------|-------------------------------------|----------------|
| Component (j) | T_j, °C | Minimum | Maximum |
| Al ₂ O ₃ | 2592.09 | 0.0000 | 0.0658 |
| B ₂ O ₃ | 719.62 | 0.0202 | 0.2033 |
| CaO | 752.82 | 0.0000 | 0.1175 |
| F | 3903.48 | 0.0000 | 0.0297 |
| Fe ₂ O ₃ | 2228.99 | 0.0000 | 0.0290 |
| K ₂ O | -2705.71 | 0.0000 | 0.0059 |
| Li ₂ O | -247.14 | 0.0221 | 0.1894 |
| MgO | 2134.97 | 0.0000 | 0.0642 |
| Na ₂ O | -2113.48 | 0.0389 | 0.1703 |
| P ₂ O ₅ | 2971.73 | 0.0000 | 0.0253 |
| SiO ₂ | 1133.46 | 0.4592 | 0.6452 |
| ZrO ₂ | 7814.54 | 0.0194 | 0.0860 |
| Sum | | 0.9492 | 1.0000 |
| Input | Normalized Mol Fraction of Oxide | | |
| # data points | 64 | | |
| R ² | 0.926 | | |
| R ² (adjusted) | 0.910 | | |
| R ² (predicted) | 0.866 | | |
| s (RMSE) | 22.30 | | |

Note: Liquidus temperature is calculated using the formula:

$$T_L = \sum_{j=1}^N T_j x_j \quad (\text{S.4})$$

where j stands for the component, N is the number of components, x_j is j -th component component mol fraction where $\sum_{j=1}^N x_j = 1$, and T_j is the coefficient listed in Table S4.

Reference

P. Hrma, 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, Vol. 1 and 2, Pacific Northwest Laboratory, Richland, Washington.

Glossary

| | |
|-------|---|
| BNFL | British Nuclear Fuels, Limited |
| CCC | canister centerline cooled |
| CUA | Catholic University of America |
| CVS | composition variation study |
| DOE | U.S. Department of Energy |
| DWPF | Defense Waste Processing Facility |
| EA | environmental assessment |
| EDS | energy dispersive spectroscopy |
| HAW | high-activity waste |
| HLW | high-level waste |
| HWVP | Hanford Waste Vitrification Plant |
| HTWOS | Hanford Tank Waste Optimization Simulator |
| INEEL | Idaho National Engineering and Environmental Laboratory |
| INTEC | Idaho Nuclear Technology and Engineering Center |
| LAW | low-activity waste |
| MCC | Materials Characterization Center |
| MS | melter study |
| MSE | mean squared error |
| NCAW | neutralized current acid waste |
| LM | light microscopy |
| PCT | product consistency test |
| PNNL | Pacific Northwest National Laboratory |
| PVTD | PNNL Vitrification Technology Development |
| Q | quenched (glasses) |
| QA | quality assurance |
| RPP | River Protection Project |
| RFETS | Rocky Flats Environmental Technology Site |
| RSD | relative standard deviation |
| RSME | root mean squared error |
| SEM | scanning electron microscopy |
| SD | standard deviation |

| | |
|--------|---|
| SA/V | surface area-to-volume ratio |
| SP | spinel study |
| SRTC | Savannah River Technology Center |
| TCLP | Toxicity Characteristic Leaching Procedure |
| TEM | transmission electron microscopy |
| THERMO | Thermodynamic Hydration Energy Reaction Model |
| TRU | transuranic |
| TWRS | Tank Waste Remediation System |
| WAPS | Waste Acceptance Product Specifications |
| WTP | Waste Treatment Plant |
| WVDP | West Valley Demonstration Plant |
| WVNS | West Valley Nuclear Services |
| WVST | West Valley Support Task |
| XRD | x-ray diffraction |

List of Symbols

| Symbol | Definition | Equation |
|----------------|---|---------------|
| A, A_{VFT} | composition-dependent coefficients | (1.9), (1.10) |
| A_j | j -th component coefficient in viscosity equation | (1.11) |
| A_j, A_0 | j -th component constraint constants | (4.2) |
| B, B_{VFT} | composition-dependent coefficients | (1.9), (1.10) |
| B_j | j -th component coefficient in viscosity equation | (1.11) |
| B_j | j -th component atomic/thermodynamic characteristic | (1.6) |
| b_{ij} | j -th component coefficient for i -th element (PCT release) | (3.2) |
| $b_{\alpha j}$ | j -th component coefficient for α -th property | (1.3) |
| c_α | α -th property constraint constant | (4.1) |
| f_α | α -th property-composition function | (1.3) |
| \mathbf{F}_W | composition vector function | |
| g_α | α -th property-composition function (inverse) | (1.4) |
| K | number of constraints | (4.1) |
| N | number of components in glass | (1.2) |
| \mathbf{p} | property vector | |
| p_α | α -th property | (1.3) |
| r_i | i -th element normalized PCT release from quenched glass | (3.2) |
| r_α | α -th property empirical coefficient | (1.6) |
| q_α | α -th property empirical coefficient | (1.6) |
| T | Temperature | |
| T_g | glass transition temperature | |
| T_j | j -th component coefficient in viscosity equation | (1.11) |
| T_j | liquidus temperature j -th component coefficient | (3.5) |
| T_L | liquidus temperature | (3.5) |
| T_M | nominal melter operating temperature | |
| T_0 | composition-dependent coefficient | (1.9) |
| V | glass composition region with acceptable properties | (4.3) |
| W | waste loading | (4.3) |
| \mathbf{x} | composition vector | (1.8) |
| x_j | j -th component mol fraction | (1.2) |

| | | |
|----------------|------------------------------------|-------|
| \mathbf{x}_0 | optimized glass composition vector | |
| ε | melt electrical conductivity | |
| η | melt viscosity | (1.9) |

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Quality Assurance

Ordinary “good practices” QA was performed in developing the database and models. Formal QA documentation such as would be required for Nuclear Quality Assurance Requirements and Descriptions (NQARD) was not performed because of the interim nature of the work.

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1.0 Introduction

This report discusses interim property-composition models developed for Hanford high-level waste (HLW) glasses. This effort is aimed at increasing the efficiency and decreasing the cost of vitrifying the large amount of radioactive waste in Hanford tank farms. Increasing the waste loading will decrease the amount of waste to be vitrified, and this in turn will decrease both operational and long-term storage costs.

The interim models were developed from a HLW property-composition database compiled for this purpose. Because the compiled database covers a large fraction of the region of HLW glass compositions considered potentially of interest for Hanford, the resulting interim property-composition models are considered *global models* (Piepel et al. 1998). Global models are useful when it is necessary to make property predictions over a wide HLW glass composition region. Global models may yield less-accurate property predictions, but still can be useful. Eventually, when target compositions and composition-variation regions around target compositions for specific waste types^(a) are better defined, it may be advisable to develop *local models* to predict HLW glass properties over the composition-variation region corresponding to a target composition for a given waste type. *Local models*, because they cover smaller composition regions centered near the glass composition of interest, are typically more accurate.

The HLW glass property-composition models presented in this report are referred to as *interim models* for several reasons. The most obvious reason is that property-composition models will continue to be developed as more property-composition data become available and better information about HLW compositions^(b) and corresponding HLW glass compositions becomes available. However, the models should also be considered interim due to limitations in the data used to develop them. Ideally, to provide good support for developing property-composition models (per Piepel et al. 1998), a waste-glass-composition region of interest should be defined and covered with property-composition data using statistical experimental design methods.

The interim models presented in this report were developed from a compilation of existing data. The data were screened so that only relevant data were used (as described in Section 3.1); however, the coverage of the HLW glass-composition region of interest is not as good as is desirable. For example, due to contractual issues between British Nuclear Fuels, Limited (BNFL), and the U.S. Department of Energy (DOE), the compiled database does not yet contain the data generated by the River Protection Project-Waste Treatment Plant (RPP-WTP) Project. Hence, the quality of the property-composition models discussed in this report may be affected by the limitations in the available data they were based upon. Further, time to develop, evaluate, and validate the interim-property models was limited. The available time only permitted using certain statistical regression diagnostic methods (Draper and Smith 1998; Montgomery and Peck 1992) to identify outlying or influential data points and to identify the subset of waste-glass components that should be included in the interim model for a given property. Statistical model-validation methods (Montgomery and Peck 1992, Chapter 10) were not applied. In

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- (a) A *waste type* is defined in the Waste Acceptance Product Specifications (WAPS) (DOE 1996) as “the waste material fed to each vitrification plant, the composition and properties of which will remain relatively constant over an extended period of time during waste form production.”
 - (b) It is expected that waste feed compositions will be updated as tank characterization, retrieval/blending scenarios, and definition of chemical impacts from separations and pretreatment processes are improved.

summary, although the interim property-composition models presented in this report have certain limitations, they should be useful for the needs at the present early stages of planning for the waste-retrieval, blending, and waste-glass development processes. These models are expected to give improved glass-property prediction over those previously developed for Hanford HLW waste glasses.

The following subsections in this introduction address the role of property-composition models, property constraints implemented through models, the need for property-composition data to develop models, the forms of property-composition models, model fitting and reduction, and previous work to develop property models for Hanford HLW glasses. Section 2.0 presents a property-composition database compiled from previous studies to provide a basis for developing HLW property-composition models. Section 3.0 discusses the interim property-composition models developed for Hanford HLW glasses, the data used to develop the models, and the glass composition regions over which the models are valid for predicting glass properties. Section 4.0 discusses the use of property-composition models and mathematical constrained optimization methods to develop glass formulations and estimate waste glass volumes.

1.1 The Role of Property-Composition Models

The processability and acceptability of HLW glass is specified in terms of glass properties. To make HLW glass, the waste must be mixed with glass-forming additives in proportions to obtain a target glass composition that must have properties within prescribed limits. HLW glass composition varies as a result of the changing composition of waste. The economic aspect of vitrification requires that HLW glass composition should minimize the expense.

It is practically impossible to develop an optimized waste glass for each waste composition on a purely experimental basis. Mathematical, statistical, and optimization methods are extremely useful in developing optimal glass compositions. Therefore, the task of developing optimum glass compositions must be addressed within a mathematical framework. An indispensable element of such a framework is a set of property-composition models. These models should be developed for HLW glasses covering both the HLW glass composition region of interest and a sufficiently broad range of values for HLW glass properties of interest.

Property-composition models applicable to Hanford HLW glasses have been developed at Pacific Northwest National Laboratory (PNNL) for over a decade. Initially, only one HLW waste stream was considered that would be processed in a certain type of melter without any attempt for optimization. However, the need for property-composition models broadened over time because the waste composition estimates changed, new waste streams were taken into consideration, new types of melters were tested, and economic considerations became more important. Thus, it became clear that the composition region of HLW glass for the development of property-composition models was too narrow and the range of existing property-composition models were not broad enough for practical applications.

The composition region of HLW glass is determined by four factors:

- 1) The HLW composition region
- 2) The range of glass properties that define acceptability for the repository

- 3) The processing technology
- 4) The applicable economic considerations.

These four factors are not fixed; all are continuously changing, and some are inter-dependent. Estimates of HLW compositions change with new samples and chemical analyses, pretreatment methods, retrieval strategies, and blending options. Though the acceptability conditions have been relatively stable for the last decade^(a), opinions vary as to how much crystallinity should be allowed in the glass and whether the glass can be phase-separated. It is also conceivable that additional acceptability conditions may be imposed in the future as additional concerns regarding safety are raised. Finally, different melter types have been considered in the past or are considered for the future (e.g., Joule-heated melter, stirred melter, high-temperature melter, cold-walled induction-heated melter). Different melters require different sets of glass-property values for processability. Economic considerations are often assessed in terms of waste loading in HLW glass. Maximizing waste loading generally minimizes the costs of producing and disposing of HLW glass.

With each change, whether in 1) the estimated composition of waste in the tanks currently considered for vitrification, 2) the group of tanks being considered for processing, 3) the key glass components resulting from pretreatment, or 4) the melter type being considered for vitrification, the set of property-composition models needs to be updated. Extrapolation beyond the composition region on which the models are established can lead to misleading results. There is another reason for periodic updating of property-composition models. As more glasses are being tested to support various programs, more and more glass-property data accumulate. These data can be used to validate the existing property-composition models and ultimately to update these models. The development of property-composition models must respond to continuous changes. Consequently, developing property-composition models for HLW glass is a continuous process.

1.2 Property Constraints

Three kinds of constraints on HLW glass properties exist: acceptability constraints, processing constraints, and economic constraints. Each of these kinds of constraints is discussed below.

1.2.1 Acceptability Constraints

Acceptability constraints are concerned with the acceptability of the final product. Roughly, HLW glass should have sufficiently high chemical durability and should retain this durability over thousands of years. Although the engineering barriers in the repository and the geology of the repository itself will prevent the spreading of radioactive elements into the environment, the glass itself should have good resistance against corrosion by water. The benchmark test for U. S. HLW glass is the Product Consistency Test (PCT) (ASTM 1998). A rough statement of an applicable PCT constraint is that no acceptable HLW glass should have a higher release of boron, sodium, or lithium than the Environmental Assessment (EA) glass after normalization for their fractions in glass (DOE 1996). As our knowledge of glass behavior increases, glasses are routinely formulated that surpass the EA constraint by nearly an order of magnitude. However, to implement this constraint, various uncertainties (in PCT measurement,

^(a) The acceptability of HLW glass is described in the Waste Acceptance Product Specifications (WAPS) (DOE 1996).

release predictions from models that are functions of glass composition, and glass compositions used in predicting PCT release) must be accounted for.

HLW glass properties may strongly depend on the temperature history of the glass. Slowly cooled glass is prone to amorphous phase-separation and crystallization. Crystals are usually durable, which means that they remove from the amorphous phase components that endow glass with durability. Thus, crystallization of certain minerals, such as nepheline, may produce non-durable glass. Therefore, PCT performance should be studied and modeled for glass that is quickly cooled (quenched glass) and glass with the slowest rate of cooling (canister-centerline-cooled glass), see Marra and Jantzen (1993) and Riley et al. 2001. The formation of additional phases (crystalline or amorphous) also impacts glass acceptability by making the prediction of PCT release less certain. This imposes a further restriction on glass composition by increasing the error margin in PCT release that must be accounted for.

1.2.2 Processing Constraints

The second kind of constraint is added to ensure the processability of glass in the melter. The acceptable ranges for processability-related glass properties differ for different melter types. Generally, glass is processable when its viscosity (η) is lower than 10 Pa·s. The lower is the viscosity, the higher the rate of processing. However, when η is below 2 Pa·s, glass becomes more corrosive to the melter walls and introduces concerns of steam excursions. Therefore, 2 Pa·s is generally considered the lower limit for melt viscosity, although 1 Pa·s is likely to be acceptable.

An important property of HLW glass is its liquidus temperature (T_L), the highest temperature at which a solid phase can exist in the melt at equilibrium. With increasing waste loading, T_L increases until it reaches and exceeds the temperature of glass in the melter. When this happens, solids can precipitate in the melter. If these solids are not removed from the melter with the waste glass, they accumulate and can eventually obstruct melter operation. To prevent a premature shutdown of these melters, T_L is required to be lower than a certain temperature pertinent to the melter. Typically, a 100°C safety margin is used so that $T_L \leq T_M - 100^\circ\text{C}$, where T_M is the nominal melter operating temperature.

Processability constraints may be modified in the future. In particular, the T_L constraint currently limits waste loading in most of Hanford and Savannah River HLW glasses and thus has a huge economic impact. Hence, the T_L constraint is likely to be subjected to scrutiny and made less restrictive without putting solid-phase-sensitive melters at risk. For example, it may be acceptable to allow some small volume fraction of certain crystals in the melter as long as they do not segregate to the melter bottom, cause other processing problems, or affect the acceptability of the HLW glass. Other constraints may be added to the existing list. For example, constraints could be developed that would prevent the segregation of molten salts in the melter or prevent unacceptably low melting rate or high corrosion rate.

Another property that has been required to be within certain limits is electrical conductivity (ϵ) of the melt. Because glass is heated by an electric current passing through it, the glass conductivity must be substantially higher than that of the melter walls and sufficiently low to prevent electrode damage or thermal instability. The permitted range of ϵ of molten glass is wide, usually 10 to 100 S/m. With this wide range, ϵ is unlikely to affect the formulation of HLW glasses that meet viscosity and PCT constraints. Once the power system for the melter has been built, the acceptable range for ϵ may be

narrowed to meet the specific power output of the system. Because of the broad range of acceptable ε , this property rarely limits the waste loading of HLW glasses and therefore was not modeled in this study.

1.2.3 Economic Constraints

The cost of producing HLW glass depends on the total volume of glass to be produced and the required processing time. By increasing the waste loading of HLW glass (i.e., the fraction of HLW incorporated in the glass), the volume of HLW glass will be reduced. Thus, the cost will be reduced by decreasing the time required to process the waste (assuming the same rate), and by decreasing the space and handling required for the canistered waste. Hence, constraints may be placed on the waste loading of HLW glass to control the cost of producing the glass. For example, the contract for the RPP-WTP to be built at Hanford contains waste-loading constraints for HLW glass.

Acceptability constraints and processing constraints are typically placed on HLW properties, whereas waste loading (economic) constraints are placed directly on the HLW glass composition itself. For glass development and qualification work, property-composition models provide a way to implement property constraints as functions of glass composition.

1.3 Property-Composition Models

Property-composition models (or constitutive equations) are functions of the form

$$p_{\alpha} = f_{\alpha}(\mathbf{x}) \quad (1.1)$$

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 vector is defined as $\mathbf{x} = (x_1, x_2, \dots, x_{N-1})$, where x_j is the j -th component mass or mol fraction, and N is the number of components. Only $N-1$ components are independent because the mass and mol fractions must sum to 1:

$$\sum_{j=1}^N x_j = 1 \quad (1.2)$$

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 not applicable to the prediction of multi-component waste-glass properties but may be useful in understanding fundamental relationships that guide model development.

The following two subsections discuss property models linear in composition, and property models linear in composition and nonlinear in temperature. The final subsection briefly discusses the concept of first principles.

1.3.1 Property Models Linear in Composition

A simple but very useful property-composition model form is given by

$$p_{\alpha} = f_{\alpha} \left(\sum_{j=1}^N b_{\alpha j} x_j \right) \quad (1.3)$$

or, more conveniently,

$$g_{\alpha}(p_{\alpha}) = \sum_{j=1}^N b_{\alpha j} x_j \quad (1.4)$$

where $b_{\alpha j}$ is the j -th component coefficient for α -th property and g_{α} is the inverse of f_{α} . Note that the mathematical transformation g_{α} could be the identity transformation (i.e., no transformation). Also note that the sum runs from 1 to N , and thus not all x_i are independent. This form enabled us to write Equation (1.4) without a constant (intercept term) because, by Equation (1.2),

$$x_N = 1 - \sum_{j=1}^N x_j \quad (1.5)$$

Because $g_{\alpha}(p_{\alpha})$ in Equation (1.4) is also a property, we can identify the $b_{\alpha j}$ coefficients as partial-specific or partial-molar properties. Models of the form (1.4) are often referred to as *first-order (or linear) mixture experiment models* (Cornell 1990) because the functional form is a first-order (linear) polynomial. Note that in classical thermodynamics, Equation (1.4) is used also for non-ideal mixtures. In these mixtures, partial specific or molar properties are functions of composition. Glass is generally a non-ideal mixture. Fortunately, individual components in waste glasses are usually confined to sufficiently narrow ranges of concentrations as to allow non-linear functions of composition to be approximated as linear with acceptable error.

Glass composition (the \mathbf{x} vector) can be expressed in three basic ways.

- 1) Glass composition is traditionally expressed as a mixture of single metal oxides (SiO_2 , Fe_2O_3 , SO_3 , Na_2O , etc.) and halogens (e.g., F). Multivalent oxides are all represented with the prevalent valency. Though the oxygen content in the glass is not counted accurately, the composition is uniquely defined and is probably the most suitable for technological and engineering applications, especially when mass fractions are used. Accounting for the true oxidation-reduction states of all components is not practicable because this state depends on glass-making conditions (selection of raw materials, temperature, and atmosphere during glass making). However, models have been developed that account for variations in oxygen fugacity by including separate terms for FeO and Fe_2O_3 .
- 2) Glass can be viewed as a mixture of electronegative constituents (O^{2-} , F^-) and electropositive constituents (Si^{4+} , B^{3+} , Fe^{2+} , Fe^{3+} , Na^+ , etc.). The problem with the redox state and the fraction of

oxygen does not arise if only electropositive constituents and F^- are considered. This may be advantageous for semi-empirical models that include fundamental properties of ionic species, such as the size or charge of the ions.

- 3) Glass composition can be resolved into simple silicates and borates. This representation is not unique and can be accomplished in different ways for different properties, dependent on which structural units are associated with different transport properties, hydration reactions, or crystallization behavior. This may be advantageous for modeling the effects of elements that fill multiple structural roles in glass, depending on composition.

Approach 2) has been used for the spinel T_L model^(a) (Section 3.4.3), Approach 3) has been applied for the hydration energy model (Jantzen 1992), and Approach 1) is useful for technological calculations. Approach 1) with mass fractions is directly related to the weighing operation of materials and thus is preferred by glassmakers. Approach 1) with mol fractions of components is used for η , PCT release, and the zircon T_L models in this report.

The disadvantage of an empirical model, such as Equation (1.4), is that a large number of coefficients must be estimated from data. Waste glass can have up to 40 elements, and some of these elements can be in multiple oxidation states. It would be difficult to cover a large composition region with enough compositions to estimate 50 or more coefficients. However, in practice most glass properties are only significantly affected by “major” glass components (e.g., those appearing at mass or mol fractions greater than 0.005). Hence, the number of components for which $b_{\alpha j}$ coefficients in Equation (1.4) must be estimated is usually much smaller than the total number of glass components.

The problem of empirically estimating a large number of component coefficients in Equation (1.4) can be resolved if the coefficients are related to some basic atomic or thermodynamic characteristic of the components. If such relationships are simple, the number of empirical coefficients can drastically decrease. Suppose that

$$b_{\alpha j} = r_{\alpha} + q_{\alpha} B_j \quad (1.6)$$

where B_j is the atomic or thermodynamic characteristic of the j -th component, and r_{α} and q_{α} are empirical coefficients for α -th property. Combining Equations (1.4) and (1.6), we obtain a semi-empirical relationship

$$g_j(p_j) = r_j + q_j \sum_{i=1}^N B_i x_i \quad (1.7)$$

Because Equation (1.7) has only two empirical coefficients, it will generally yield less accurate property predictions than the fully empirical Equation (1.4). However, Equation (1.7) may yield better results if

(a) Element concentrations were used as components in the model for liquidus temperature in the spinel primary phase field because it was found that in this form the coefficients scaled with the ion potential of the components. Vienna et al. (2001) describe the application of ion potential to liquidus temperature prediction in detail.

$b_{\alpha j}$ coefficients are not known for some influential components. A semi-empirical relationship such as Equation (1.7) is easier to develop and use, and N can be larger than for an empirical relationship represented by Equation (1.4). Comparing empirical and semi-empirical $b_{\alpha j}$ values can identify shortcomings in the assumptions inherent in Equation (1.7) (see for example, Piepel et al. 1996 and 1997).

1.3.2 Property Models Linear in Composition and Nonlinear in Temperature

Some glass properties, such as η and ε , are functions of temperature (T) as well as composition. For such properties, models are of the form

$$p_{\alpha} = f_{\alpha}(\mathbf{x}, T) \quad (1.8)$$

For a given waste glass, the temperature dependence of a property, such as viscosity, is often approximated by the Vogel-Fulcher-Tammann equation

$$\eta = \exp(A_{VFT} + \frac{B_{VFT}}{T - T_0}) \quad (1.9)$$

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

$$\eta = \exp(A + \frac{B}{T}) \quad (1.10)$$

where A_{VFT} , B_{VFT} , T_0 , A , and B are temperature-independent coefficients.

In any of these equations, the parameters A_{VFT} , B_{VFT} , T_0 , A , and B can be expressed as functions of composition to also capture the dependence of the property on composition. Expanding the parameters in Equations (1.9) and (1.10) as linear functions of composition (linear mixture models) yields

$$\ln(\eta) = \sum_{i=1}^N (A_i + \frac{B_i}{T - \sum_{j=1}^n T_j x_j}) x_i \quad (1.11)$$

and

$$\ln(\eta) = \sum_{i=1}^N (A_i + \frac{B_i}{T}) x_i \quad (1.12)$$

Here subscripts VFT were dropped from the partial specific/molar coefficients in Equation (1.11). Coefficients A_{VFT} , B_{VFT} , T_0 , A , and B can be treated as composition-dependent properties, and thus their reparameterization as in Equation (1.7) is conceivable.

1.3.3 A Comment About First Principles

In classical field theory, material parameters or properties are mathematically established as constitutive equations that relate these parameters to state variables (such as temperature, pressure, and composition). These relationships are distinct from the first-principles that postulate the basic laws of physics, such as the balance of energy. The constitutive equations themselves are not first-principles. They just define material objects whose behavior is subject to the basic laws (the first-principles).

Can constitutive equations themselves be based on first-principles? Yes, if these equations were based on quantum mechanics, as in the *ab initio* calculations. In such models, no empirical coefficients would be needed. They would be based solely on the first-principles or basic laws. Such an approach is not realistic at present. For example, properties of even a single-component glass (SiO_2) are much easier to measure than to accurately calculate from first-principles. The term “first-principle” is occasionally used for semi-empirical models of the type (1.7). This terminology is inappropriate and confusing.

1.4 Need for Property-Composition Data

Partial properties in Equation (1.4) or empirical coefficients in Equation (1.7) can only be measured or estimated from data. The temperature dependence of a property, such as η , can be determined by: 1) measuring the property at a series of constant temperatures, or 2) continuously measuring the property while the temperature is gradually increasing or decreasing. To establish a η - T relationship in analytical terms, an empirical model is fitted to measured data. Such a relationship or model^(a) is ready for use in applications, for example, in the Navier-Stokes equation for fluid flow with a variable temperature. It can also be used for computing viscosity at a given temperature if such a number is needed for understanding a more complex behavior, such as the settling of solid particles. When using empirical models, it is important to be aware of uncertainties, such as the uncertainty of measured data, the uncertainty of the empirical model form (how closely it represents or approximates the real behavior), and the uncertainty of parameters that define the application (e.g., the mass and composition of the tank waste or the degree of nonuniformity of the melter feed).

To determine the empirical coefficients in property-composition models, an adequate set of property-composition data is needed. Historical data sets can be compiled for this purpose, or a test matrix of compositions can be designed and the properties measured. Unlike temperature, which is expressed by one number, composition is expressed as a vector with $N-1$ dimensions. The goal in compiling property-composition data to develop property-composition models is to adequately cover the $(N-1)$ -dimensional glass-composition region with a manageable number of compositions.

Several approaches can be used to select a test matrix to explore an $(N-1)$ -dimensional composition region. Three common approaches are to: 1) vary each component one-at-a-time (i.e., adding or removing a single component to or from a baseline composition with the remaining components adjusting for the change while maintaining constant proportions), 2) replacing one component with another, and 3) changing the fractions of several (up to $N-1$) components at a time. Some advantages and disadvantages of these three approaches are summarized in Table 1.

(a) The terms “model” and “relationship” are interchangeable in this report, though their connotations are different in materials science and statistics

Table 1.1. Advantages and Disadvantages of Three Approaches for Exploring a Glass Composition Region of Interest

| Approach | Advantages | Disadvantages |
|--|---|---|
| One-at-a-time variations from baseline composition or replacing one component with another | <ol style="list-style-type: none"> 1. Component effects can be graphically visualized 2. Linearity or nonlinearity of component effects are immediately apparent 3. Does not require sophisticated software for design or evaluation 4. Component replacement is useful if one component makes up the majority of the glass | <ol style="list-style-type: none"> 1. Results may depend on the baseline composition 2. Does not provide information about non-linear blending (“interaction”) effects of the components 3. Inefficient way to cover composition space and generate data for property-composition models |
| Many-at-a-time variations within a defined glass composition region | <ol style="list-style-type: none"> 1. Provides information about nonlinear blending (“interaction”) effects of the components 2. Provides information about linear effects of components over the region 3. Provides for best coverage of the composition region | <ol style="list-style-type: none"> 1. Requires statistical optimal experimental design methods and software to implement 2. Requires models to assess whether components have linear or non-linear (curvilinear or interaction) blending effects |

The large number of components in Hanford HLW glass indicates that there is hardly ever enough data to develop highly accurate constitutive equations over the whole glass composition region in question. Moreover, the dependence of waste-glass properties on glass composition is fundamentally nonlinear, and thus the linear representation in Equations (1.4) or (1.7) has limited validity. Fortunately, the “true” (but unknown) property-composition relationships are generally expected to be smooth or piecewise smooth (as in the case of T_L) functions of composition. For smooth functions of composition, linear functions provide satisfactory approximations over sufficiently small portions of the composition space. Luckily, in many-component HLW glasses, the range of interest for each component is likely to be sufficiently narrow so that a linear function provides a reasonable approximation to the “true” property-composition relationship.

Linear mixture models such as (1.4) can be expanded to include nonlinear blending terms in cases where a linear approximation is not adequate, and there are sufficient data to estimate the coefficients of linear and nonlinear blending terms (Cornell 1990; Piepel and Szychowski 2000). If glass components are likely to have significant nonlinear blending effects for a given waste-glass composition region, more property-composition data points covering the composition space will be needed to support fitting models with nonlinear blending terms.

1.5 Data Reduction: Partial Specific/Molar Coefficients

As was discussed in Section 1.4, databases alone are insufficient for developing an adequate HLW glass formulation because too many constraints need to be satisfied, and the waste-glass volume should be as small as possible (i.e., the waste loading in the glass should be as high as possible). Therefore, data reduction is necessary. As discussed in Section 1.1, the goal of data reduction for formulation purposes is to develop property-composition models that adequately approximate the “true”, unknown property-composition relationships. Such models can then be used to predict waste-glass property values as functions of waste-glass composition (and temperature, where applicable) anywhere within the composition region of validity for the models.

In this report, we focus attention on models with linear composition dependence, such as in Equations (1.4), (1.11), and (1.12). Such models can be fit to an appropriate property-composition data set, thereby reducing the data to partial-specific or molar properties. Composition in the models can be expressed in one of the three possible divisions of the mixture to constituents discussed in Section 1.3. Partial properties have been well established in thermodynamics, including their physical meaning and methods of evaluation from data. They can be themselves functions of composition. Hence, Equation (1.4) is useful, even when the composition relationship is nonlinear, that is, $b_{\alpha j} = f_{\alpha j}(\mathbf{x})$. Attempts have been made to use this approach (to develop higher-order models), but these attempts were discontinued for the lack of sufficient data (for some properties) or because of the limited time available to develop models for inclusion in this report.

After fitting a model linear in composition (Equation (1.4)) to property-composition data (and thus estimating partial specific or molar properties for the components in the model), the next step is to assess the adequacy of the model. As noted previously, a model linear in composition may or may not adequately approximate the “true”, unknown property-composition relationship over the composition region covered by the available data. Provided the data set includes sufficient replicate data points, or adequate estimates of experimental and property measurement uncertainties exist, statistical methods for assessing model lack-of-fit (Draper and Smith 1998; Montgomery and Peck 1992) can be applied. If a model does not have a statistically significant lack-of-fit, then it should be validated using data not used to develop it, or cross-validated using the data used to develop it (Montgomery and Peck 1992, Chapter 10). However, empirical models with statistically significant lack-of-fits or less than ideal validation or cross-validation performance can still be useful in earlier stages of glass development and formulation studies, provided the models provide reasonable fits and predictive ability. Global models linear in composition may fall into this category, but would still be useful in supporting early waste-retrieval, waste-blending, and glass-development activities. As waste composition and variation information improve, local models can be developed to more accurately predict glass properties over smaller glass-composition regions corresponding to specific waste types.

If a model linear in composition (Equation (1.4)) for a given property provides an adequate fit to the data, the next step in the data reduction is to focus more attention on the estimated partial-specific or molar properties obtained from the model fit. For example, the partial properties can be further analyzed to find correlations between or relationships with more fundamental characteristics of the constituents, such as the electric charge and radius of ions or the free enthalpy of simple silicates and borates (Vienna et al. 2001). Such a semi-empirical approach to developing property-composition models reduces property-composition data to the maximum practicable degree.

1.6 Existing Property Composition Models for Hanford HLW Glass

Historically, simple relations between properties and composition have been developed for commercial glasses for nearly a century. The book by Scholze (1990) provides a good review of property-composition relationships for simple glasses. A similar approach became a necessity for HLW glass to deal with the large composition region of Hanford HLWs. Before Hanford experience, a semi-empirical equation, originally developed by Paul for assessing glass durability (Paul 1981), was applied to HLW at Savannah River (Jantzen 1992).

The Hanford HLW composition region is not fully known, but reasonable estimates of its boundaries have been made based on HLW sample analyses and process inventories. For this estimated HLW composition region, a glass-composition region for neutralized current acid waste (NCAW) was assessed and represented by more than 100 compositions, for which a number of properties were measured (Hrma et al. 1994; Piepel et al. 1995). Property-composition models were then developed from these data (Hrma et al. 1994, 1995a, 1995b).

The basic processing properties measured and modeled (Hrma et al. 1995b, Vienna et al. 1996b) were η , ε , and T_L . Other properties were also characterized and modeled: glass-transition temperature, thermal-expansion coefficients of solid and molten glass, and density (Hrma et al. 1994). Considerable attention focused on PCT (Hrma 1995a; Vienna et al. 1996a), and other studies for Hanford HLW glass have focused some attention on Toxicity Characteristic Leach Procedure (TCLP) to a lesser extent. These outcomes of specific tests are, strictly speaking, not properties, but can be treated as such because they are reproducible results of well-defined experimental procedures. For Idaho HLW glass-composition regions, preliminary property-composition models were developed for η , T_L , and PCT (Edwards et al. 2000; Piepel et al. 2000).

The form of the function g_α in Equations (1.4) and (1.7) is the natural logarithmic function for η , ε , and normalized PCT elemental releases. For other properties, g_α was the identity function. The transport properties, η and ε , are also functions of temperature, as discussed in Section 1.3. For η , Hrma et al. (1995a) developed property-composition-temperature models of the form (1.11) and (1.12) as presented in Section 1.3. For ε , they developed models of the form (1.12). Models for η and ε at a constant temperature were also developed. Hrma et al. (1995b) also used a model of the form (1.4) for PCT normalized elemental releases. A semi-empirical model based on the hydration energies of silicate, borate, and oxide components of glass did not work well for Hanford HLW glass (Piepel et al. 1996 and 1997). Feng et al. (1990) and Feng and Metzger (1996) developed a semi-empirical model for viscosity and PCT release based on the heat of formation of oxide components in glass. Jantzen (1991) developed a model for T_L based on the free energies of formation of three mineral phases. Jantzen (1991) also developed a model for viscosity based on a calculation of the number of non-bridging oxygen atoms.

2.0 Property-Composition Database

This section describes the waste-glass property-composition database that was compiled to support developing property-composition models. Section 2.1 briefly describes the structure and contents of the database. Section 2.2 lists the major sources of data incorporated in the database and used for model development in Section 3.0.

The database certainly does not contain all property values of HLW glasses ever measured. Some available data sets were omitted because of incomplete documentation or other reasons, which are given below. Moreover, some relevant recent data could not be included: for example, the data generated in Part B-1 of the RPP-WTP Project were not available. More data will be collected after this interim report is issued to validate and improve property-composition models.

2.1 Description of Database

The current database was compiled in an Excel spreadsheet with IDs of glasses in rows and compositions and properties in columns as described below. Because of the size of the database, two versions of the report were printed, one version with the database attached as Appendix A and one version without the database attached.

- *Study, Data Source, and Glass ID*: Each set of data is distinguished by a study name (i.e., the names for a group or groups of data) and the source of the data (i.e., a reference). The same Glass IDs are used as given in the original Data Source.
- *Glass Composition (mass fraction)*: Target (-t) and analyzed (-a) compositions are entered in separate columns in alphabetical order for 61 components. The “Others” component is used only when there is no information available to separate “Others” into individual component concentrations, and the sum of oxide components in target composition did not equal one.
- *Melting Temperature (T_M in $^{\circ}\text{C}$)*: The melting temperatures are the actual temperatures used to fabricate the glass. When a glass was melted two or three times, only the final melting temperature was entered.
- *Liquidus Temperature (T_L in $^{\circ}\text{C}$)*: The liquidus temperatures measured by a gradient-furnace method and by a uniform-temperature method are given in separate columns. The primary phase was also recorded in a column.
- *Crystallinity and Homogeneity*: The information on the crystalline and amorphous phase separation was given for quenched, canister centerline cooled (CCC), and heat-treated glasses. The results from visual/light microscopic (LM) observation, electron microscopic (scanning electron microscopy/electron-dispersive spectroscopy [SEM/EDS] or transmission electron microscopy [TEM]), and X-ray diffraction (XRD) were recorded in separate columns.
- *Density (ρ in g/cm^3)*: Density data are available for limited number of glasses.

- *Viscosity (η in Pa·s)*: The coefficients for Vogel-Fulcher-Tamann and Arrhenius equations; the calculated viscosity at 1150°C; and temperatures at 2, 5, and 10 Pa·s (based on these coefficients) are entered as provided in the references. The T_n and V_n ($n \equiv$ data point number = 1 to 14) columns are for the viscosity-at-temperature data.
- *PCT Normalized Releases (r_i in g/m²)*: Normalized elemental releases of $i = \text{B, Li, Na, and Si}$ and final pH values from standard 7-day PCT at 90°C and target surface area-to-volume ratio (SA/V) of 2000 m⁻¹ are given for quenched (Q) and CCC glasses. The releases are all normalized to SA/V in addition to element concentration in glass, giving r_i values in g/m². In some of the studies, the reported releases are not normalized to SA/V and are reported in g/L. Some studies measured PCT at 20°C; these results are in separate columns.
- *TCLP (in ppm)*: The TCLP data are available for a limited number of glasses.

The database compiled in this report contains glasses designed for the vitrification of HLW and selected low-activity waste (LAW) glasses with compositions within the composition region of typical HLW glasses that were used for the model development.

2.2 Discussion of Data Sets Used in Model Development

This subsection provides a list of studies represented in the database with brief explanations of each study. Table 2.1 summarizes these studies in terms of the number of glasses tested, their compositions, and properties provided. The figures in parentheses in the “property” column indicate the number of glasses for which the property data are provided.

2.2.1 Idaho National Engineering and Environmental Laboratory Composition Variation Studies

This series of studies includes the three phases of glass composition variation study (CVS) conducted at Idaho National Engineering and Environmental Laboratory (INEEL) to develop glass compositions for immobilizing the HLW calcine stored at the Idaho Nuclear Technology and Engineering Center (INTEC).

INEEL CVS Phase 1 (Staples et al. 1999)

The first phase of the CVS addressed waste compositions based on the high-activity waste (HAW) fraction from the initial separations flowsheet. This study investigated how glass properties depend on composition within a region compatible with the expected range of INEEL INTEC HAW. Given the range of the HAW compositions, statistical design techniques were applied to derive a formulation matrix for the first phase of the CVS (Piepel et al. 1999). Formulations selected from this matrix were characterized with respect to crystallinity of both quenched and CCC glasses, PCT releases of quenched glasses, η , and T_L . The T_M data are provided for all 44 glasses. Because of batching errors that were discovered after the report was issued, the original report contained some incorrect target compositions and PCT releases calculated based on the target compositions. The correct compositions and PCT releases were recalculated later from the original batch sheets and entered in the database. The corrected compositions are documented in a report by Piepel et al. (2000). Analyzed compositions were not given in the original report; the analyzed compositions entered in this database were those obtained after the Staples et al. (1999) report was issued.

Table 2.1. Summary of Number of Glasses Tested and Properties Measured in Each Data Set

| Study | Reference | # of Glasses | Comp ^(a) | Property (# of glasses) |
|-----------------------------|--------------------------------------|--------------|---|---|
| INEEL CVS Phase 1 | Staples et al. (1999) | 44 | t, a | T_M (44); GT_L (23); UT_L (28); Q (44); CCC (8); η VFT (36), η (1150°C) (36), $\eta(T)$ (36); Q PCT (44) |
| INEEL CVS Phase 2 | Staples et al. (2000) | 37 | t, a | T_M (37); UT_L (26); Q (37); CCC (15); ρ (37); η VFT (36), η (1150°C) (36), $\eta(T)$ (36); Q PCT (37) |
| INEEL CVS Phase 3 | Scholes et al. (2000) | 30 | t, a | T_M (30); UT_L (24); Q (30); CCC (28); ρ (30); η A (30), η (1150°C) (30), $\eta(T)$ (30); Q PCT(30) |
| Hanford CVS 1 and 2 | Hrma et al. (1994) | 146 | t, a (t only for roughly 1/2 of the glasses) | For 122 glasses of CVS1-1 ~ CVS2-101 except CVS2-53, 54: GT_L , CCC; η VFT@A; η (1150°C); $\eta(T)$; Q PCT; CCC PCT For 22 glasses of CVS2-102 ~ CVS2-123: Q PCT; CCC PCT |
| Hanford CVS 3 | Vienna et al. (1996c) | 40 | t | UT_L (31); Q (16); CCC (38); η VFT (32), η A (39), $\eta(T)$ (39); Q PCT (40); CCC PCT (40) |
| TRU ^(b) Study | Crum et al. (1997) | 44 | t | UT_L (42) |
| SP ^(c) | Mika et al. (1997) | 41 | t | UT_L (41) |
| Zr Study | Vienna et al. (1999) | 29 | t | T_M (29); UT_L (29); Q PCT (28) |
| MS | Hrma (1999) and Wilson et al. (2001) | 28 | t | UT_L (28) |
| SG | Hrma et al. (1999) | 63 | t | T_M (63); UT_L (63) |
| SP3, SPx4, Misc. | Vienna et al. (2001) | 50 | t | UT_L (50) |
| Comp. V's Properties Study | Chick et al. (1981) | 102 | a | T_M (102); Q (77); CCC (44); η @ 1250°C (102) |
| WV HLW Formulation Study | Chick et al. (1984) | 103 | t, a | Q (103); CCC (103); HT (103); T @ 10 Pa-s (88); T @ 3 Pa-s (96) |
| HWVP 85 | Bates (1985) | 1 | t | $\eta(T)$; ρ |
| WV Glasses by CUA and PNL | Johnston et al. (1990) ^a | 128 | | Q PCT (128) – 98 glasses r_B only, 30 glasses r_B , r_{Li} , r_{Na} , r_{Si} and pH |
| WVDP ^(d) Support | Olson (1993) and (1994) | 20 | t, a | η (1150°C) (20), $\eta(T)$ (20); Q PCT (20) |

^(a) Johnston, J. W., G. F. Piepel, and B. A. Pulsipher. 1990. "Evaluation of Empirical Models for Glass Durability," Letter Report Prepared for West Valley Nuclear Services, Pacific Northwest National Laboratory.

Table 2.1 (Contd)

| Study | Reference | # of Glasses | Comp ^(a) | Property (# of glasses) |
|---|-------------------------------------|--------------|---------------------|---|
| West Valley CVS Glasses PCT | Olson et al. (1994) | 16 | a | Q PCT (16) |
| Glass Dissolution Chemistry | Ramsey (1995) | 30 | t, a | Q PCT (30) |
| West Valley WQR ^(e) | West Valley Nuclear Services (1995) | 48 | t | η (1150°C) (10), $\eta(T)$ (10); Q PCT (48) |
| DWPF ^(f) PCT Model | Jantzen et al. (1995) | 177 | t, a | Q PCT (177) |
| Plutonium Vitrification | Bulkley and Vienna (1997) | 45 | t | T_M (41); η_A (40), η (1150°C) (36), $\eta(T)$ (40); Q PCT (39) |
| TWRS LAW Formulation ^(g) | Muller and Pegg (1998) | 51 | t, a | UT_L (46); ρ (4); $\eta(T)$ (46); Q PCT @ 20°C (51); TCLP (4) |
| TWRS LAW Formulation 2 ^(g) | Ferrara et al. (1998) | 3 | t, a | Q PCT @ 20°C (3); TCLP (3) |
| <p>(a) Compositions given in the database; t = target and a = analyzed. (b) TRU = transuranic (c) SP = spinel study (d) WVDP = West Valley Demonstration Project (e) WQR = Waste Form Qualification Report (f) DWPF = Defense Waste Processing Facility (g) LAW glasses Other abbreviations: A and VFT = Arrhenius and Vogel-Fulcher-Tammann viscosity coefficients, respectively, CCC and Q = crystallinity of canister-centerline-cooled and quenched glasses, respectively, CCC PCT and Q PCT = r_i ($i = B, Na, Li$) from canister-centerline-cooled and glasses, respectively, $G\bar{T}_L$ and $UT_L = T_L$ measured using gradient temperature and uniform temperature furnace methods, respectively, HT = heat-treated</p> | | | | |

INEEL CVS Phase 2 (Staples et al. 2000)

A test matrix of 37 glasses was developed (Edwards et al. 2000) and tested in Phase 2 to investigate property-composition relationships within the alkali borosilicate glass-composition region compatible with estimates of INTEC calcined compositions using a direct vitrification flowsheet and of HAW fractions proposed to be separated from dissolved calcine. A secondary objective of the Phase 2b test matrix was to investigate the composition boundaries of P_2O_5 , F, CaO, and Al_2O_3 .^(a) These glasses were characterized with respect to crystallinity of quenched and CCC glasses, PCT releases of quenched glasses, η , T_L , and density. T_M data are provided for all 37 glasses.

INEEL CVS Phase 3 (Scholes et al. 2000)

Phase 3 of the INEEL CVS focused on glass compositions that may be appropriate for either the INEEL separations/pretreatment scenario or the direct vitrification of calcined HLW. Through application of statistical techniques, a test matrix was defined to augment Phase 1 and 2 data with additional data points (Piepel et al. 2000). These glasses were characterized for crystallinity of quenched and CCC glasses, PCT releases of quenched glasses, η , T_L , and density. T_M data are provided for all 30 glasses.

2.2.2 Hanford CVS Investigations

This series includes the three stages of CVS performed within the Hanford Waste Vitrification Plant (HWVP) and PNNL Vitrification Technology Development (PVTD) programs in support of a future HLW vitrification plant at the Hanford site.

Hanford CVS 1 and 2 (Hrma et al. 1994)

The report presents two Composition Variation Study data sets, CVS-1 and -2. These studies were performed at PNNL for the Hanford HLW program. Property-composition relationships were obtained for 146 glasses in 5 statistically designed experimental phases. The properties measured include η , ϵ , glass transition temperature (T_g), thermal-expansion coefficients of solid glass and molten glass, crystallinity (quenched and CCC glasses), T_L , and durability based on normalized elemental releases from the Materials Characterization Center-1 28-day dissolution test (MCC-1) (quenched glasses) and the standard PCT (quenched and CCC glasses). Amorphous phase separation was also evaluated with transmission electron microscopy. The statistical experimental design strategy used in the CVS involved defining a glass-composition region expected to contain glasses that might be made from NCAW expected to be processed by the previously planned HWVP (scoping tests considering some additional waste types were also included), and then selecting specific compositions for study so as to appropriately cover this region. Ten glass components, SiO_2 , B_2O_3 , Na_2O , Li_2O , CaO, MgO, Fe_2O_3 , Al_2O_3 , ZrO_2 , and "Others" (the remaining waste constituents) were systematically varied in the study. The individual component concentrations contained in the "Others" component were separated and entered in the database. The compositions in the database are the target mass-fraction values with analyzed compositions for roughly half of the glasses.

(a) Before the test matrix for Phase 2b, scoping tests were performed in Phase 2a for 17 glasses (Edwards et al. 2000) of which results are not included in the current database but to be included in the future version.

Hanford CVS 3 (Vienna et al. 1996c)

This data set, CVS-3, covers a different glass composition region than CVS-1 and -2 to allow for higher-temperature-melting glasses with higher waste loadings to be produced. The properties measured include the viscosity-temperature relationship, T_g , ϵ , T_L , CCC crystallinity, and PCT from quenched and CCC glasses. This study varied glass components one-at-a-time from a boron-free alkali-aluminosilicate baseline glass while maintaining constant ratios of all other components. The components varied were SiO_2 , B_2O_3 , Na_2O , Li_2O , Fe_2O_3 , Al_2O_3 , ZrO_2 , Bi_2O_3 , UO_2 , P_2O_5 , and Others. The compositions in the database are the target mass-fraction values.

2.2.3 Liquidus Temperature Studies

These studies are specifically concentrated on the effect of glass compositions on the T_L of important crystalline phases, such as spinel and zirconium silicate, that can occur in the HLW glass melter during operation. The T_L models described in Section 3.4 are primarily based on the data from these studies.

TRU Study (Crum et al. 1997)

This study of glasses was based on a simulated transuranic waste with high concentrations of ZrO_2 and Bi_2O_3 to determine the composition dependence of primary crystalline phase and T_L . Starting from a baseline composition, glasses were formulated by changing one-at-a-time the mass fractions of Al_2O_3 , B_2O_3 , Bi_2O_3 , CeO_2 , Li_2O , Na_2O , P_2O_5 , SiO_2 , and ZrO_2 , while keeping the remaining components in the same relative proportions as in the baseline glass. The T_L values are given along with the corresponding primary crystalline phases, which were mostly zircon (ZrSiO_4) with some baddeleyite (ZrO_2) and cerium oxide.

SP (Mika et al. 1997)

This study was performed to measure the T_L of melts in the spinel primary phase field as a function of glass composition. The test glasses were based on high-iron Hanford tank wastes. A test matrix was designed containing 33 glasses with 10 components (Al_2O_3 , Cr_2O_3 , Fe_2O_3 , MgO , MnO , Na_2O , NiO , SiO_2 , B_2O_3 , and Li_2O) and Others. The test matrix was derived from the baseline glass containing 47 mass% water-washed Hanford nominal waste blend. The baseline composition was altered, one-component-at-a-time, while maintaining the same relative proportions of the remaining components. All glasses tested had spinel as the primary phase.

Zr Study (Vienna et al. 1999)

The objective of this study was to develop preliminary glass formulations for the HAW fraction of INEEL zirconia calcine and then to recommend a waste loading and frit composition for use in an INEEL scaled melter test. This study focused on the development of glass compositions with a high concentration of ZrO_2 because the estimated waste composition contained 92.58 wt% ZrO_2 . In 29 glass compositions tested, the concentrations of ZrO_2 , Al_2O_3 , B_2O_3 , and Li_2O were varied independently, and then the concentrations of SiO_2 and Na_2O were adjusted to maintain a calculated viscosity of 6 Pa·s at 1150°C. The PCT releases and T_L values with the corresponding primary crystalline phases are given. The primary phases identified in this study were mostly zircon (ZrSiO_4), baddeleyite (ZrO_2), and parakelydshite ($\text{Na}_2\text{ZrSi}_2\text{O}_7$).

MS (Hrma 1999; Wilson et al. 2001)

The goal of the study by Hrma (1999) was to develop a basic understanding of the dynamics of spinel formation and motion in velocity, temperature, and redox fields that are characteristic for the glass melting process. Nine glasses with different compositions (MS-1 to MS-9) were formulated and measured for T_L . In a subsequent study (Wilson et al. 2001), the glasses were formulated by increasing or decreasing concentrations of Al_2O_3 , Cr_2O_3 , Fe_2O_3 , Li_2O , MgO , Na_2O , or NiO , one-at-a-time, from a baseline composition (MS-7). The T_L data from this study were also included in this data set.

SG (Hrma et al. 1999)

A T_L versus composition study was performed for the DWPF. The main objective of the study was to decrease the uncertainty in T_L model predictions of glasses produced at SRS by developing a database for glass-composition effects on T_L . A series of 53 glass compositions was statistically designed to cover the DWPF composition region using a layered design approach (Edwards 1997). The test matrix contained glass compositions within and just outside the DWPF composition region. The components varied (in mass fractions in parentheses) were SiO_2 (0.43 to 0.59), B_2O_3 (0.05 to 0.10), Na_2O (0.06 to 0.11), Li_2O (0.03 to 0.06), Fe_2O_3 (0.06 to .015), Al_2O_3 (0.025 to 0.08), CaO (0.003 to 0.02), MgO (0.005 to 0.025), K_2O (0.015 to 0.038), U_3O_8 (0 to 0.055), MnO (0.01 to 0.03), NiO (0.001 to 0.02), TiO_2 (0.002 to 0.006), and Cr_2O_3 (0.001 to 0.003). The properties measured and reported included T_L with primary phases. Spinel was the primary phase for most of glasses while some glasses had clinopyroxene primary phase. The compositions of the glasses were confirmed by chemical analyses after the report was issued. Those analyzed compositions, although not currently included in the database, did not show any significant deviation from target values.

SP-3, SP×4, Misc. (Vienna et al. 2001)

This study compiled all the glasses in the spinel primary phase field including MS, SG and SP studies previously described to develop a new model that can accurately predict the T_L of spinel. This reference includes the results of further studies on the spinel crystallization, designated as SP-3 and SP×4. The SP-3 study expanded the SP series by five components, CaO , K_2O , RuO_2 , TiO_2 , and ZrO_2 , and the range of variation for SiO_2 , Li_2O , and Fe_2O_3 was increased. Another study was also performed to determine T_L in the spinel primary crystalline phase field. This study, designated as SP×4, was based on the original baseline glass SP-1 but varied four components-at-a-time while maintaining the concentrations of all other components in constant relative proportions. The four components varied were Al_2O_3 , Cr_2O_3 , Na_2O , and NiO , which were found to have the strongest impact on the T_L of those that were varied in the original study. A number of glasses that had been fabricated for different purposes or studies were grouped into the “Misc.” study and were used in T_L model validation.

2.2.4 Other Property-Composition Relation Studies

Composition vs. Properties Study (Chick et al. 1981)

The purpose of this study was to evaluate and refine the statistical methods used to produce the empirical property models. Ninety simplified waste glass compositions (102 glasses including replicates) within an 11-component oxide composition matrix were tested for crystallinity, η , and MCC-1 releases. The η at 1250°C data and the results of crystallinity observations on quenched and CCC treated glasses were entered in the database.

WV HLW Formulation Study (Chick et al. 1984)

This report describes the statistically designed study performed at PNNL to develop the glass composition recommended for the vitrification of HLW stored at West Valley, New York. This study assessed the effects of seven oxide components (SiO_2 , B_2O_3 , CaO , Fe_2O_3 , Al_2O_3 , Na_2O , and waste mix) on glass properties. Over 100 melts combining the seven components into a wide variety of compositions were tested for η , ϵ , thermal expansion, crystallinity, and MCC-1 releases. The estimated temperatures at 10 Pa·s and 3 Pa·s and the results of crystallinity observation on quenched, CCC treated, and heat-treated glasses were recorded in the database.

HWVP 85 (Bates 1985)

This report describes the result of development of a reference glass composition for the HWVP. The reference glass composition developed from this study was designated HW39 and characterized for melt η , ϵ , and density.

WV Glasses by CUA and PNL (Johnston et al. 1990)^(a)

This report describes the development of a database of PCT leach test results. The compositional and leach data pertinent to West Valley waste forms from the Catholic University of America (CUA) and PNNL were gathered to compare the free energy of hydration model with several empirical models that predict boron releases from chemical composition. The data from PNNL were included in another data set (Reimus et al. 1988) and so were excluded in this data set. The CUA PCT data, which were entered in the database, were those transferred to PNNL via diskettes at the time of this study.

WVDP Support (Olson 1993 and 1994)

These data are from two studies conducted as part of glass-composition variability testing under the PNNL West Valley Support Program to support establishment of a glass composition control strategy by West Valley Nuclear Services (WVNS). The results of PCT releases for 20 glasses (PNL series, Alkali series) were reported in Olson (1993) while the results of viscosity measurement for the same 20 glasses and 10 more glasses of the Ratio series are reported in Olson (1994). The PCT releases and η at T data from this data set were entered in the database. The viscosity data for 10 glasses of the Ratio series were entered as part of another data set, "West Valley WQR" (WVNS 1995), which contained also the PCT data along with other West Valley waste-form qualification glasses.

West Valley CVS Glasses PCT (Olson et al. 1994)

To assist WVDP, the PCT method was used to evaluate 44 West Valley glasses. These glasses were fabricated as sets of Compositional Variation Glasses for studies performed by the West Valley Support Task (WVST) at PNNL and were initially tested using a modified MCC-3 test method. The glasses were retested using the PCT method after WAPS included the PCT in an acceptance specification.

Glass Dissolution Chemistry (Ramsey 1995)

This data set includes glasses from a statistically designed study of a 6-component (SiO_2 , Al_2O_3 , B_2O_3 , Fe_2O_3 , CaO , and Na_2O) glass composition region, which was intended to include alkali borosilicate glasses that successfully encapsulate the high-level defense wastes. The analyzed compositions in the database contain the concentrations of iron oxides in both FeO and Fe_2O_3 , which were calculated from the result of glass redox analysis. PCT releases in elemental leachate concentrations given in the reference

(a) The Johnston et al. 1990 report is the only (incomplete) source available to us for CUA data.

were converted to normalized releases and entered in the database. Oksoy et al. (1994) used this data set to perform a study on the canonical correlation of glass compositions and PCT releases.

West Valley WQR (West Valley Nuclear Services 1995)

WVNS developed a data set consisting of 58 glass compositions. These data were used to develop PCT release models for use in WVDP, a high-level nuclear waste glass facility. The 58 glasses were selected to evenly cover a glass-composition region centered on the WVDP target glass composition with the boundary taken to be three times the expected process variation. Only nine components known to influence PCT releases were varied in these glasses, and the composition data were provided based on these nine components. The full composition data entered in the database were those found in Piepel et al. (1996). Out of 58 glasses given in this report, 10 glasses of the alkali series (Alkali1 to Ref6Qtr2) were already included in data set of “WVDP Support” (Olson 1993 and 1994) and were not included in this data set. The viscosity data for 10 glasses of the Ratio series (Ratio2 to PNL190) were from Olson (1994).

DWPF PCT Model (Jantzen et al. 1995)

This study was conducted to develop the Thermodynamic Hydration Energy Reaction Model (THERMO) to predict glass PCT releases from glass composition based on the estimated glass hydration free energy. The THERMO is being used in DWPF to assess product consistency and quality. The result of this study was registered as a U.S. patent (Jantzen et al. 1998). The glasses examined in this study were fabricated under a variety of laboratory and pilot-scale conditions by various researchers and vendors. The target compositions and PCT data entered in the database were those supplied by SRTC to PNNL in electronic data form. The analyzed compositions are from the SRTC report (Jantzen et al. 1995), which is not yet publicly available. PCT releases were converted to g/m^2 from g/L reported.

Plutonium Vitrification (Bulkley and Vienna 1997)

The objective of this study was to examine how variations in the waste-stream compositions would affect the key properties of glasses for immobilization of plutonium-bearing materials at Rocky Flats Environmental Technology Site (RFETS), Hanford, and other DOE sites. A one-component-at-a-time change matrix was designed. The glasses were tested for viscosity and PCT releases. The published reference (Bulkley and Vienna 1997) contains only a part of the data, the temperature at 5 Pa·s, and PCT releases for B and Na, whereas the database contains all the data obtained during this study, including viscosity-at-temperature, Arrhenius coefficients for viscosity, PCT releases for Li and Si, and final pH from PCT. The database also contains 9 more glasses with different or replicate compositions that were not included in the reference.

2.2.5 LLW Formulation Studies

TWRS LAW Formulation (Muller and Pegg 1998)

This report presented the results of glass-formulation development with Tank Waste Remediation System (TWRS) LAW simulants during TWRS Phase I, Part A. Glasses were formulated based on the LAW Envelope A, B, and C composition specifications provided by the TWRS contract. After specific glass formulation design parameters were identified, glasses were formulated on the basis of previous experience with the objective of meeting the constraints imposed on those parameters and characterized with respect to T_L , η , ε , and PCT releases. It should be noted that the measurement of PCT releases was conducted at 20°C instead of standard 90°C used in HLW glasses. The T_L , η at T , ρ , 20°C PCT releases

of quenched glasses, and TCLP results were entered in the database. The T_L data were given as “greater or less than a reference temperature” without information on the primary phase.

TWRS LAW Formulation 2 (Ferrara et al. 1998)

This study characterized three LAW glasses produced from Hanford radioactive waste samples as part of a demonstration for BNFL. The three LAW glasses were produced from radioactive supernate samples that had been treated to remove most of the radionuclides. The TCLP results and PCT releases of quenched glasses are recorded in the database.

3.0 Interim Property-Composition Models

This section discusses the interim property-composition models developed for Hanford HLW glasses and the portions of the database (discussed in Section 2.0) used to develop the models.

3.1 Initial Data Evaluation and Screening

The initial database available for developing the property-composition models (see Section 2.0) contained data from 1570 glass compositions expressed in terms of 61 components. However, 4 of the glasses did not have composition information. These 4 glasses were therefore removed from the modeling process, leaving 1566 usable glasses.^(a) The compositions of the 1566 glasses were converted from mass fractions to mol fractions of oxides and halogens, except for those glasses whose mol fraction compositions were available and included in the database. The target (or as batched) compositions were used for most glasses. For those glasses without target compositions, analyzed compositions were used. The 1566 glasses were graphically analyzed and assessed based on subject-matter knowledge to select the components and initial subset of data to be used for developing property-composition models. The methods used to assess the data and the resulting description of components and data points (glass compositions) initially used to develop property-composition models are discussed in this section.

3.1.1 Initial Component Screening

Data plots (Minitab 2000) were produced to display and assess the range and distribution of mol-fraction values for each of 61 glass components contained in the database. A glass component was selected for possible inclusion in property-composition models only if it had a sufficient range of mol fractions and a sufficient distribution of mol-fraction values within the range.^(b) After the initial database evaluation in terms of the 61 components, the oxides of some components were combined as follows:

$$\begin{aligned} \text{UO}_x &= \text{UO}_3 + \text{UO}_2 + 3\text{U}_3\text{O}_8 \\ \text{MnO}_x &= \text{MnO} + \text{MnO}_2 \\ \text{LN}_2\text{O}_3 &= 0.5\text{CeO}_2 + \text{Ce}_2\text{O}_3 + \text{Eu}_2\text{O}_3 + \text{Gd}_2\text{O}_3 + \text{La}_2\text{O}_3 + \text{Nd}_2\text{O}_3 + \text{Pr}_2\text{O}_3 + 3\text{Pr}_6\text{O}_{11} + \text{Sm}_2\text{O}_3 + \text{Y}_2\text{O}_3 \end{aligned} \quad (3.1)$$

The combined components (UO_x , MnO_x , and LN_2O_3) were formed because the constituent components often did not have sufficient ranges or distributions to support separate terms in property-composition models. The UO_x and MnO_x components combine components involving the same metal,^(c) whereas the LN_2O_3 component combines all of the lanthanide components (which are expected to have

-
- (a) The compositions of these four glasses were discovered and subsequently included in an updated version of the database after the interim property models were developed.
- (b) What was considered a sufficient range was dependent on the component. The distribution of values within a range was considered sufficient if most of the values were not clustered in a small sub-range.
- (c) It is assumed that all glasses were equilibrated with air during melting or heat-treatment and thus the proportions of valence states of multivalent oxides are uniquely determined for each glass by the temperature at which the glass has been equilibrated with the partial pressure of oxygen of 2.13×10^4 Pa. However, this proportion is rarely determined experimentally. The oxides are listed in databases as a certain nominal valency that may (Fe_2O_3) or may not (MnO_2) represent the dominant valence state of that oxide in glass.

similar effects on glass properties). The FeO and Fe₂O₃ components were not combined because the vast majority of the data points in the database did not have separate determinations of FeO and Fe₂O₃. FeO had a zero value for the vast majority of glasses in the database, and so only Fe₂O₃ was used as a component.

After forming the combined components, the 1566 glass compositions were re-expressed as normalized mol fractions of 49 components ($61 - 15 + 3 = 49$). The database-evaluation process identified 20 of these 49 components as having sufficient ranges and distributions of values within the ranges to consider including them in property-composition models. These 20 components were Al₂O₃, B₂O₃, CaO, Cr₂O₃, F, Fe₂O₃, K₂O, Li₂O, LN₂O₃, MgO, MnO_x, Na₂O, NiO, P₂O₅, SiO₂, ThO₂, TiO₂, UO_x, ZnO, and ZrO₂. Note that the three combined components, UO_x, MnO_x, and LN₂O₃ from (3.1), are included in the list of 20 components. In selecting the 20 components, no consideration was given to whether the components were known or expected to influence one or more glass properties. Also, no consideration was given to whether compositions had values for a given property. Such considerations were left to the model development effort for each property.

Table 3.1 lists the 61 glass components contained in the database, along with minimum and maximum component values (in the “Original Range” column) over the entire set of 1566 usable glass compositions. An “X” in the column labeled “Sufficient Range” indicates that the component had an adequate range to be included in the model-building process. Components marked with “(X)” were included in one of the combined components. The “Restricted Range” column contains the minimum and maximum component values after the initial filtering of the data set described in Section 3.1.2.

Table 3.1. Summary of Component Ranges and Initial Component Screening

| Component | Original Range | | Sufficient Range for Modeling | Restricted Range (After Filters from Table 3.2) | |
|--------------------------------|----------------|----------|----------------------------------|--|----------|
| | Minimum | Maximum | | Minimum | Maximum |
| Al ₂ O ₃ | 0 | 0.183502 | X | 0.00119 | 0.161 |
| B ₂ O ₃ | 0 | 0.2466 | X | 0.009761 | 0.196727 |
| K ₂ O | 0 | 0.333316 | X | 0 | 0.099857 |
| Li ₂ O | 0 | 0.497582 | X | 0 | 0.200593 |
| Na ₂ O | 0 | 0.421649 | X | 0.036245 | 0.391913 |
| P ₂ O ₅ | 0 | 0.06802 | X | 0 | 0.015952 |
| SiO ₂ | 0 | 0.88662 | X | 0.362322 | 0.675968 |
| ZrO ₂ | 0 | 0.095745 | X | 0 | 0.090803 |
| CaO | 0 | 0.534198 | X | 0 | 0.12011 |
| F | 0 | 0.267694 | X | 0 | 0.02984 |
| Fe ₂ O ₃ | 0 | 0.144226 | X | 0 | 0.116849 |
| FeO | 0 | 0.566733 | | 0 | 0 |
| NiO | 0 | 0.058275 | X | 0 | 0.034 |
| MoO ₃ | 0 | 0.008829 | | 0 | 0.0034 |
| SrO | 0 | 0.369823 | | 0 | 0.003637 |
| TiO ₂ | 0 | 0.100003 | X | 0 | 0.039 |
| Ag ₂ O | 0 | 0.000497 | | 0 | 0.000497 |
| As ₂ O ₃ | 0 | 0.00034 | | 0 | 0.00034 |

Table 3.1 (Contd)

| Component | Original Range | | Sufficient Range for Modeling | Restricted Range (After Filters from Table 3.2) | |
|---------------------------------|----------------|----------|----------------------------------|--|----------|
| | Minimum | Maximum | | Minimum | Maximum |
| BaO | 0 | 0.281539 | | 0 | 0.004781 |
| Bi ₂ O ₃ | 0 | 0.028188 | | 0 | 0.009595 |
| CdO | 0 | 0.007197 | | 0 | 0.007074 |
| CeO ₂ | 0 | 0.0258 | (X) | 0 | 0.0258 |
| Ce ₂ O ₃ | 0 | 0.005601 | (X) | 0 | 0.004133 |
| Cl | 0 | 0.018317 | | 0 | 0.013722 |
| Co ₂ O ₃ | 0 | 0.010269 | | 0 | 0.0007 |
| Cr ₂ O ₃ | 0 | 0.036 | X | 0 | 0.015 |
| Cs ₂ O | 0 | 0.333379 | | 0 | 0.0027 |
| CuO | 0 | 0.049626 | | 0 | 0.005401 |
| Eu ₂ O ₃ | 0 | 0.0086 | (X) | 0 | 0.0086 |
| Gd ₂ O ₃ | 0 | 0.0123 | (X) | 0 | 0.0123 |
| I | 0 | 1.46E-05 | | 0 | 1.42E-05 |
| La ₂ O ₃ | 0 | 0.012588 | (X) | 0 | 0.012588 |
| MgO | 0 | 0.598517 | X | 0 | 0.129695 |
| MnO | 0 | 0.038564 | (X) | 0 | 0.038564 |
| MnO ₂ | 0 | 0.037368 | (X) | 0 | 0.037368 |
| Nb ₃ O ₅ | 0 | 4.4E-05 | | 0 | 0.000044 |
| Nd ₂ O ₃ | 0 | 0.01964 | (X) | 0 | 0.012427 |
| PbO | 0 | 0.0323 | | 0 | 0.0035 |
| PdO | 0 | 0.000786 | | 0 | 0.000758 |
| PdO ₂ | 0 | 5.26E-05 | | 0 | 5.26E-05 |
| Pr ₂ O ₃ | 0 | 5.73E-06 | (X) | 0 | 5.3E-06 |
| Pr ₆ O ₁₁ | 0 | 0.000121 | (X) | 0 | 0.000121 |
| Rb ₂ O | 0 | 0.33333 | | 0 | 0.000326 |
| ReO ₂ | 0 | 0.000239 | | 0 | 0.000239 |
| Rh ₂ O ₃ | 0 | 0.000244 | | 0 | 0.00024 |
| RhO ₂ | 0 | 0.000106 | | 0 | 0.000106 |
| RuO ₂ | 0 | 0.001391 | | 0 | 0.001367 |
| Sb ₂ O ₃ | 0 | 0.000608 | | 0 | 0.000608 |
| SeO ₂ | 0 | 0.002043 | | 0 | 0.002014 |
| Sm ₂ O ₃ | 0 | 0.0087 | (X) | 0 | 0.0087 |
| SnO ₂ | 0 | 0.031 | | 0 | 0.000296 |
| SO ₃ | 0 | 0.758236 | | 0 | 0.009553 |
| TeO ₂ | 0 | 0.001922 | | 0 | 0.00046 |
| Y ₂ O ₃ | 0 | 0.009093 | (X) | 0 | 0.009093 |
| ThO ₂ | 0 | 0.019971 | X | 0 | 0.016678 |
| UO ₃ | 0 | 0.018952 | (X) | 0 | 0.018952 |
| UO ₂ | 0 | 0.01571 | (X) | 0 | 0.01571 |
| U ₃ O ₈ | 0 | 0.013961 | (X) | 0 | 0.004747 |
| V ₂ O ₃ | 0 | 3.76E-06 | | 0 | 0 |
| WO ₃ | 0 | 0.000575 | | 0 | 0.000359 |
| ZnO | 0 | 0.082636 | X | 0 | 0.062 |

3.1.2 Initial Glass Screening

After the 20 components were selected, several compositional filters were developed to screen data for the initial subset of the composition portion of the database to be used for modeling. In some cases, all data from certain studies in the database were excluded as not representative of glass compositions appropriate for Hanford HLW. In other cases, only certain glass compositions from a study were excluded as not being applicable for Hanford HLW. Finally, certain compositions were excluded because they had one or more components with values too far from the main distribution of component values. Compositions with such outlying component values can be very influential in developing property-composition models. It is not desirable to have coefficients in an empirical or semi-empirical model determined by, or highly influenced by, one or even a few outlying data points. The database filters and the corresponding reasons are summarized in Table 3.2. The filters in Table 3.2 are based only on applicability of data to the Hanford HLW situation and elimination of outlying data. Additional filters were applied on a property-by-property basis for other reasons, as discussed in subsequent sections discussing the model development process for each property.

Before applying the filters summarized in Table 3.2, the database contained information for 1566 compositions. The filters eliminated 742 compositions, leaving 824 glasses as the initial set for use in developing property-composition models. The minimum and maximum component values after applying the filters listed in Table 3.2 are summarized in the “Restricted Range” column of Table 3.1. However, not all 824 of the remaining compositions had values for a given property. More specific information about the initial and final data sets used to develop the model for each property is provided in the following sections.

After first filtering the glass compositions, and then deciding on using 20 components for initial modeling efforts, the compositions were renormalized to sum to one over those components. Thus, each of the property models discussed hereafter begin their development using this reduced data set having 20 components and 824 normalized glass compositions.

3.2 Models for PCT Normalized Releases of B, Li, and Na

This section describes how interim property-composition models were developed for the natural logarithms of normalized releases of B, Li, and Na from PCT. The normalized elemental releases are denoted r_i ($i = \text{B, Li, and Na}$), and are expressed in units of g/m^2 . Models were developed for r_B , r_{Li} , and r_{Na} because those are the three elements included in Specification 1.3 of the WAPS (DOE 1996). This section also discusses the subsets of the 824 glasses described in Section 3.1.2 that were used to develop the PCT models.

Table 3.2. Filters Applied to the Database to Select the Initial Subset for Property-Composition Modeling (concentrations in mole fractions)

| Filter No. | Filter of Compositions Deleted (component values in mol fractions) | Reason |
|------------|--|---|
| 1 | SRC-Ce-1, SRC-Ce-4, SRC-Gd-1, SRC-Gd-4 from Plutonium Vitrification Study | No compositions in database |
| 2 | GLA 78-9-11, GLA 78-9-15, GLA 78-9-18 from INEL DZr Process Demonstration Study | Mol fractions sum not close enough to 1 |
| 3 | Johnston et al. (1990) | BaO, CaO, and MgO were combined into a single component “AEO” (information on BaO, CaO, and MgO concentrations was not available at the time of model fitting). |
| 4 | $Al_2O_3 < 0.0001$ | Only glasses containing Al_2O_3 of interest |
| 5 | $B_2O_3 < 0.0084$ | Only glasses containing B_2O_3 of interest |
| 6 | $B_2O_3 > 0.20$ | Glasses with very high B_2O_3 not of interest |
| 7 | Sasek (1977) | Simple 1–4 component glasses |
| 8 | Bottinga (1972) | Simple 1–4 component glasses |
| 9 | $Na_2O < 0.036$ | Glasses with very low Na_2O not of interest |
| 10 | $P_2O_5 > 0.016$ | To avoid multi-phase glasses |
| 11 | $SiO_2 < 0.36$ | Glasses with no or very low SiO_2 not of interest |
| 12 | $SiO_2 > 0.68$ | Glasses with very high SiO_2 not of interest |
| 13 | $CaO > 0.1202$ | Glasses with higher CaO not of interest |
| 14 | $F > 0.03$ | Glasses with high $F > 0.03$ phase separated |
| 15 | $FeO > 0$ | Very few glasses with $FeO > 0$ |
| 16 | $MoO_3 > 0.005$ | Glasses with high $MoO_3 > 0.005$ phase separated |
| 17 | $SrO > 0.03$ | Very few glasses, not of interest |
| 18 | $TiO_2 > 0.04$ | Small number of glasses with $TiO_2 > 0.04$ |
| 19 | $Bi_2O_3 > 0.01$ | Very few glasses with $Bi_2O_3 > 0.01$ |
| 20 | $Cr_2O_3 > 0.015$ | To avoid glass with high T_L |
| 21 | $Cs_2O > 0.005$ | Very few glasses, not of interest |
| 22 | $CuO > 0.01$ | Very few glasses, not of interest |
| 23 | $MgO > 0.1325$ | Small number of such glasses, not of interest |
| 24 | $PbO > 0.01$ | Very few glasses, not of interest |
| 25 | $Rb_2O > 0.01$ | Very few glasses, not of interest |
| 26 | $SnO_2 > 0.005$ | Very few glasses, not of interest |
| 27 | $SO_3 > 0.01$ | Small number of such glasses, not of interest |
| 28 | CU49 from CUA Data Study, Envelope D from TWRS HLW Formulation Study, 5% Ba glass from the HWVP Comp. Variability Scoping Tests Study. | Extreme component values based on data plots |

3.2.1 General Form of the PCT Models

The general form of the PCT models for r_B , r_{Li} , and r_{Na} can be written as

$$\ln(r_i) = \sum_{j=1}^N b_{ij} x_j \quad (3.2)$$

where r_i is as defined in Section 3.2, x_j is the j -th component mol fraction, b_{ij} is the j -th component coefficient for i -th element, and N is the number of components used in the model. These models are linear mixture models (Cornell 1990) of the form of Equation (1.4). According to Equation (1.2), the N components selected must be normalized to sum to one before the least-squares regression. Such normalization corresponds to the assumption that the property depends only on the relative proportions (mol fractions) of the N selected components (Cornell 1990). Including components in the model that have little or no impact on PCT response will not improve the fit, whereas omitting components that do impact PCT response will degrade the fit of the model.

The natural logarithm transformation of PCT normalized elemental releases is used for several reasons. First, experience has shown that linear mixture and other mixture model forms fit PCT release data better after a logarithmic transformation. Second, ordinary least-squares regression requires that the experimental error variance be the same for all data points. However, this requirement is not directly met for PCT normalized releases, which can vary over one to two orders of magnitude in many PCT-composition data sets. Experimental error variances tend to increase proportionally to the magnitude of the PCT normalized elemental release. Logarithm transformations of such data stabilize (make constant) the experimental error variances. Third, the natural logarithm is used rather than the common logarithm because of the strong approximate relationship

$$SD[\ln(y)] \approx RSD(y) \quad (3.3)$$

where $y = r_i$ ($i = B, Li, \text{ or } Na$). Hence, a standard deviation (SD) of $\ln(r_i)$ is essentially equal to the relative standard deviation (RSD) of r_i . This relationship only holds for the natural logarithm and is very useful in interpreting models fitted to data.

Because the normalized elemental releases in the database are expressed in g/m^2 units, predictions from a model of the form Equation (3.2) are in $\ln(\text{g/m}^2)$ units. Thus, the exponential transformation converts the logarithmic predicted values back to g/m^2 units.

3.2.2 Screening Glasses for PCT Modeling

Of the 824 glasses that remained in the data set following the initial screening described in Section 3.1.2, many did not have PCT data. Of the initial 824 glasses, 432 had r_B data, 406 had r_{Li} data, and 441 had r_{Na} data. Before conducting PCT modeling, some additional glasses were removed from the data set because they exhibited characteristics that are considered undesirable for PCT modeling. The glasses removed from the data set are discussed in the following paragraphs.

Glasses identified in the database as multi-phase^(a) were removed because PCT behavior for such glasses can be significantly different than for single-phase glasses. However, it is extremely important to note that most of the glasses in the database did not have information indicating whether they were single-phase or multi-phase. Hence, some multi-phase glasses could remain in the subsets of glasses used to develop PCT models. The presence of such glasses could degrade the fits of PCT models to the data, potentially resulting in biased predictions or predictions with increased uncertainty (imprecision).

Glasses with high PCT release values (specifically, $r_B > 20 \text{ g/m}^2$) were also deleted from the data set used to develop PCT models. These data were removed to address concerns that glasses with higher PCT releases could degrade predictive performance of models for glasses with lower releases (which are of primary interest for use with the models).

A summary of the PCT-specific data screening is given in Table 3.3. The Xs in Table 3.3 indicate glasses that were deleted from the PCT model-development process for the specified elements based on the reasons listed. Having deleted the glasses mentioned in Table 3.3 from the data set, there were 420 glasses available for r_B modeling, 400 glasses available for r_{Li} modeling, and 429 glasses available for r_{Na} modeling.

Table 3.3. Glasses Deleted During Screening for PCT Model Development

| Glass | Study | Deleted for PCT | | | Reason |
|--|----------------------------|-----------------|-----|----|-------------|
| | | B | Li | Na | |
| IG2-06 | INEL CVS | X | X | X | Multi-phase |
| IG1-31 | INEL CVS | X | X | X | Multi-phase |
| IG1-36 | INEL CVS | X | X | X | Multi-phase |
| HTB825 | Waste-Loading Maximization | X | (a) | X | Multi-phase |
| IG1-13 | INEL CVS | X | X | X | $r_B > 20$ |
| CVS2-82 | Second Hanford CVS | X | X | X | $r_B > 20$ |
| CVS2-83 | Second Hanford CVS | X | X | X | $r_B > 20$ |
| 7 | Ramsey | X | (a) | X | $r_B > 20$ |
| 9 | Ramsey | X | (a) | X | $r_B > 20$ |
| 18 | Ramsey | X | (a) | X | $r_B > 20$ |
| MG-9 | DWPF | X | (a) | X | $r_B > 20$ |
| MG-18 | DWPF | X | (a) | X | $r_B > 20$ |
| (a) Glasses that were not included in PCT modeling for a specified element because the glass did not contain the indicated oxide, thus no PCT release data could be generated. | | | | | |

3.2.3 Component Screening for PCT Modeling

The PCT modeling began with the 20 components retained after the initial screening discussed in Section 3.1.1. Recall that the 20 components were selected because the database provides support for including them in property-composition models, not because they necessarily influence one or more glass

(a) Glasses were considered to be multi-phase if any of the three columns in the database relating to homogeneity had a negative indication.

properties (including PCT). Also, the initial selection of the 20 components did not account for whether the glasses actually had r_B , r_{Li} , or r_{Na} values. Statistical least-squares regression techniques appropriate for mixture-experiment models (Cornell 1990) were applied to fit 20-component models of the form (3.2) for $\ln(r_B)$, $\ln(r_{Li})$, and $\ln(r_{Na})$. Then, other mixture-experiment methods were used to identify components that 1) did not have adequate support in the data for inclusion or 2) on average had little effect on PCT behavior. These methods were used to develop models of the form Equation (3.2) with fewer than 20 components.

Piepel (1982), Cornell (1990), and Piepel and Redgate (1997) discuss statistical mixture-experiment methods to identify mixture components that: 1) do not affect a response or property or 2) have essentially the same effect on a response or property. However, the short deadline for this work did not allow such a complete, structured analysis of component effects on $\ln(r_i)$. Rather, we relied on the methods described below. While some of these methods are not statistically rigorous, they are related to rigorous methods. Also, a rigorous statistical method to assess model reductions was employed, as is subsequently discussed.

In mixture-model settings such as this study, the effect of a component cannot be completely assessed by comparing the fitted coefficient to the coefficient's standard deviation (e.g., via a t-test) as discussed by Cornell (1990). However, comparing a component coefficient to its standard deviation can still be useful as an indicator of the uncertainty associated with the coefficient. Components having coefficients less than 1.5 to 2 times the magnitude of their standard deviations typically do not strongly affect the property of interest.^(a) Such considerations were taken into account as components were screened.

The coefficient for each component was also compared to the average property [i.e., $\ln(r_i)$] value. Components whose coefficients are close to the average property value may be considered as having a less-important effect on a property than components whose coefficients are farther from the average property value. Components that exhibit negligible or less-important effects are candidates to be dropped from the model.

One goal of regression analysis is to obtain a parsimonious model, one that provides an adequate fit to the data, but at the same time is as simple as possible. Using the methods described in the previous paragraph, glass components to be deleted from subsequent models were identified. Models with 15 and 12 components were considered following consideration of the 20-component models. Each time a model of the form (3.2) with fewer components was considered, the compositions were renormalized to sum to one based on the components included in the model.

Table 3.4 indicates which components were included in the 20-, 15-, and 12-component PCT models. Summary statistics from the regression analysis for each of these models are also presented in Table 3.4. The coefficients and standard errors of the coefficients for the 12-component models for $\ln(r_B)$, $\ln(r_{Li})$, and $\ln(r_{Na})$ are presented and discussed later in this section. The coefficients are not provided for the 20-component and 15-component PCT models because of the accelerated, concurrent process used to reduce the number of components at the same time the data assessment was being performed. For example,

(a) This conclusion is based on experience of one of the authors in applying statistical mixture experiment methods for calculating and testing the significance of component effects. These methods are time consuming to apply, and so it proves helpful to have experience-based rules such as this for making faster determinations of the likely significance of a component's effect.

roughly only one-fourth of the 1566 glasses used to select the 20 components for consideration in developing property-composition models survived the filtering process and had r_i values. Hence, the data actually available to fit models did not adequately support the inclusion of some of the 20 components. Also, regression diagnostics and residual plots produced by the regression software employed (Minitab 2000) were used to identify outlying or influential data points as the number of components in models was reduced. Reducing the number of components as well as many glasses not having PCT release values made it necessary to re-assess whether the remaining data points had sufficient ranges and did not involve outlying data points, which could be very influential in regression modeling. Hence, the 20-component and 15-component models may have been affected by poor composition-region support, or by outlying or influential data points. Thus, the coefficients of those models are not reported in Table 3.4.

The definitions of the R^2 , $R^2(\text{adjusted})$, and $R^2(\text{predicted})$ statistics in Table 3.4 are given in the following equations

$$R^2 = 1 - \frac{\sum_{i=1}^n (\hat{y}_i - y_i)^2}{\sum_{i=1}^n (y_i - \bar{y})^2}$$

$$R^2(\text{adjusted}) = 1 - \frac{\sum_{i=1}^n (\hat{y}_i - y_i)^2 / (n - p)}{\sum_{i=1}^n (y_i - \bar{y})^2 / (n - 1)}$$

$$R^2(\text{predicted}) = 1 - \frac{\sum_{i=1}^n (\hat{y}_{(i)} - y_i)^2}{\sum_{i=1}^n (y_i - \bar{y})^2},$$

where n denotes the number of data points used to fit a model, p denotes the number of model parameters estimated from the data, y_i denotes the measured property value for the i -th data point, \bar{y} denotes the average of the y_i ($i = 1, 2, \dots, n$) values, \hat{y}_i denotes the predicted property value for the i -th data point, and $\hat{y}_{(i)}$ denotes the predicted property value for the i -th data point without using the i -th data point to fit the model.

The R^2 and $R^2(\text{adjusted})$ statistics are two measures of the proportion of variation in property values [$\ln(r_i)$ in this case] over a data set accounted for by a model. Hence, these two statistics must be between zero and one. $R^2(\text{predicted})$ is obtained by comparing predicted property values for each data point, with and without each data point used to determine the prediction. $R^2(\text{predicted})$ must be less than 1, but can be negative if one or more data points are highly influential. Generally, $R^2 > R^2(\text{adjusted}) > R^2(\text{predicted})$. A difference larger than about 0.03 to 0.05 between R^2 and $R^2(\text{adjusted})$ indicates the model may contain some unneeded terms, while a difference of that magnitude or larger between $R^2(\text{adjusted})$ and $R^2(\text{predicted})$ suggests there is one or more highly influential data points (which should be investigated).

Table 3.4. Summary Statistics for Preliminary PCT Model Regression Analyses

| Component | Model | | |
|---|--------------------|--------------------|--------------------|
| | 20-Component | 15-Component | 12-Component |
| Al ₂ O ₃ | X | X | X |
| B ₂ O ₃ | X | X | X |
| CaO | X | X | X |
| Cr ₂ O ₃ | X | | |
| F | X | X | |
| Fe ₂ O ₃ | X | X | X |
| K ₂ O | X | X | X |
| Li ₂ O | X | X | X |
| LN ₂ O ₃ | X | X | |
| MgO | X | X | X |
| MnO _x | X | X | X |
| Na ₂ O | X | X | X |
| NiO | X | | |
| P ₂ O ₅ | X | X | X |
| SiO ₂ | X | X | X |
| ThO ₂ | X | | |
| TiO ₂ | X | X | |
| UO _x | X | | |
| ZnO | X | | |
| ZrO ₂ | X | X | X |
| ln(<i>r_B</i>) Model Statistics | | | |
| Number of Glasses | 409 ^(a) | 386 ^(a) | 391 ^(a) |
| R ² | 0.757 | 0.821 | 0.814 |
| R ² (Adjusted) | 0.745 | 0.814 | 0.808 |
| R ² (Predicted) | 0.711 | 0.800 | 0.798 |
| s (RMSE) | 0.6658 | 0.5471 | 0.531 |
| ln(<i>r_{Li}</i>) Model Statistics | | | |
| Number of Glasses | 389 | 374 | 380 |
| R ² | 0.776 | 0.802 | 0.797 |
| R ² (Adjusted) | 0.764 | 0.794 | 0.791 |
| R ² (Predicted) | 0.741 | 0.778 | 0.779 |
| s (RMSE) | 0.5133 | 0.4768 | 0.4675 |
| ln(<i>r_{Na}</i>) Model Statistics | | | |
| Number of Glasses | 409 | 386 | 390 |
| R ² | 0.747 | 0.815 | 0.824 |
| R ² (Adjusted) | 0.735 | 0.808 | 0.819 |
| R ² (Predicted) | 0.696 | 0.793 | 0.809 |
| s (RMSE) | 0.6288 | 0.5017 | 0.4754 |

(a) After all models were initially fitted, errors in the PCT r_B , r_{Li} , and r_{Na} values for the Bulkley and Vienna (1997) study glasses contained in the compiled database were detected and corrected. Also, it was detected that data points for a few glasses having r_{Li} and/or r_{Na} values but not r_B values were accidentally deleted in the data screening process. Only the 12-component models were refitted using the corrected data, which explains why: (i) the numbers of data points for 20 components are smaller than mentioned previously in the text, and (ii) the number of data points for 12 components is larger than the number for 15 components. The model goodness-of-fit statistics changed very little for the 12-component models, so it is assumed that the goodness-of-fit statistics for the 20-component and 15-component models would also have changed very little if those models had been refitted.

Root mean squared error (MSE) in Table 3.4 refers to the square root of the MSE from the regression analysis. Because PCT models are fitted to natural logarithms of normalized releases, the “root MSE” (RMSE) statistic can be interpreted as a relative standard deviation of normalized release (i.e., without the natural logarithm) per Equation (3.3). RMSE values for $\ln(r_i)$ models larger than the r_i RSDs associated with making a glass and performing the PCT indicates a potential model lack-of-fit (because the property variation accounted for by the model is larger than what can be explained by experimental and measurement variation in making glasses and performing PCTs).

The numbers of glasses used to develop the models summarized in Table 3.4 indicate that additional glasses were deleted from the modeling when changing from the 20-component model to the 15-component model and then to the 12-component model. Table 3.5 lists the additional glasses deleted for the 15-component PCT modeling. Table 3.6 lists the glasses deleted for the 12-component PCT modeling. The Xs in Tables 3.5 and 3.6 indicate glasses that were deleted from the PCT modeling for the specified elements based on the reasons listed. The preliminary diagnostic techniques employed to identify outlying and influential data points included residual plots, normal probability plots, and predicted-versus-measured plots. Because the details of these statistical methods are not critical to the discussion, they are not discussed further here. The interested reader is referred to Draper and Smith (1998) or Montgomery and Peck (1992) for additional information about these methods.

3.2.4 The Final PCT Models

The final PCT models are the 12-component models described in Table 3.4. The components included in the final models were Al_2O_3 , B_2O_3 , CaO , Fe_2O_3 , K_2O , Li_2O , MgO , MnO_x , Na_2O , P_2O_5 , SiO_2 , and ZrO_2 . Table 3.7 lists the coefficients for the 12 components of the final PCT models, their respective standard deviations, the number of data points used to fit the models, and the model fit statistics (repeated from Table 3.4). The numbers of data points used to fit the $\ln(r_B)$, $\ln(r_{Li})$, and $\ln(r_{Na})$ models were not the same because some compositions did not contain B_2O_3 or Li_2O , or because PCT normalized elemental releases for B and Li were not available. Table 3.7 also lists the minimum, maximum, and average values of r_i and $\ln(r_i)$ for the data used to fit the models. As discussed in Section 3.2.3, model coefficients can be compared to the average $\ln(r_i)$ values to assess whether components are likely to have significant or negligible effects.

Note that the appearance of a component in the final PCT models does not necessarily mean it has a significant effect on r_B , r_{Li} , and r_{Na} . It was decided to use the same 12 components in each of the $\ln(r_B)$, $\ln(r_{Li})$, and $\ln(r_{Na})$ models. It was decided to retain in all three models the nine main components (Al_2O_3 , B_2O_3 , CaO , Fe_2O_3 , Li_2O , MgO , Na_2O , SiO_2 , and ZrO_2) studied and included in Hanford property-composition models by Hrma et al. (1994). The additional three components included in all three PCT release models are K_2O , MnO_x , and P_2O_5 .

The coefficients in Table 3.7 are consistent with those published previously (Hrma et al. 1995a). Al_2O_3 and ZrO_2 strongly decrease r_i ($i = \text{B, Na, Li}$) because of their strong network-forming action. P_2O_5 decreases solution pH, thus making the solution less aggressive. MnO_x is a rather minor component; it is surprising that it increases durability as much as ZrO_2 . Compared to Na_2O and Li_2O , K_2O has a smaller and possibly negligible effect on r_i ($i = \text{B, Na, Li}$).

Table 3.5. Glasses Deleted for 15-Component PCT Modeling

| Glass | Study | Deleted for PCT | | | Reason Deleted |
|--|-------------------------------|-----------------|-----|----|-------------------------------------|
| | | B | Li | Na | |
| IG2-14 | INEL CVS | X | (a) | X | Excessive Stand. Resid. (c) |
| IG1-37 | INEL CVS | X | X | X | Excessive Stand. Resid. (c) |
| CVS2-22 | Second Hanford CVS | X | X | X | Excessive Stand. Resid. (c) |
| CVS2-65 | Second Hanford CVS | X | X | X | Excessive Stand. Resid. (c) |
| Ratio5 | West Valley | X | X | X | Excessive Stand. Resid. (c) |
| Sigma3 | West Valley | X | X | X | Excessive Stand. Resid. (c) |
| PFP-0P | Student Study 1994 (D Heckle) | X | X | X | Excessive Stand. Resid. (c) |
| PFP-3.3P | Student Study 1994 (D Heckle) | X | X | X | Excessive Stand. Resid. (c) |
| LAWA22 | TWRS LAW Formulation | (b) | (b) | X | Excessive Stand. Resid. (c) |
| LAWA23 | TWRS LAW Formulation | (b) | (b) | X | Excessive Stand. Resid. (c) |
| LAWB29 | TWRS LAW Formulation | (b) | (b) | X | Excessive Stand. Resid. (c) |
| LAWPC1 | TWRS LAW Formulation | (b) | (a) | X | Excessive Stand. Resid. (c) |
| LAWPC3 | TWRS LAW Formulation | (b) | (a) | X | Excessive Stand. Resid. (c) |
| LAWPC9 | TWRS LAW Formulation | (b) | (b) | X | Excessive Stand. Resid. (c) |
| LAWPC7 | TWRS LAW Formulation | (b) | (b) | X | Excessive Stand. Resid. (c) |
| LAWPC8 | TWRS LAW Formulation | (b) | (b) | X | Excessive Stand. Resid. (c) |
| LAWPC10 | TWRS LAW Formulation | (b) | (b) | X | Excessive Stand. Resid. (c) |
| CVS2-68 | Second Hanford CVS | X | X | X | $\text{Cr}_2\text{O}_3 > 0.005$ (d) |
| CVS2-69 | Second Hanford CVS | X | X | X | $\text{Cr}_2\text{O}_3 > 0.005$ (d) |
| CU41 | CUA Data | X | X | X | $\text{ZnO} > 0.004$ (d) |
| CU42 | CUA Data | X | X | X | $\text{ZnO} > 0.004$ (d) |
| CU43 | CUA Data | X | X | X | $\text{ZnO} > 0.004$ (d) |
| LAWPC6 | TWRS LAW Formulation | X | (b) | X | $\text{ZnO} > 0.004$ (d) |
| LAWC-63B | TWRS LAW Formulation | X | (a) | X | $\text{ZnO} > 0.004$ (d) |
| LAWC-88A | TWRS LAW Formulation | X | (a) | X | $\text{ZnO} > 0.004$ (d) |
| LAWC-95D | TWRS LAW Formulation | X | (a) | X | $\text{ZnO} > 0.004$ (d) |
| LAWC-99B | TWRS LAW Formulation | X | (a) | X | $\text{ZnO} > 0.004$ (d) |
| LAWBF-62G | TWRS LAW Formulation | X | (b) | X | $\text{ZnO} > 0.004$ (d) |
| LAWBF-70D | TWRS LAW Formulation | X | (b) | X | $\text{ZnO} > 0.004$ (d) |
| Envelope A | TWRS LAW Formulation | X | X | X | $\text{ZnO} > 0.004$ (d) |
| Envelope B | TWRS LAW Formulation | X | X | X | $\text{ZnO} > 0.004$ (d) |
| Envelope C | TWRS LAW Formulation | X | X | X | $\text{ZnO} > 0.004$ (d) |
| <p>(a) Glasses that were not included in PCT modeling for a specified element i because the glass did not contain the indicated oxide, thus no r_i value could be generated.</p> <p>(b) Glasses that did contain the indicated oxide, but that were not included in the PCT modeling for a specified element because no r_i value was available for that element.</p> <p>(c) The standardized residual from at least one of the PCT model regression analyses was beyond approximately ± 2.4. In most cases, the standardized residuals were beyond ± 3.</p> <p>(d) Based on 20-component normalized mol fraction compositions.</p> | | | | | |

Table 3.6. Glasses Deleted for 12-Component PCT Modeling

| Glass | Study | Deleted for PCT | | | Reason Deleted |
|---|-------------------------------|-----------------|-----|----|------------------------------|
| | | B | Li | Na | |
| IG2-14 | INEL CVS | X | (a) | X | See Table 3.5 |
| IG1-37 | INEL CVS | X | X | X | See Table 3.5 |
| CVS2-22 | Second Hanford CVS | X | X | X | See Table 3.5 |
| CVS2-65 | Second Hanford CVS | X | X | X | See Table 3.5 |
| Ratio5 | West Valley | X | X | X | See Table 3.5 |
| Sigma3 | West Valley | X | X | X | See Table 3.5 |
| PFP-0P | Student Study 1994 (D Heckle) | X | X | X | See Table 3.5 |
| PFP-3.3P | Student Study 1994 (D Heckle) | X | X | X | See Table 3.5 |
| LAWA22 | TWRS LAW Formulation | (b) | (b) | X | See Table 3.5 |
| LAWA23 | TWRS LAW Formulation | (b) | (b) | X | See Table 3.5 |
| LAWB29 | TWRS LAW Formulation | (b) | (b) | X | See Table 3.5 |
| LAWPC1 | TWRS LAW Formulation | (b) | (a) | X | See Table 3.5 |
| LAWPC3 | TWRS LAW Formulation | (b) | (a) | X | See Table 3.5 |
| LAWPC9 | TWRS LAW Formulation | (b) | (b) | X | See Table 3.5 |
| LAWPC7 | TWRS LAW Formulation | (b) | (b) | X | See Table 3.5 |
| LAWPC8 | TWRS LAW Formulation | (b) | (b) | X | See Table 3.5 |
| LAWPC10 | TWRS LAW Formulation | (b) | (b) | X | See Table 3.5 |
| CVS2-68 | Second Hanford CVS | X | X | X | See Table 3.5 |
| CVS2-69 | Second Hanford CVS | X | X | X | See Table 3.5 |
| CU41 | CUA Data | X | X | X | See Table 3.5 |
| CU42 | CUA Data | X | X | X | See Table 3.5 |
| CU43 | CUA Data | X | X | X | See Table 3.5 |
| LAWPC6 | TWRS LAW Formulation | X | (b) | X | See Table 3.5 |
| LAWC-63B | TWRS LAW Formulation | X | (a) | X | See Table 3.5 |
| LAWC-88A | TWRS LAW Formulation | X | (a) | X | See Table 3.5 |
| LAWC-95D | TWRS LAW Formulation | X | (a) | X | See Table 3.5 |
| LAWC-99B | TWRS LAW Formulation | X | (a) | X | See Table 3.5 |
| LAWBF-62G | TWRS LAW Formulation | X | (b) | X | See Table 3.5 |
| LAWBF-70D | TWRS LAW Formulation | X | (b) | X | See Table 3.5 |
| Envelope A | TWRS LAW Formulation | X | X | X | See Table 3.5 |
| Envelope B | TWRS LAW Formulation | X | X | X | See Table 3.5 |
| Envelope C | TWRS LAW Formulation | X | X | X | See Table 3.5 |
| IG2-04 | INEL CVS | X | X | X | Excessive Stand. Resid. (c) |
| IG1-12 | INEL CVS | X | (a) | X | K ₂ O > 0.057 (d) |
| IG2-13 | INEL CVS | | | X | Excessive Stand. Resid. (c) |
| <p>(a) Glasses that were not included in PCT modeling for a specified element because the glass did not contain the indicated oxide, thus no PCT release data could be generated.</p> <p>(b) Glasses that did contain the indicated oxide, but that were not included in the PCT modeling for the specified element because no PCT release data were available for that element.</p> <p>(c) The standardized residual from at least one of the PCT model-regression analyses was beyond ± 2.38. In most cases, the standardized residuals were beyond ± 3.</p> <p>(d) Based on 20-component normalized mol fraction compositions.</p> | | | | | |

Table 3.7. Component Coefficients and Standard Deviations, Fit Statistics, and Property Ranges for the Final 12-Component PCT Models

| | $\ln(r_B)$ | | $\ln(r_{Li})$ | | $\ln(r_{Na})$ | |
|--------------------------------|---------------------------------------|------------------------------|--|---------------------------------|--|---------------------------------|
| Component | Coefficient | SD (Coeff.) | Coefficient | SD (Coeff.) | Coefficient | SD (Coeff.) |
| Al ₂ O ₃ | -33.419 | 1.318 | -29.999 | 1.251 | -32.668 | 1.184 |
| B ₂ O ₃ | 13.403 | 0.719 | 11.238 | 0.649 | 9.558 | 0.644 |
| CaO | -9.183 | 1.257 | -6.144 | 1.188 | -3.488 | 1.128 |
| Fe ₂ O ₃ | -11.947 | 2.006 | -13.028 | 1.812 | -10.357 | 1.797 |
| K ₂ O | -1.547 | 2.365 | -0.814 | 2.099 | 2.363 | 2.119 |
| Li ₂ O | 9.382 | 0.804 | 9.279 | 0.793 | 7.434 | 0.721 |
| MgO | 3.513 | 1.219 | 1.719 | 1.091 | 3.549 | 1.093 |
| MnO _x | -21.220 | 4.015 | -15.880 | 3.585 | -16.419 | 3.598 |
| Na ₂ O | 17.013 | 0.718 | 13.404 | 0.651 | 18.794 | 0.646 |
| P ₂ O ₅ | -41.830 | 10.790 | -31.893 | 9.554 | -39.952 | 9.680 |
| SiO ₂ | -4.106 | 0.285 | -3.431 | 0.258 | -4.243 | 0.255 |
| ZrO ₂ | -14.458 | 2.614 | -12.906 | 2.316 | -16.091 | 2.395 |
| | | | | | | |
| Fit Statistics | | | | | | |
| Number of Glasses | 383 | | 380 | | 390 | |
| R ² | 0.814 | | 0.797 | | 0.824 | |
| R ² (Adjusted) | 0.808 | | 0.791 | | 0.819 | |
| R ² (Predicted) | 0.798 | | 0.779 | | 0.809 | |
| s (RMSE) | 0.531 | | 0.468 | | 0.475 | |
| | | | | | | |
| Property Ranges | $\ln(r_B)$ [ln(g/m ²)] | r_B (g/m ²) | $\ln(r_{Li})$ [ln(g/m ²)] | r_{Li} (g/m ²) | $\ln(r_{Na})$ [ln(g/m ²)] | r_{Na} (g/m ²) |
| Minimum | -2.7181 | 0.066 | -2.3969 | 0.091 | -3.2127 | 0.040 |
| Maximum | 2.9226 | 18.590 | 2.5575 | 12.903 | 2.5513 | 12.824 |
| Average | 0.0613 | 0.148 | 0.0524 | 0.094 | 0.0565 | 0.108 |

The mol-fraction ranges of the components for glasses used to fit the PCT models are given in Tables 3.8 and 3.9. Table 3.8 lists the ranges of mol fractions for the original 61 components (before re-normalization for the components in the model), while Table 3.9 lists the ranges of mol fractions for the 12-component normalized compositions used to develop the models. Glass compositions that were dropped (i.e., not used to develop the models) were not included in determining the component ranges. The ranges in Tables 3.8 and 3.9 are based on the 391 glass compositions used to obtain the 12-component $\ln(r_B)$ model. Although fewer compositions were used to obtain the $\ln(r_{Li})$ and $\ln(r_{Na})$ models, the component mol-fraction ranges in Tables 3.8 and 3.9 should still be reasonable for those models as well.

**Table 3.8. Mol-Fraction Ranges of the Original Components for the Data
Used to Develop the Final PCT Models**

| Component | Range Used to Develop PCT Models | | Component | Range Used to Develop PCT Models | |
|--------------------------------|----------------------------------|---------|---------------------------------|----------------------------------|---------|
| | Minimum | Maximum | | Minimum | Maximum |
| Al ₂ O ₃ | 0.00168 | 0.12629 | La ₂ O ₃ | 0 | 0.01259 |
| B ₂ O ₃ | 0.03880 | 0.19571 | MgO | 0 | 0.12970 |
| K ₂ O | 0 | 0.05640 | MnO | 0 | 0.03460 |
| Li ₂ O | 0 | 0.18210 | MnO ₂ | 0 | 0.01124 |
| Na ₂ O | 0.04512 | 0.24543 | Nb ₃ O ₅ | 0 | 0.00004 |
| P ₂ O ₅ | 0 | 0.01248 | Nd ₂ O ₃ | 0 | 0.01199 |
| SiO ₂ | 0.36232 | 0.64677 | PbO | 0 | 0.00350 |
| ZrO ₂ | 0 | 0.07174 | PdO | 0 | 0.00071 |
| CaO | 0 | 0.12011 | PdO ₂ | 0 | 0 |
| F | 0 | 0.01912 | Pr ₂ O ₃ | 0 | 0 |
| Fe ₂ O ₃ | 0 | 0.08067 | Pr ₆ O ₁₁ | 0 | 0.00012 |
| FeO | 0 | 0 | Rb ₂ O | 0 | 0.00033 |
| NiO | 0 | 0.02735 | ReO ₂ | 0 | 0.00024 |
| MoO ₃ | 0 | 0.0034 | Rh ₂ O ₃ | 0 | 0.00024 |
| SrO | 0 | 0.00364 | RhO ₂ | 0 | 0.00011 |
| TiO ₂ | 0 | 0.02586 | RuO ₂ | 0 | 0.00137 |
| Ag ₂ O | 0 | 0.00029 | Sb ₂ O ₃ | 0 | 0.00011 |
| As ₂ O ₃ | 0 | 0.00034 | SeO ₂ | 0 | 0.00201 |
| BaO | 0 | 0.00478 | Sm ₂ O ₃ | 0 | 0.00870 |
| Bi ₂ O ₃ | 0 | 0.00197 | SnO ₂ | 0 | 0.00023 |
| CdO | 0 | 0.00707 | SO ₃ | 0 | 0.00568 |
| CeO ₂ | 0 | 0.02580 | TeO ₂ | 0 | 0.00022 |
| Ce ₂ O ₃ | 0 | 0.00413 | Y ₂ O ₃ | 0 | 0.00027 |
| Cl | 0 | 0.01090 | ThO ₂ | 0 | 0.01668 |
| Co ₂ O ₃ | 0 | 0.00040 | UO ₃ | 0 | 0.00459 |
| Cr ₂ O ₃ | 0 | 0.01005 | UO ₂ | 0 | 0 |
| Cs ₂ O | 0 | 0.00270 | U ₃ O ₈ | 0 | 0.00218 |
| CuO | 0 | 0.00540 | V ₂ O ₃ | 0 | 0 |
| Eu ₂ O ₃ | 0 | 0.00860 | WO ₃ | 0 | 0.00031 |
| Gd ₂ O ₃ | 0 | 0.01230 | ZnO | 0 | 0.00395 |
| I | 0 | 0.00001 | | | |

Table 3.9. Mol-Fraction Ranges of the Normalized 12 Components for the Data Used to Develop the Final PCT Models

| Normalized 12 Components | Minimum | Maximum |
|--------------------------------|---------|---------|
| Al ₂ O ₃ | 0.00169 | 0.12748 |
| B ₂ O ₃ | 0.04141 | 0.19857 |
| CaO | 0 | 0.12081 |
| Fe ₂ O ₃ | 0 | 0.08363 |
| K ₂ O | 0 | 0.05766 |
| Li ₂ O | 0 | 0.18267 |
| MgO | 0 | 0.13673 |
| MnO _x | 0 | 0.03515 |
| Na ₂ O | 0.0466 | 0.24543 |
| P ₂ O ₅ | 0 | 0.01280 |
| SiO ₂ | 0.36444 | 0.68148 |
| ZrO ₂ | 0 | 0.07216 |

It is important to emphasize several considerations regarding the use of the PCT models presented in Table 3.7.

- Because the PCT models were derived using mol-fraction compositions, using the models requires that compositions be specified in mol fractions. If composition data are initially given in mass fractions, they must be converted to mol fractions before use in the PCT models.
- Mol-fraction compositions must sum to one across the components included in the PCT models. This will require that mol-fraction compositions containing more than the components included in the models be renormalized before applying the PCT models.
- The PCT models should only be used for compositions within the original component mol-fraction ranges listed in Table 3.8 and the 12-component normalized mol-fraction ranges listed in Table 3.9. Predictions obtained for compositions outside these ranges are extrapolations and may be subject to bias (depending on the extent of extrapolation).
- The PCT models should only be used for single-phase glasses. Multi-phase glasses may have different PCT behavior than single-phase glasses. Unfortunately, no reliable model or method currently exists to predict, as a function of composition, when a glass will be multi-phase.
- The PCT models were developed with $\ln(\text{g/m}^2)$ values as the response. Hence, predictions resulting from the models are in $\ln(\text{g/m}^2)$ units. PCT values (without the natural logarithm) can be determined in g/m^2 units, if desired, by applying the exponential function (with base e) to the $\ln(\text{g/m}^2)$ values obtained using the PCT models.

Finally, we emphasize that while the PCT models of the form (3.2) account for approximately 80% of the variation in the $\ln(r_i)$ results, the remaining ~20% is not accounted for. Of course, experimental uncertainties can never be accounted for by models, but the ~20% variation is larger than can be attributed to experimental uncertainties. Some of this lack-of-fit could be due to unknown multi-phase glasses being used to develop the models. Or it could be due to the larger uncertainty in PCT results generated at many different sites and times. It could also be due to non-linear blending behavior of glass

components not captured by the linear model. Finally, it could be due to the fact that the compositions for given glasses used to develop models may not exactly represent the true compositions of the glasses. Each of these reasons probably partially explains why the linear mixture models only account for roughly 80% of the variation in $\ln(r_i)$ values. In any case, predictions of PCT behavior from the models in Table 3.7 are subject to considerable uncertainty, which may take the form of bias and/or imprecision. The uncertainty in predictions for those glasses used to develop the models is displayed graphically in the following section. Despite the uncertainties in the model fits and predictions, the models still account for enough of the effects of composition on PCT behavior to be useful.

3.2.5 Predicted Versus Measured Plots for PCT Models

Figures 3.1 through 3.3 are predicted-versus-measured plots for the data points used to fit the PCT models. The top and right axes are r_i in g/m^2 . The bottom and left axes are $\ln(r_i)$ in $\ln(\text{g/m}^2)$. Each plot also includes a 45° line representing perfect agreement between the predicted and measured r_i values. In each figure, the plotted points clearly follow the linear pattern established by the 45° line, indicating that the models provide reasonable fits to the data. However, certain features also suggest some degree of lack of fit. For example, Figures 3.1 and 3.2 show indications of biased predictions for different ranges of $\ln(r_B)$ and $\ln(r_{Li})$, respectively. Specifically, these figures show the models tend to overpredict when measured $\ln(r_i)$ values are negative and underpredict when measured $\ln(r_i)$ values are positive. Preliminary investigations indicate the biased model predictions result from at least two contributing factors. First, nonlinear blending (i.e., curvature and/or interaction) effects of the components are not captured by models of the form (3.2), which are linear in composition. Second, the large cluster of glasses with moderately small PCT releases seem to cause a bias in the unweighted least squares regression analysis, where each data point has equal weight. These issues will be addressed in future property-composition model development and validation efforts.

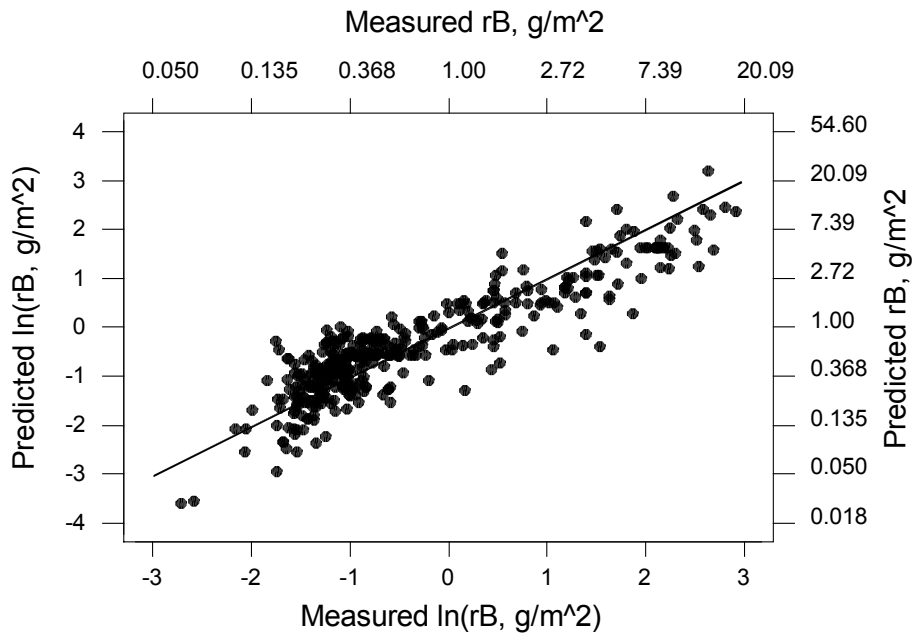


Figure 3.1. Plot of Predicted Versus Measured $\ln(r_B)$ Values

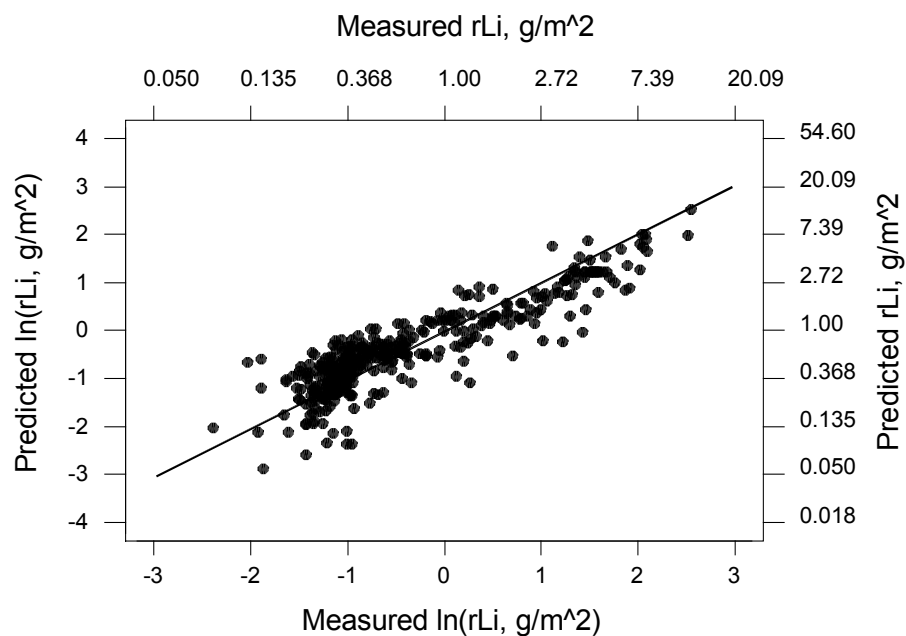


Figure 3.2. Plot of Predicted Versus Measured $\ln(r_{Li})$ Values

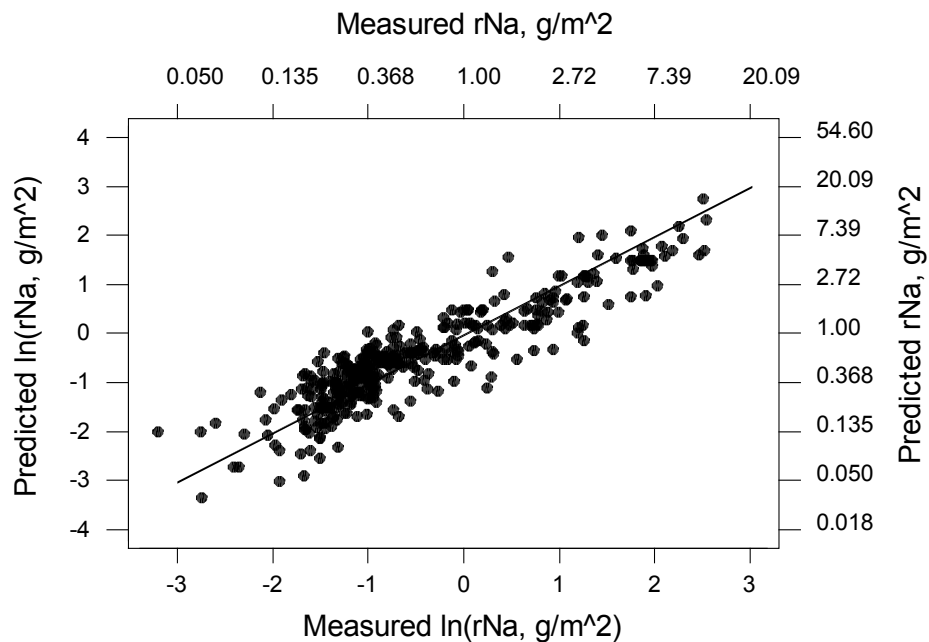


Figure 3.3. Plot of Predicted Versus Measured $\ln(r_{Na})$ Values

3.3 Models for Viscosity

This section describes how the interim viscosity model was developed. This section also discusses the subset of the 824 glasses described in Section 3.1.2 that was used to develop the viscosity model.

3.3.1 General Form of the Viscosity Model

The general form of the viscosity model can be written as

$$\ln(\eta) = A + \frac{B}{T} = \sum_{j=1}^N \left(A_j + \frac{B_j}{T} \right) x_j \quad (3.4)$$

where A_j and B_j are the j -th component coefficients. The viscosity model is of the Arrhenius form (1.10) expanded to (1.12) as presented in Section 1.3. As with the PCT models discussed in Section 3.2, the mol fractions x_j must sum to one across the N components included in the model (see [1.2] and the discussion of normalization in Section 3.2).

As with the PCT models, the natural logarithm transformation is employed in the viscosity model. Reasons for the natural logarithm transformation are presented in Section 3.2 and apply to the viscosity model as well. Viscosity was measured in Pascal-seconds (Pa·s), and Equation (3.4) implies that predicted viscosity values are in $\ln(\text{Pa}\cdot\text{s})$ units.

An obvious difference between the viscosity model and the PCT models is the inclusion of temperature in the viscosity model. Viscosity readings were typically recorded at several temperatures for a given composition. That is, while a particular glass composition is in a liquid state, the temperature of the melt is varied, and viscosity readings are taken at various temperatures. The temperatures were initially recorded in degrees Celsius ($^{\circ}\text{C}$), but were later converted to Kelvin (K) in order to apply Equation (3.4).

3.3.2 Screening Glasses for Viscosity Modeling

Of the 824 glasses that remained in the data set following the initial database screening described in Section 3.1.2, only 254 had viscosity data. For each of these 254 compositions, viscosity readings were typically recorded at several temperature levels, resulting in 1796 composition-temperature combinations (data points). Following renormalization over the 20 components discussed in Section 3.1.1, the 1796 composition-temperature combinations were screened to delete composition-temperature combinations from the data set that were not considered suitable for viscosity modeling as described below. The following paragraph describes how this data screening was conducted.

The melt temperature (i.e., temperature of the melt during viscosity measurements) is a primary concern when studying viscosity. To minimize the impact of nonlinearities in the $\ln(\eta)$ versus $1/T$ relationship, we imposed upper and lower limits on the melt temperature. For this reason, 10 composition-temperature combinations were dropped from the analysis because they had temperatures below 900°C . Similarly, 10 composition-temperature combinations were dropped where the temperatures

were above 1420°C. These data points were dropped because they were extreme in temperature space and if retained, might have the potential to overly influence the viscosity models.

A preliminary regression analysis was conducted using the 20 components in Equation (3.4), and 47 composition-temperature combinations were subsequently dropped because their corresponding standardized residuals (Montgomery and Peck 1992) were extreme (they were all beyond ± 2.7 for the ones we chose to drop). While such large standardized residuals do not necessarily mean there is any problem with the corresponding data, it was decided to drop them for conservatism in developing interim viscosity models. An additional 33 composition-temperature combinations were dropped due to unusually high concentrations of Fe_2O_3 , MnO_x , Na_2O , or NiO . These high concentrations were within the component ranges of interest for Hanford HLW, but were extreme compared to the concentrations for the remaining glass compositions. Hence, these data points were dropped to avoid having a small number of data points potentially drastically affecting the resulting model. Seven composition-temperature combinations corresponding to glass IG2-14 from the INEEL CVS were dropped because IG2-14 was considered to have yielded outlying results in that study. Similarly, one composition-temperature combination of glass CVS2-79 from the Hanford CVS was dropped because it had a higher than average residual.^(a) Finally, 102 composition-temperature combinations were dropped because they had unusually high F, P_2O_5 , or TiO_2 concentrations compared to the remaining glass compositions. Overall, the data screening during development of the 20-component viscosity model removed 210 composition-temperature combinations, thereby reducing the number of composition-temperature combinations available for viscosity modeling from 1796 to 1586. These data screening results are summarized in Table 3.10.

3.3.3 Component Screening for Viscosity Modeling

After screening glasses (deleting inappropriate composition-temperature combinations), a 20-component viscosity model was derived. We emphasize again that the 20 components were selected because the database provided support to consider including them in property-composition models, not because they had a significant influence on one or more of the glass properties. Statistical least-squares regression techniques appropriate for mixture-experiment models (Cornell 1990) were applied to the 20-component viscosity model, Equation (3.4) with $N = 20$. Other mixture-experiment methods (as discussed in Section 3.2.3) were employed to identify components that did not significantly influence viscosity behavior. Models of the form (3.4) with fewer than 20 components were subsequently investigated. Each time a new model was considered, the following steps were taken:

- Compositions were renormalized to sum to one based on the number of components being considered in the model.
- Regression analysis was conducted using the 1586 composition-temperature combinations that remained after the viscosity-specific screening discussed above.

Techniques were applied to evaluate the terms in the model. See Section 3.2 for additional discussion and references.

(a) In fact, all composition-temperature combinations for CVS2-79 were ultimately dropped before deriving the final viscosity model because of outlying aspects of the data noted in Appendix B of Hrma et al. (1994).

Table 3.10. Glasses Deleted During 20-Component Viscosity Model Screening

| Glass | Study | Temperature(s), (°C) | Reason |
|--------------|---------------------------|--|--|
| IG2-11 | INEL CVS | 857.1 | Melt Temp < 900°C |
| IG1-36 | INEL CVS | 155.9 | Melt Temp < 900°C |
| CVS1-3 | First Hanford CVS | 852 | Melt Temp < 900°C |
| 22-27 | Chick et al. (1984) | 897 | Melt Temp < 900°C |
| 70-55 | Chick et al. (1984) | 886 | Melt Temp < 900°C |
| PBG3/Ce | Plutonium Vitrification | 895 | Melt Temp < 900°C |
| BAZ-R | Italian HLW | 645, 710, 785, 860 | Melt Temp < 900°C |
| IG2-14 | INEL CVS | 1452.9, 1452.8 | Melt Temp > 1420°C |
| CVS1-10 | First Hanford CVS | 1449 | Melt Temp > 1420°C |
| 33-06 | Chick et al. (1984) | 1503 | Melt Temp > 1420°C |
| 59-06 | Chick et al. (1984) | 1589 | Melt Temp > 1420°C |
| 21-36 | Chick et al. (1984) | 1436 | Melt Temp > 1420°C |
| 41-63 | Chick et al. (1984) | 1555 | Melt Temp > 1420°C |
| 25-64 | Chick et al. (1984) | 1582 | Melt Temp > 1420°C |
| 51-66 | Chick et al. (1984) | 1542 | Melt Temp > 1420°C |
| 91-89 | Chick et al. (1984) | 1469 | Melt Temp > 1420°C |
| IG2-14 | INEL CVS | 1204.9, 1155.4, 1205.1 | Stand. Resid. Beyond ± 2.7 |
| PNL 4 | WVDP Rad Testing | 1052 | Stand. Resid. Beyond ± 2.7 |
| CVS1-16 | First Hanford CVS | 1049 | Stand. Resid. Beyond ± 2.7 |
| CVS2-30 | Second Hanford CVS | 998 | Stand. Resid. Beyond ± 2.7 |
| CVS2-79 | Second Hanford CVS | 1203, 1151, 1151, 1101, 1102, 1051 | Stand. Resid. Beyond ± 2.7 |
| CVS2-80 | Second Hanford CVS | 1252, 1200, 1150, 1150, 1149, 1101, 1100 | Stand. Resid. Beyond ± 2.7 |
| CVS2-81 | Second Hanford CVS | 949 | Stand. Resid. Beyond ± 2.7 |
| LAWPC7 | TWRS LAW Formulation | 950, 1000, 1050, 1100, 1150, 1200, 1250 | Stand. Resid. Beyond ± 2.7 |
| LAWPC8 | TWRS LAW Formulation | 950, 1000, 1050, 1100, 1150, 1200, 1250 | Stand. Resid. Beyond ± 2.7 |
| LAWBF-98E | TWRS LAW Formulation | 950, 1000, 1050, 1100, 1150, 1200, 1250, 1300 | Stand. Resid. Beyond ± 2.7 |
| 21 | Comp. Vs Properties Study | 1250 | Stand. Resid. Beyond ± 2.7 |
| 86 | Comp. Vs Properties Study | 1250 | Stand. Resid. Beyond ± 2.7 |
| 91 | Comp. Vs Properties Study | 1250 | Stand. Resid. Beyond ± 2.7 |
| 92 | Comp. Vs Properties Study | 1250 | Stand. Resid. Beyond ± 2.7 |
| 100 | Comp. Vs Properties Study | 1250 | Stand. Resid. Beyond ± 2.7 |
| CVS2-55 | Second Hanford CVS | 1247, 1197, 1147, 1147, 1147, 1097, 1096, 1046, 997, 946 | MnO _x > 0.012 |
| CVS2-56 | Second Hanford CVS | 1247, 1197, 1146, 1147, 1147, 1097, 1096, 1047, 996, 946 | MnO _x > 0.012 |
| 27-02 | Chick et al. (1984) | 1431 | Na ₂ O > 0.258 |
| 72-02 | Chick et al. (1984) | 1332 | Na ₂ O > 0.258 |
| 55-27 | Chick et al. (1984) | 910 | Na ₂ O > 0.258 |
| 35-35 | Chick et al. (1984) | 1039 | Na ₂ O > 0.258 |
| 05-40 | Chick et al. (1984) | 1026 | Na ₂ O > 0.258 |
| 24-41 | Chick et al. (1984) | 1240 | Na ₂ O > 0.258 |
| 80-46 | Chick et al. (1984) | 1215 | Fe ₂ O ₃ > 0.074 |
| 11-57 | Chick et al. (1984) | 998 | Na ₂ O > 0.258 |

Table 3.10 (Contd)

| Glass | Study | Temperature(s), (°C) | Reason |
|----------|---------------------------|---|---------------------------------|
| 89-77 | Chick et al. (1984) | 1422 | $\text{Fe}_2\text{O}_3 > 0.074$ |
| 17 | Comp. Vs Properties Study | 1250 | $\text{ZnO} > 0.036$ |
| 37 | Comp. Vs Properties Study | 1250 | $\text{NiO} > 0.015$ |
| 83 | Comp. Vs Properties Study | 1250 | $\text{ZnO} > 0.036$ |
| 95 | Comp. Vs Properties Study | 1250 | $\text{NiO} > 0.015$ |
| IG2-14 | INEL CVS | 1255.5, 1254.3, 1303.8, 1403, 1353.7, 1254.7, 1353.8 | Remaining IG2-14 points |
| CVS2-79 | Second Hanford CVS | 1002 | Mod. Outlying CVS2-79 Glass |
| IG2-06 | INEL CVS | 1007.7, 958, 1157.4, 1206.7, 1256.1, 1157.1 | $\text{P}_2\text{O}_5 > 0.0065$ |
| IG2-11 | INEL CVS | 1059.4, 1007.4, 956.9, 906.9, 957.5, 1057.1, 1106.7, 1156.3, 1205.7, 1255.2, 1156, 1056.3, 1156.6 | $\text{P}_2\text{O}_5 > 0.0065$ |
| IG1-37 | INEL CVS | 1157.5, 1106.8, 1056.7, 1107, 1156.5, 1205.5, 1254.4, 1155.6, 1006.7, 957.6 | $\text{P}_2\text{O}_5 > 0.0065$ |
| CVS2-69 | Second Hanford CVS | 1251, 1201, 1151, 1150, 1151, 1101, 1101, 1051, 1000 | $\text{P}_2\text{O}_5 > 0.0065$ |
| LAWPC1 | TWRS LAW Formulation | 950, 1000, 1050, 1100, 1150, 1200, 1250 | $\text{F} > 0.020$ |
| LAWPC3 | TWRS LAW Formulation | 950, 1000, 1050, 1100, 1150, 1200, 1250 | $\text{F} > 0.020$ |
| LAWPC6 | TWRS LAW Formulation | 950, 1000, 1050, 1100, 1150, 1200, 1250 | $\text{F} > 0.020$ |
| LAWPC9 | TWRS LAW Formulation | 950, 1000, 1050, 1100, 1150, 1200, 1250 | $\text{F} > 0.020$ |
| LAWC-30C | TWRS LAW Formulation | 1000, 1050, 1100, 1150, 1200, 1250, 1300 | $\text{F} > 0.020$ |
| LAWC-81B | TWRS LAW Formulation | 950, 1000, 1050, 1100, 1150, 1200, 1250, 1300 | $\text{F} > 0.020$ |
| LAWC-93A | TWRS LAW Formulation | 950, 1000, 1050, 1100, 1150, 1200, 1250, 1300 | $\text{F} > 0.020$ |
| 18 | Comp. Vs Properties Study | 1250 | $\text{TiO}_2 > 0.011$ |
| 19 | Comp. Vs Properties Study | 1250 | $\text{TiO}_2 > 0.011$ |
| 20 | Comp. Vs Properties Study | 1250 | $\text{TiO}_2 > 0.011$ |
| 43 | Comp. Vs Properties Study | 1250 | $\text{TiO}_2 > 0.011$ |
| 44 | Comp. Vs Properties Study | 1250 | $\text{TiO}_2 > 0.011$ |
| 45 | Comp. Vs Properties Study | 1250 | $\text{TiO}_2 > 0.011$ |
| 71 | Comp. Vs Properties Study | 1250 | $\text{TiO}_2 > 0.011$ |
| 73 | Comp. Vs Properties Study | 1250 | $\text{TiO}_2 > 0.011$ |
| 75 | Comp. Vs Properties Study | 1250 | $\text{TiO}_2 > 0.011$ |
| 79 | Comp. Vs Properties Study | 1250 | $\text{TiO}_2 > 0.011$ |
| 81 | Comp. Vs Properties Study | 1250 | $\text{TiO}_2 > 0.011$ |
| 88 | Comp. Vs Properties Study | 1250 | $\text{TiO}_2 > 0.011$ |
| 89 | Comp. Vs Properties Study | 1250 | $\text{TiO}_2 > 0.011$ |

Table 3.11 indicates which components were used in the various models considered and gives the summary statistics from the regression analyses. The coefficients are not provided for the various “intermediate” viscosity models because of the accelerated, concurrent process used to reduce the number of components at the same time the data assessment was being performed. For example, roughly only $\frac{1}{6}$ of the 1566 glasses used to select the 20 components for consideration in developing property-composition models survived the filtering process (described in Sections 3.1.2 and 3.3.2) and had viscosity values. Hence, the data actually available to fit a viscosity model did not adequately support the inclusion of some of the 20 components. Hence, the 20-component and fewer-component models considered on the way to the final model may have been affected by poor composition-region support. Also some additional data points were discarded before fitting the final model, as described in Section 3.3.4. Thus the coefficients of the interim models considered along the way in developing the final models are not reported in Table 3.11.

The first 12-component model mentioned in Table 3.11 was obtained from the 13-component model, except that ThO_2 and ZrO_2 were combined because they are expected to have a similar effect on viscosity. Because ThO_2 appeared to have a less significant effect on $\ln(\eta)$ than ZrO_2 , a 12-component model wherein ZrO_2 was retained but ThO_2 was deleted was also considered. Based on the regression analyses, the 12-component model without ThO_2 yielded as good or better fit to the data than the 13-component model or the 11-component model. Therefore, possible similarities between the effects of ThO_2 and ZrO_2 were not pursued further. The 12-component model without ThO_2 (described in the final column of Table 3.11) was selected as the final viscosity model. However, note that the 12 components are not the same 12 used in the PCT models. As is well known (see, e.g., Hrma et al. 1995b), virtually all components affect melt viscosity, either as network formers or as network modifiers. However, the effects of minor components are relatively small, and thus such components can be deleted without affecting the accuracy of viscosity prediction.

3.3.4 The Final Viscosity Model

As indicated from Table 3.11, the 12 components included in the final $\ln(\eta)$ model were Al_2O_3 , B_2O_3 , CaO , F , Fe_2O_3 , K_2O , Li_2O , LN_2O_3 , MgO , Na_2O , SiO_2 , and ZrO_2 . Before determining the regression coefficients for the final model, 12 additional composition-temperature combinations were dropped from the analysis because crystals in the melt may have affected the viscosity measurements (Hrma et al. 1994, Appendix B). The composition-temperature combinations dropped are listed in Table 3.12.

Having dropped the 12 composition-temperature combinations listed in Table 3.12, the final regression analysis was conducted using the remaining 1574 composition-temperature combinations. The coefficients and coefficient standard deviations for the 12-component terms and the 12-component-temperature terms of the final viscosity model are given in Table 3.13. Table 3.13 also lists the summary statistics for the final regression analysis. A comparison of these statistics with those for the 12-component model in Table 3.11 indicate that deleting the 12 composition-temperature combinations listed in Table 3.12 did improve the model fit.

Table 3.11. Summary Statistics for Preliminary Viscosity Model Regression Analyses

| Component | Model | | | | | |
|--------------------------------|----------|----------|----------|----------|----------------------------|----------|
| | 20-Comp. | 15-Comp. | 13-Comp. | 11-Comp. | 12-Comp. | 12-Comp. |
| Al ₂ O ₃ | X | X | X | X | X | X |
| B ₂ O ₃ | X | X | X | X | X | X |
| CaO | X | X | X | X | X | X |
| Cr ₂ O ₃ | X | | | | | |
| F | X | X | X | X | X | X |
| Fe ₂ O ₃ | X | X | X | X | X | X |
| K ₂ O | X | X | X | | X | X |
| Li ₂ O | X | X | X | X | X | X |
| LN ₂ O ₃ | X | X | X | | X | X |
| MgO | X | X | X | X | X | X |
| MnO _x | X | X | | | | |
| Na ₂ O | X | X | X | X | X | X |
| NiO | X | X | | | | |
| P ₂ O ₅ | X | | | X | | |
| SiO ₂ | X | X | X | X | X | X |
| ThO ₂ | X | X | X | | X (with ZrO ₂) | |
| TiO ₂ | X | | | | | |
| UO _x | X | | | | | |
| ZnO | X | | | | | |
| ZrO ₂ | X | X | X | X | X (with ThO ₂) | X |
| Statistics | | | | | | |
| # glass-temp. | 1586 | 1586 | 1586 | 1586 | 1586 | 1586 |
| R ² | 0.981 | 0.978 | 0.977 | 0.964 | 0.977 | 0.977 |
| R ² (Adjusted) | 0.980 | 0.978 | 0.977 | 0.964 | 0.977 | 0.977 |
| R ² (Predicted) | 0.980 | 0.977 | 0.976 | 0.963 | 0.976 | 0.976 |
| s (RMSE) | 0.160 | 0.171 | 0.174 | 0.218 | 0.175 | 0.174 |

Table 3.12. Composition-Temperature Combinations Deleted Prior to Final 12-Component Viscosity Model

| Glass | Study | T (°C) | Reason ^(a) |
|---|--------------------|--------|---------------------------|
| CVS2-68 | Second Hanford CVS | 1250 | Possible Crystals in Melt |
| CVS2-68 | Second Hanford CVS | 1201 | Possible Crystals in Melt |
| CVS2-68 | Second Hanford CVS | 1151 | Possible Crystals in Melt |
| CVS2-68 | Second Hanford CVS | 1150 | Possible Crystals in Melt |
| CVS2-68 | Second Hanford CVS | 1151 | Possible Crystals in Melt |
| CVS2-68 | Second Hanford CVS | 1101 | Possible Crystals in Melt |
| CVS2-68 | Second Hanford CVS | 1101 | Possible Crystals in Melt |
| CVS2-68 | Second Hanford CVS | 1051 | Possible Crystals in Melt |
| CVS2-68 | Second Hanford CVS | 1000 | Possible Crystals in Melt |
| CVS2-68 | Second Hanford CVS | 950 | Possible Crystals in Melt |
| CVS2-79 | Second Hanford CVS | 1252 | Possible Crystals in Melt |
| CVS2-79 | Second Hanford CVS | 1152 | Possible Crystals in Melt |
| (a) These observations were made during the viscosity measurement process, as discussed by Hrma et al. (1994). The T _L of CVS2-68 was >1114°C and that of CVS2-79 was > 1154°C (Hrma et al. 1994). | | | |

Table 3.13. Coefficients, Coefficient Standard Deviations, Fit Statistics, and Property Ranges for the Final 12-Component $\ln(\text{Viscosity})$ Model

| Model Term | Coefficient | SD of Coeff. |
|--|--|--|
| Al ₂ O ₃ | -2.860 | 3.046 |
| B ₂ O ₃ | -13.594 | 1.619 |
| CaO | -25.804 | 2.348 |
| F | -83.850 | 15.630 |
| Fe ₂ O ₃ | -3.490 | 4.082 |
| K ₂ O | -16.589 | 4.535 |
| Li ₂ O | -7.100 | 1.596 |
| LN ₂ O ₃ | 43.46 | 13.530 |
| MgO | -19.102 | 2.104 |
| Na ₂ O | -9.974 | 1.472 |
| SiO ₂ | -10.136 | 0.668 |
| ZrO ₂ | -55.621 | 4.459 |
| Al ₂ O ₃ /T | 27599 | 4213 |
| B ₂ O ₃ /T | 8765 | 2230 |
| CaO/T | 27511 | 3240 |
| F/T | 108852 | 21601 |
| Fe ₂ O ₃ /T | -835 | 5635 |
| K ₂ O/T | 14436 | 6261 |
| Li ₂ O/T | -10377 | 2224 |
| LN ₂ O ₃ /T | -78677 | 18928 |
| MgO/T | 25120 | 2903 |
| Na ₂ O/T | 632 | 2033 |
| SiO ₂ /T | 26427 | 926 |
| ZrO ₂ /T | 95153 | 6156 |
| Statistics | | |
| Number of glass-temperature combinations | 1574 | |
| R ² | 0.979 | |
| R ² (Adjusted) | 0.979 | |
| R ² (Predicted) | 0.978 | |
| s (RMSE) | 0.167 | |
| Property Ranges | | |
| | $\ln(\eta/\text{Pa}\cdot\text{s})$ | $\eta, \text{Pa}\cdot\text{s}$ |
| Minimum | -1.02 | 0.36 |
| Maximum | 5.61 | 273.14 |
| Average | 1.95 | 7.03 |

Note that the appearance of a component in the final viscosity model does not necessarily mean that it has a significant effect on viscosity. It was decided to retain in the model the nine main components (Al_2O_3 , B_2O_3 , CaO , Fe_2O_3 , Li_2O , MgO , Na_2O , SiO_2 , and ZrO_2) studied and included in Hanford property-composition models by Hrma et al. (1994). The component coefficients in Table 3.13 have similar values as those published previously (Hrma et al. 1995b). Briefly, Al_2O_3 , ZrO_2 , and SiO_2 increase viscosity. Alkali oxides (K_2O , Li_2O , and Na_2O) strongly decrease viscosity, while alkali-earth oxides (CaO and MgO), F, and B_2O_3 decrease viscosity to a lesser extent. The component coefficients for activation energy in the Arrhenius equation express the effect of components on the response of the glass to changing temperature (i.e., the viscous “length” of the glass). According to Table 1.13, the leading components that make glass “shorter” with respect to viscosity are F and ZrO_2 . SiO_2 , Al_2O_3 , MgO , and CaO also make glass shorter, though to a lesser extent. The most outstanding components that increase glass “length” are LN_2O_3 and Li_2O . Other glass-“lengthening” components, Fe_2O_3 , Na_2O , and B_2O_3 , are much less effective than Li_2O . K_2O has little effect.

The mol-fraction ranges of the components and temperature ranges for glasses used to fit the viscosity model are given in Tables 3.14 and 3.15. Table 3.14 lists the ranges of mol fractions for the original 61 components (before re-normalization for the components in the model), while Table 3.15 lists the ranges of mol fractions for the 12-component normalized compositions used to develop the model. Glass composition-temperature combinations that were dropped (i.e., not used to develop the model) were not included in determining the component and temperature ranges. The ranges in Tables 3.14 and 3.15 are based on the 1574 composition-temperature compositions used to obtain the 12-component viscosity model.

Considerations such as those discussed for the PCT models at the end of Section 3.2.4 apply to the viscosity model of the form (3.4) with coefficients taken from Table 3.13. Because of the importance of these considerations, they are listed below, appropriately modified for the viscosity model.

- Because the viscosity model was derived using mol-fraction compositions and temperature in Kelvin, using the model requires that compositions be specified in mol fractions of oxides and that temperature be specified in Kelvin. If composition data are initially given in mass fractions, they must be converted to mol fractions before use in the model. Similarly, if temperatures are initially given in degrees Celsius, they must be converted to Kelvin before using the model.
- Mol-fraction compositions must sum to one across the components included in the viscosity model. This will require that mol-fraction compositions containing more than the components included in the model be renormalized before applying the model.
- The viscosity model should only be used for compositions within the original component mol-fraction ranges listed in Table 3.14, the 12-component normalized mol-fraction ranges listed in Table 3.15, and the temperature range given in both Tables 3.14 and 3.15. Predictions obtained for compositions and temperatures outside these ranges are extrapolations and are subject to possible bias.
- The viscosity model was developed with $\ln(\text{Pa}\cdot\text{s})$ values as the response. Hence, predictions resulting from the models are in $\ln(\text{Pa}\cdot\text{s})$ units. Viscosity values (without the natural logarithm) can be determined, if desired, by applying the exponential function (with base e) to the $\ln(\text{Pa}\cdot\text{s})$ values obtained using the viscosity model.

Table 3.14. Mol-Fraction Ranges of the Original Components and Temperature Range for the Data Used to Develop the Final 12-Component Viscosity Model

| Component | Range Used to Develop the Viscosity Model | | Component | Range Used to Develop the Viscosity Model | |
|--------------------------------|---|---------|---------------------------------|---|---------|
| | Minimum | Maximum | | Minimum | Maximum |
| Al ₂ O ₃ | 0.00168 | 0.161 | La ₂ O ₃ | 0 | 0.0031 |
| B ₂ O ₃ | 0.01807 | 0.19651 | MgO | 0 | 0.1297 |
| K ₂ O | 0 | 0.08 | MnO | 0 | 0.0346 |
| Li ₂ O | 0 | 0.20059 | MnO ₂ | 0 | 0 |
| Na ₂ O | 0.04512 | 0.39191 | Nb ₃ O ₅ | 0 | 0.00004 |
| P ₂ O ₅ | 0 | 0.01594 | Nd ₂ O ₃ | 0 | 0.01199 |
| SiO ₂ | 0.36232 | 0.67597 | PbO | 0 | 0.0035 |
| ZrO ₂ | 0 | 0.0802 | PdO | 0 | 0.00071 |
| CaO | 0 | 0.12011 | PdO ₂ | 0 | 0 |
| F | 0 | 0.02984 | Pr ₂ O ₃ | 0 | 0.00001 |
| Fe ₂ O ₃ | 0 | 0.11685 | Pr ₆ O ₁₁ | 0 | 0.00012 |
| FeO | 0 | 0 | Rb ₂ O | 0 | 0.00033 |
| NiO | 0 | 0.034 | ReO ₂ | 0 | 0.00024 |
| MoO ₃ | 0 | 0.0034 | Rh ₂ O ₃ | 0 | 0.00024 |
| SrO | 0 | 0.00364 | RhO ₂ | 0 | 0 |
| TiO ₂ | 0 | 0.039 | RuO ₂ | 0 | 0.00137 |
| Ag ₂ O | 0 | 0.00029 | Sb ₂ O ₃ | 0 | 0.00011 |
| As ₂ O ₃ | 0 | 0.00034 | SeO ₂ | 0 | 0.00201 |
| BaO | 0 | 0.00478 | Sm ₂ O ₃ | 0 | 0.0087 |
| Bi ₂ O ₃ | 0 | 0.00197 | SnO ₂ | 0 | 0.00026 |
| CdO | 0 | 0.00707 | SO ₃ | 0 | 0.0064 |
| CeO ₂ | 0 | 0.0258 | TeO ₂ | 0 | 0.00022 |
| Ce ₂ O ₃ | 0 | 0.00072 | Y ₂ O ₃ | 0 | 0.00909 |
| Cl | 0 | 0.01372 | ThO ₂ | 0 | 0.01538 |
| Co ₂ O ₃ | 0 | 0.0004 | UO ₃ | 0 | 0.00168 |
| Cr ₂ O ₃ | 0 | 0.015 | UO ₂ | 0 | 0 |
| Cs ₂ O | 0 | 0.0027 | U ₃ O ₈ | 0 | 0.00053 |
| CuO | 0 | 0.00229 | V ₂ O ₃ | 0 | 0 |
| Eu ₂ O ₃ | 0 | 0.0086 | WO ₃ | 0 | 0.00031 |
| Gd ₂ O ₃ | 0 | 0.0123 | ZnO | 0 | 0.062 |
| I | 0 | 0.00001 | | | |
| T (°C) | 920 | 1395 | | | |
| T (K) | 1193.2 | 1668.2 | | | |

Table 3.15. Mol-Fraction Ranges of the Normalized 12 Components and Temperature Range for the Data Used to Develop the Final Viscosity Model

| Normalized 12 Components | | |
|--------------------------------|---------|---------|
| | Minimum | Maximum |
| Al ₂ O ₃ | 0.00169 | 0.12721 |
| B ₂ O ₃ | 0.02834 | 0.19807 |
| CaO | 0 | 0.12052 |
| F | 0 | 0.0198 |
| Fe ₂ O ₃ | 0 | 0.07754 |
| K ₂ O | 0 | 0.07504 |
| Li ₂ O | 0 | 0.19534 |
| LN ₂ O ₃ | 0 | 0.02395 |
| MgO | 0 | 0.13404 |
| Na ₂ O | 0.04599 | 0.23582 |
| SiO ₂ | 0.36356 | 0.66436 |
| ZrO ₂ | 0 | 0.08029 |
| T (°C) | 920 | 1395 |
| T (K) | 1193.2 | 1668.2 |

Finally, we emphasize that while the viscosity model of the form (3.4) given in Table 3.13 accounts for approximately 98% of the variation in the $\ln(\text{Pa}\cdot\text{s})$ results, the model may still have some lack-of-fit relative to the true relationship between viscosity and composition. The high R^2 values result from the wide range of viscosity values as a function of temperature. Because of this, any shortcomings in the viscosity-composition relationship aspect of the model do not contribute as much to the R^2 values. As another measure of model goodness, consider the model $\text{RMSE} = 0.1671$, which corresponds to a 16.71 %RSD for viscosity. This %RSD is larger than the expected magnitude of experimental and measurement uncertainty in determining viscosity, although the uncertainty could be larger due to lab-to-lab or time-to-time differences in a combined data set such as that used in this work. In any case, viscosity predictions from the model in Table 3.13 are subject to uncertainty. The uncertainty in predictions for those glasses used to develop the models is displayed graphically in the following section. Despite some uncertainty in predicted viscosity values, the model in Table 3.13 accounts for the vast majority of variation in viscosity values due to composition and temperature effects and should be very useful over the composition and temperature region of glasses used in fitting the model.

3.3.5 Predicted Versus Measured Plot for the Viscosity Model

Figure 3.4 plots the predicted $\ln(\eta)$ values for the 1574 composition-temperature combinations from the final $\ln(\eta)$ model in Table 3.13 versus the measured $\ln(\eta)$ values for those same composition-temperature combinations. The top and right axes are in the original viscosity units, $\text{Pa}\cdot\text{s}$. The bottom and left axes are in $\ln(\eta)$ units, $\ln(\text{Pa}\cdot\text{s})$. The plot also includes a 45° line representing perfect agreement between the predicted and measured viscosity values. Plotted points above the 45° line represent over-predictions, while plotted points below the 45° line represent under-predictions. The plot in Figure 3.4 indicates that the final viscosity model provides a very reasonable fit to the data, but the model does

appear to yield slight under-predictions for compositions having measured $\ln(\eta)$ values near the extremities of the $\ln(\eta)$ range. Such biased model predictions may be due to the nonlinear blending (i.e., curvature and/or interaction) effects of the components not captured by the linear composition terms in the form (3.4), or possibly due to the need to capture the temperature dependence by a Vogel- Fulcher-Tammann equation instead of the Arrhenius equation that model (3.4) is based on.

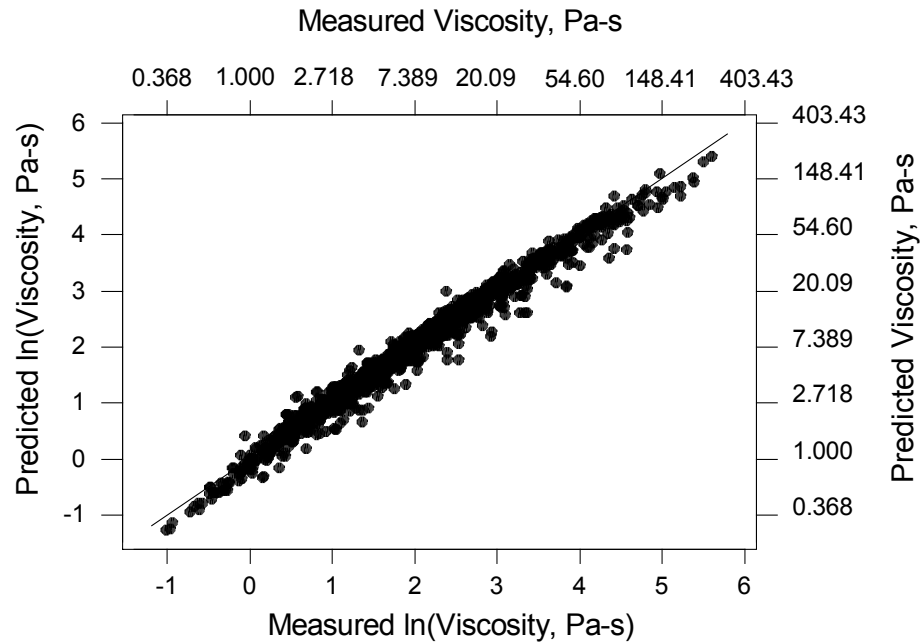


Figure 3.4. Plot of Predicted Versus Measured $\ln(\eta)$ Values

3.4 Models for Liquidus Temperature

This section describes how interim property-composition models were developed for T_L of glasses in the spinel (nominally $[\text{Fe,Mn,Ni}][\text{Fe,Cr}]_2\text{O}_4$) and zircon (nominally ZrSiO_4) primary phase fields. These models are referred to as the spinel model and zircon model, respectively. Models were developed for T_L in these two primary phase fields primarily because those are the only two phases commonly seen in Hanford HLW glasses with sufficient data available to develop models. This section also discusses the subsets of the 824 glasses described in Section 3.1 that were used to develop the T_L models.

3.4.1 General Form of the T_L Models

The general form of the composition models for T_L can be written as

$$T_L = \sum_{i=1}^N T_i x_i \quad (3.5)$$

where x_i is the i -th component mol fraction, T_i is the i -th component partial molar T_L , and N is the number of components used in the model. These models are linear-mixture models of the form (1.4) presented in Section 1.3. Because models discussed in this section are based on $N < 61$ of the components in the database, the mol fractions of the N components selected must be normalized to sum to one before the least-squares regression. Such normalization corresponds to the assumption that the response variable depends only on the relative proportions (mol fractions) of the N selected components. Including components in the model that have little or no impact on T_L behavior will not improve the fit, whereas omitting components that do impact T_L behavior will degrade the fit of the model.

For both T_L models, temperatures in $^{\circ}\text{C}$ were used. In the zircon model, the compositional components are simple oxides or halogens, e.g., Al_2O_3 , B_2O_3 , and F.^(a) In the spinel model, the compositional components are oxides on a single metal basis, e.g., $\text{AlO}_{3/2}$, $\text{BO}_{3/2}$, and SiO_2 . For simplicity, the components are labeled using only the element rather than the transformed oxide, e.g., $\text{AlO}_{3/2}$ is referred to simply as Al.

3.4.2 Zircon Model

Of the 824 glasses that remained in the data set following the initial screening described in Section 3.1, many did not have T_L data or were not in the zircon primary phase field. Of the glasses with T_L values, 70 were within the zircon primary phase field. These glasses came from three studies.

- (1) The Hanford HLW CVS (Hrma et al. 1994) in which 10 glass compositions were varied systematically across relatively broad composition ranges, and many glass properties were measured. The T_L s of these glasses were measured using a gradient-temperature-furnace method that is known to have poor precision due to convective flow of glass in the furnace (Plodinec 1999).

(a) This is equivalent to Method 2 listed in Section 1.3.1 except O is not a separate component. The fraction of oxygen in glass depends on its oxidation-reduction state.

- (2) The Hanford TRU study (Crum et al. 1997) in which the compositions of high-ZrO₂ waste glasses were varied one-component-at-a-time and many-components-at-a-time.
- (3) The INEEL zirconia calcine glass study (Zr) (Vienna et al. 2000) in which four components (Al₂O₃, B₂O₃, Li₂O, and ZrO₂) were varied systematically, and Na₂O and SiO₂ were varied to maintain a melt viscosity of roughly 5 Pa·s at 1150°C.

Three of the 70 glasses—CVS1-06, CVS1-08, and CVS2-80—did not have numeric T_L values. This left 67 possible glasses for model development. Preliminary zircon models were fitted as described in the next section. Three glasses consistently stood out as outliers in the fitted models (CVS2-39, CVS3-21, and Zr-27), which were eventually removed. These three glasses were among only four glasses with normalized B₂O₃ concentration less than 4.34 mol %, along with TRU-B-2. The details of these fits are described below.

The zircon model first considered 16 components (Al₂O₃, B₂O₃, Bi₂O₃, CaO, F, Fe₂O₃, K₂O, Li₂O, LN₂O₃, MgO, MnO, Na₂O, NiO, P₂O₅, SiO₂, and ZrO₂). Statistical least-squares-regression techniques appropriate for mixture-experiment models (Cornell 1990) were applied to fit 16-component models of the form (3.5) for T_L . Then, other mixture-experiment methods were used to identify components that did not sufficiently affect T_L and to develop models of the form (3.5) with fewer than 16 components.

In mixture-model settings such as this study, the effect of a component cannot be completely assessed by comparing the fitted coefficient to the coefficient's standard deviation (e.g., via a t-test). However, comparing a component coefficient to its standard deviation can still be useful as an indicator of the uncertainty associated with the coefficient. Components having coefficients less than 1.5 to 2 times the magnitude of their standard deviations typically do not have strong effects on the property of interest (as discussed previously in Section 3.2.3 for PCT models). The coefficient for each component was also compared to the average property (i.e., T_L) value. Components whose coefficients are close to the average property value may be considered as having a less important effect on a property than components whose coefficients are farther from the average property value. Components that exhibit negligible or less-important effects are candidates to be dropped from a subsequent model.

Table 3.16 shows which components were included and fit statistics for the sequence of zircon model fits. The first fit (a) used all 67 data points and all 16 components. The final model (f) was fit with three data points removed (Zr-27, CVS2-39, and CVS3-21) and with four components removed (Bi₂O₃, LN₂O₃, MnO, and NiO). Details of the final model are discussed below.

The components included in the final model (f) were Al₂O₃, B₂O₃, CaO, F, Fe₂O₃, K₂O, Li₂O, MgO, Na₂O, P₂O₅, SiO₂, and ZrO₂. The coefficients for the 12 components of the final zircon model are given in Table 3.17 along with their respective standard errors. With the exception of K₂O, the standard errors are less than 50% of the T_i values for each component. It can be readily seen that T_L is increased most by ZrO₂ (as could be expected), and moderately increased by F, P₂O₅, Al₂O₃, Fe₂O₃, and MgO. T_L is decreased most by K₂O, followed by Na₂O, and Li₂O. The model has R^2 , R^2 (Adjusted), R^2 (Predicted), Avg. T_L , and s values of 0.926, 0.910, 0.866, 1062.4, and 22.3, respectively. The large difference between R^2 and R^2 (Predicted) suggests that a small number of data points have a significant influence on the model fit. A Cook's D Influence test shows that the points with the highest influence on the model

are CVS2-65 and CVS2-03. The T_L values for these glasses were confirmed from notes and reports. Also listed in Table 3.17 are the ranges of normalized component concentrations of glasses used to fit the zircon model. The sums of these 12 components ranged from 0.9492 to 0.9996 mol fraction before normalization.

Table 3.16. Summary of Zircon Model Fit Sequence

| Model | a | b | c | d | e | f(inal) |
|--------------------------------|----------|----------|----------|----------|----------|----------------|
| Al ₂ O ₃ | X | X | X | X | X | 2592.1 |
| B ₂ O ₃ | X | X | X | X | X | 719.6 |
| Bi ₂ O ₃ | X | X | | | | |
| CaO | X | X | X | X | X | 752.8 |
| F | X | X | X | X | X | 3903.5 |
| Fe ₂ O ₃ | X | X | X | X | X | 2229.0 |
| K ₂ O | X | X | X | X | X | -2705.7 |
| LN ₂ O ₃ | X | X | | | | |
| Li ₂ O | X | X | X | X | X | -247.1 |
| MgO | X | X | X | X | X | 2135.0 |
| MnO | X | X | X | X | | |
| Na ₂ O | X | X | X | X | X | -2113.5 |
| NiO | X | X | X | X | X | |
| P ₂ O ₅ | X | X | X | X | X | 2971.7 |
| SiO ₂ | X | X | X | X | X | 1133.5 |
| ZrO ₂ | X | X | X | X | X | 7814.5 |
| MnO+NiO | | | | | X | |
| R ² | 0.916 | 0.916 | 0.932 | 0.936 | 0.925 | 0.926 |
| R ² (Adjusted) | 0.892 | 0.891 | 0.916 | 0.919 | 0.908 | 0.910 |
| s | 27.85 | 24.60 | 24.52 | 23.68 | 22.61 | 22.30 |
| Average T _L | 1068.5 | 1063.5 | 1067 | 1067.5 | 1062.4 | 1062.4 |
| Number of Glasses | 67 | 66 | 66 | 64 | 64 | 64 |

Figure 3.5 compares the measured T_L values for the data points used to fit the model with predicted T_L values from the final zircon model. The T_L values of all glasses used in model fitting were predicted within 55°C of the measured values (within 33°C for 90% of the glasses). The T_L values of those glasses excluded from the model fit were all under-predicted by more than 100°C. The measurement uncertainty may be different depending on the data source, but is typically $\pm 4^\circ\text{C}$ to $\pm 20^\circ\text{C}$.

**Table 3.17. Zircon Model Coefficients, Standard Errors, and Component Ranges
(in normalized mole fractions of oxides)**

| Component | T_i | Std. Error | Min | Max |
|--------------------------------|----------|------------|--------|--------|
| Al ₂ O ₃ | 2592.09 | 347.70 | 0.0000 | 0.0658 |
| B ₂ O ₃ | 719.62 | 100.83 | 0.0202 | 0.2033 |
| CaO | 752.82 | 165.21 | 0.0000 | 0.1175 |
| F | 3903.48 | 512.13 | 0.0000 | 0.0297 |
| Fe ₂ O ₃ | 2228.99 | 500.84 | 0.0000 | 0.0290 |
| K ₂ O | -2705.71 | 4811.92 | 0.0000 | 0.0059 |
| Li ₂ O | -247.14 | 116.26 | 0.0221 | 0.1894 |
| MgO | 2134.97 | 302.33 | 0.0000 | 0.0642 |
| Na ₂ O | -2113.48 | 153.79 | 0.0389 | 0.1703 |
| P ₂ O ₅ | 2971.73 | 793.18 | 0.0000 | 0.0253 |
| SiO ₂ | 1133.46 | 54.05 | 0.4592 | 0.6452 |
| ZrO ₂ | 7814.54 | 472.36 | 0.0194 | 0.0860 |

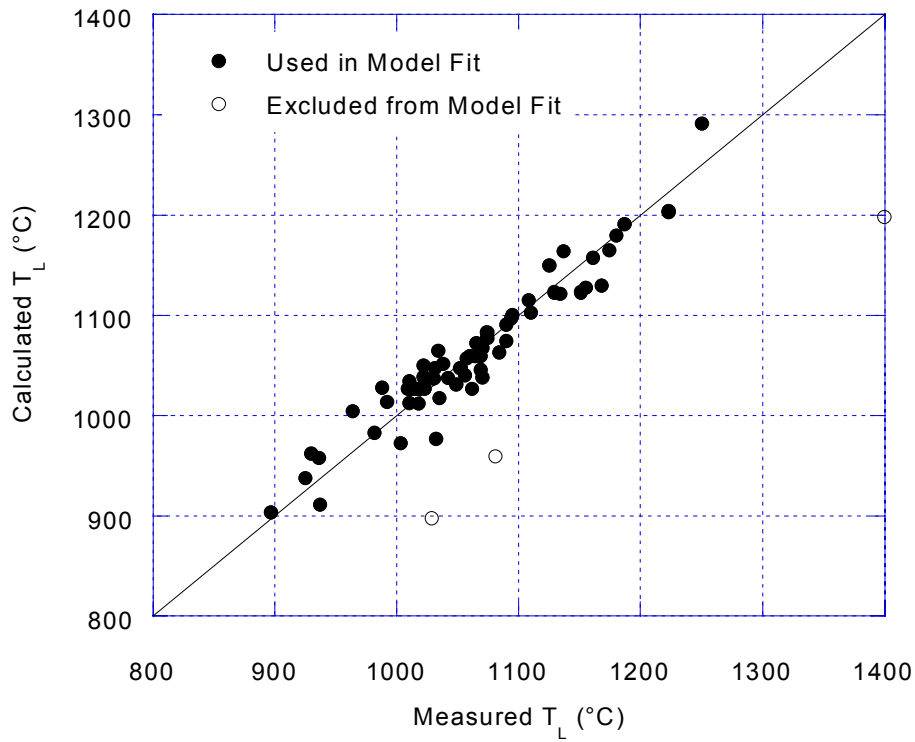


Figure 3.5. Predicted vs. Measured T_L Values for Data Used to Develop the Zircon Model

3.4.3 Spinel Model

Of the 824 glasses that remained in the data set following the initial screening described in Section 3.1, many did not have T_L data or were not in the spinel primary phase field. A total of 209 glasses were within the spinel primary phase field. Twenty-five alkali-aluminosilicate glasses from the HTM study (Vienna et al. 1996b) were excluded because they did not contain boron. Glasses not associated with any systematic study (14) were reserved for model validation, leaving a data set of 170 points. The 170 glasses came from five studies.

- (1) The initial spinel study (SP) (Mika et al. 1997; Vienna et al. 2001) was designed with a central or baseline glass composition (SP-1), which was representative of a typical Hanford HLW glass. The concentrations of 14 glass components were varied one-component-at-a-time from this baseline.
- (2) A study of DWPF glass compositions, labeled SG for Savannah River Glasses, was statistically designed to cover the extremes of outer and inner composition regions centered at the expected DWPF glass composition (Hrma et al. 1999). In this study, the concentrations of 14 components were varied systematically, many-at-a-time.
- (3) A third study, SP×4, was based on the SP-1 baseline glass but varied Al, Cr, Na, and Ni all-at-a-time while maintaining the concentrations of all other components in constant relative proportions (Vienna et al. 2001).
- (4) A small study (5 glasses), SP-MC, was designed to vary several components many-at-a-time and provide better coverage of the combined SP and SG glass-composition region (Vienna et al. 2001).
- (5) An ongoing study to model the behavior of spinel in HLW glass melter (denoted MS for melter study) also generated T_L data for HLW glasses as a function of composition. In this study described by Hrma (1999), several components were varied many-at-a-time to form nine glasses, and then several components were varied one-at-a-time from a baseline glass (MS-7). By one-at-a-time we mean by adding or subtracting single components from the baseline glass. This does literally involve varying components one-at-a-time, because changes in the varied component are offset by changes in other components proportional to their values in the baseline glass.

Preliminary spinel models were fitted as described in the next section. Several glasses were found to be outliers and were excluded from the fit: SG-06 (a, b, and c), SG-18c and SG-52a (found in Hrma et al. 1994 to be inaccurate), SP-B-5 ($x_B = 0.2646$, the highest in the data set), SP-Li-6 ($x_{Li} = 0.2209$, the highest in the data set), SP-Na-1 ($T_L = 1350^\circ\text{C}$, the second highest in the data set), SP-Si-4 ($x_{Si} = 0.2297$, the lowest in the data set), SP3-1envD ($x_{Si} = 0.2507$, the second lowest in the data set), SP-MC-8 (the lowest x_B and x_{Cr} in the data set), and SP-MC-9 ($x_B = 0.1966$, the second highest in the data set). These excluded data indirectly help define the composition space over which Equation (3.2) adequately approximates the T_L – composition relationship.

The spinel model considered 15 components (Al, B, Ca, Cr, Fe, K, Li, Mg, Mn, Na, Ni, Si, Ti, U, and Zr), the only 15 that were varied systematically in the available database. Statistical least-squares regression techniques appropriate for mixture-experiment models (Cornell 1990) were applied to fit

15-component models of the form (3.5) for T_L . All 15 components were found to influence the T_L of glasses within the spinel primary-phase field.

The coefficients for the 15 components of the spinel model are given in Table 3.18 along with their respective standard errors. With the exception of Mn, the standard errors are less than 50% of the T_i values for each component. It can be readily seen that T_L is increased most by Cr and Ni (as could be expected), and moderately increased by Zr, Fe, Mg, Al, U, and Ti. The T_L is decreased most by K, and is also decreased by Na, Li, Mn, B, and Si. The model has R^2 , $R^2(\text{Adjusted})$, Average T_L , and s values of 0.936, 0.930, 1080, and 29.8, respectively. The $R^2(\text{Predicted})$ statistic was not calculated for the spinel model fit. Also listed in Table 3.18 are the ranges of normalized component concentrations of glasses used to fit the spinel model.

Figure 3.6 compares the measured T_L values for the data points used to fit the model with those predicted from the final zircon model. The T_L values of all glasses used in model fitting were predicted within 80°C of the measured values (within 50°C for 93% of the glasses).

Table 3.18. Spinel Model Coefficients, Standard Errors, and Component Ranges (in normalized mol fractions of components) (values in bold represent ranges of model validity that are reduced from the range of current data)

| | Coefficient | Std. Error | Min. | Max. |
|----|-------------|------------|---------|---------|
| Al | 3,063.70 | 115.18 | 0.00551 | 0.15316 |
| B | 548.48 | 104.96 | 0.00000 | 0.17000 |
| Ca | 1,650.97 | 441.82 | 0.00000 | 0.04000 |
| Cr | 31,857.26 | 2,300.57 | 0.00000 | 0.00770 |
| Fe | 3,737.48 | 147.33 | 0.02701 | 0.14689 |
| K | -687.67 | 325.81 | 0.00000 | 0.04000 |
| Li | 156.93 | 72.99 | 0.00000 | 0.18700 |
| Mg | 3,224.76 | 293.06 | 0.00000 | 0.03200 |
| Mn | 32.40 | 565.15 | 0.00000 | 0.02772 |
| Na | -263.75 | 65.42 | 0.08767 | 0.30000 |
| Ni | 13,842.64 | 579.08 | 0.00000 | 0.01969 |
| Si | 986.88 | 52.81 | 0.32000 | 0.48000 |
| Ti | 2,316.13 | 653.04 | 0.00000 | 0.02900 |
| U | 2,919.40 | 1,040.95 | 0.00000 | 0.01060 |
| Zr | 4,073.25 | 454.23 | 0.00000 | 0.02409 |

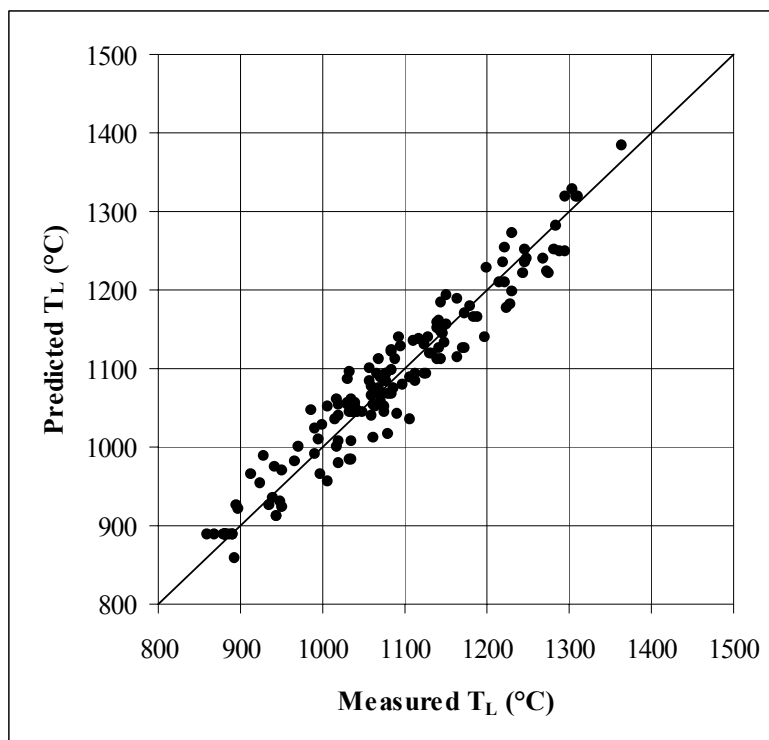


Figure 3.6. Predicted vs. Measured T_L Values for Data Used to Develop the Spinel Model (the line shows equal predicted and measured T_L).

4.0 Model Applications

As mentioned in Section 1.2, HLW glass must meet property and composition constraints. The task is to determine, for a given waste stream, the composition (or composition region) of glass that has admissible properties and the minimum possible volume. Thus, we first need to solve the reverse problem to developing property-composition relationships (i.e., to find the relationship $\mathbf{x} = F_w[\mathbf{p}]$, where $\mathbf{p} \equiv [p_1, p_2, \dots, p_K]$ is the property vector, and the parameter \mathbf{w} stands for waste composition). The next step is to identify the composition region \mathbf{V} of glasses with acceptable properties (the region of glasses made from the given waste composition and meeting all acceptability and processability constraints). Finally, we need to find on \mathbf{V} a glass $\mathbf{x}_0 \in \mathbf{V}$ with maximum waste loading.

HLW glass is produced by adding to the waste glass-forming and modifying additives such as SiO_2 , B_2O_3 , Li_2O , Na_2O , Al_2O_3 as well as some others if necessary. The majority of Hanford wastes contain sufficient concentrations of Al_2O_3 , so only SiO_2 , B_2O_3 , Li_2O , and Na_2O , are added.

Note that \mathbf{x}_0 is subject to Equation (1.2). Property constraints have a form $\pm p_\alpha \leq c_\alpha$, where p_α is the α -th property and c_α is a constant (the \pm sign depends on whether the constraint is an upper or a lower limit). By Equation (1.4), a property constraint assumes the form^(a)

$$\pm \sum_{j=1}^N b_{\alpha j} x_j - c_\alpha \geq 0 \quad (4.1)$$

for each $\alpha = 1, 2, \dots, K$.

Not all properties that limit glass acceptability and processability are known as functions of composition. For example, insoluble noble metals, chromium, sulfates, fluorides, and phosphates may negatively impact glass processing, or the crystallization of nepheline and cristobalite may negatively impact glass acceptability. These limitations are expressed as composition constraints, some of which are provisory and will be used until the nature of the constraining property is mathematically formulated, and the property is measured and evaluated as a function of glass composition. Composition constraints are of a general form

$$\sum_{j=1}^N A_j x_j + A_0 \geq 0 \quad (4.2)$$

Here the A_j values may be 0 for some or most components. Lower and upper bounds on single waste-glass components, on linear combinations of waste-glass components, or on ratios of linear combinations of waste-glass components can all be represented in the form of Equation (4.2). Similarly, lower and upper bounds on waste-glass properties, implemented through property-composition models of the form (1.4) or (1.7), can be represented in the form (4.1).

(a) Inequalities (4.1) and (4.2) follow the convention, common in many statistical software packages, that a nonnegative value means inside (pass) the constraint, while a negative value means outside (fail) the constraint. Thus, their form (in vector notation) is $\pm \mathbf{b} \cdot \mathbf{x} - \mathbf{c} \geq 0$.

The maximum waste-loading requirement can be expressed as

$$W = \max \text{ on } \mathbf{V} \quad (4.3)$$

where W is the waste loading.

Solution of the constrained optimization problem of finding $\mathbf{x}_0 \in \mathbf{V}$ has been outlined several times in the past; see, for example, Hrma and Robertus (1993) and Hrma (1994). This approach to developing HLW glass formulations has been widely applied at Hanford and Idaho (Vienna et al. 2000). Using this approach, glasses are being formulated for experimental melter runs.

Of course, glass for costly melter runs, not to mention vitrification plants, cannot be formulated on computers and paper only. Because of uncertainties in measured data and the property-composition models, the real-property values associated with the “optimized” glass composition are subject to uncertainty and may differ from the model-predicted property values (depending on the accuracy and precision of the property-composition models). Consequently, experimental verification of the acceptability of mathematically optimized glass formulations is absolutely necessary. Models are then used again to ensure that acceptable glass will be made from the full range of expected waste-composition variation.

To verify a mathematically optimized glass formulation, the glass is made in the laboratory, its properties are measured, and the measured and model-predicted property values are compared. If the measured and predicted property values differ beyond an acceptable tolerance (e.g., as determined by applicable statistical model-validation methods), the candidate glass formulation must be corrected. One correction approach is to start with the candidate formulation as a baseline. If the corrected glass composition is \mathbf{x}' , the property value (p_α') of the corrected glass can be expressed as

$$g_\alpha(p'_\alpha) = g_\alpha(p_\alpha) + \sum_{j=1}^N b_{\alpha j} (x'_j - x_j) \quad (4.4)$$

where p_α is the measured property value of the baseline glass. Equation (4.4) is a consequence of Equation (1.4).

However, using Equation (4.4) is insufficient to make the property-composition model appropriate for local sub-regions of glass composition space because local $b_{\alpha j}$ values may be different from the global ones (those determined for a large composition region). Therefore, we need to check the corrected glass and make as many corrections as needed.

Only a glass whose properties have been confirmed by property measurement can be used for a reduced-scale melter run. Such a run may reveal that laboratory testing did not exactly match the glass produced in the melter. For example, glass redox can have a different value because the glass from a laboratory crucible is close to redox equilibrium with furnace atmosphere, whereas the redox state of glass from the melter is governed by the feed-melting reactions. A difference in the redox state might have an impact on some properties, such as liquidus temperature. Any such discrepancies must be

resolved before the glass is committed to large-scale production. Resolutions may include modifying property-composition models to account for redox effects so that such effects are accounted for in future efforts to optimize formulations using the mathematical approach.

Generating a large number of data within a sufficiently close neighborhood of the baseline composition will make the measurement-prediction iterative process described above more effective. A local property-composition model developed from the data would adequately respond to small composition variations around a baseline glass, but could not be extrapolated beyond a close neighborhood of this glass.

Whether the “iterations” or “local response” approach is chosen depends on its effectiveness with respect to the intended application. For processing a large HLW batch of a known average composition with specified variations, a set of local property-composition models might be preferred. In this situation, the detailed knowledge of the local neighborhood is needed to show that the expected composition variations (which are unavoidable in the real process) will yield acceptable glasses. For a short-term medium-scale melter run, one or two composition iterations followed by calculations using Equation (4.4) may be enough.

Additionally, fully radioactive glasses, made from tank sludge treated according to the appropriate flowsheet unit operations, should be fabricated and tested to confirm that the chemical simulation of the waste adequately represented the real waste from a key glass-property perspective.

There are several benefits to developing HLW glasses by the process of: 1) generating property-composition data to cover a HLW glass composition region of interest, 2) developing property-composition models that adequately fit the data, 3) using mathematical constrained optimization methods to develop candidate optimized glass formulations, and 4) verifying or improving the candidate glass formulation (either via local property-composition models or measurement-calculation iterations):

- The process is much faster and cheaper than developing a glass from scratch for each new waste composition for a single waste tank or for 177 waste tanks at Hanford or when a property constraint is changed.
- Step 4) of the process provides strong evidence that the resulting glass composition is the best achievable for given constraints. Stopping after Step 3) would always leave open to question whether a better solution had been missed. As has been repeatedly shown in practice (Music et al. 2000, Peeler et al. 2001, and Vienna et al. 2000), Step 4) does provide for obtaining improved glass formulations over the result after Step 3).
- Additional data are generated in Step 4) that can be used for validating and/or improving the existing property-composition models.

Planning Hanford’s large-scale vitrification program will require considering a large number of parameters and alternatives. To help in making important decisions, optimization programs such as the Hanford Tank Waste Optimization Simulator (HTWOS) have been developed that allow working with compositions of all Hanford waste streams simultaneously. These programs can assess the effects of influential parameters on important global criteria, such as the total number of HLW glass canisters to be produced, and compare alternatives in equipment, schedules, pretreatments, etc.

A useful tool in trying to develop optimal glass formulations is to develop charts that plot glass volume (number of canisters) or cleanup cost estimates as functions of property constraints. The following hypothetical situations illustrate the usefulness of such investigations:

- Suppose a change in a certain property constraint (say, the lower limit for T_L) has a strong impact on the total number of canisters, and thus on the overall cost. This information would provide an incentive for either changing this constraint (if the risk associated with it proves exaggerated) or developing a technology that is not sensitive to the influential property.
- Suppose a certain constraint (say, the upper limit for viscosity) can be changed without a significant impact on the number of canisters, but a change in this constraint would substantially increase melter output (the production rate). In this case, large potential savings can be achieved by formulating glass with a revised constraint (e.g., lower viscosity).
- Suppose a more durable glass (when a less durable product is acceptable) can be produced at the expense of an insignificant increase of the total volume. A decision might be made to produce more durable glass. Such a decision would increase the safety margin for the environment and would be appreciated by the general public.

These and similar studies can be performed only when dependable property-composition models are available and if these models are regularly updated to meet changing demands and changes in input data. Though data generation, development of property-composition models, and development of sophisticated optimization algorithms are complex endeavors, the output can be presented in a form that is easily comprehended and convincing. This would help in adopting unbiased views and informed decisions.

5.0 References

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