Parsimonious viscosity–composition relationships for high-temperature multicomponent glass melts

Pavel Ferkl\textsuperscript{a}, Pavel Hrma\textsuperscript{b} and Albert Kruger\textsuperscript{c}

\textsuperscript{a}Energy and Environment Directorate, Pacific Northwest National Laboratory, Richland, WA, USA; \textsuperscript{b}Department of Energy, AttainX, Support Services Contractor to the Office of River Protection U.S, Richland, WA, USA; \textsuperscript{c}U.S. Department of Energy, Office of River Protection, Richland, WA, USA

**ABSTRACT**

The activation energy of glass melt viscosity, $\eta$, is nearly constant at temperatures at which $\eta < 100$ Pa s. Provided that the preexponential factor is a composition-independent constant, only the activation energy is a function of composition, and viscosity–composition relationships of utmost simplicity can be formulated to provide a welcome advantage in computational fluid dynamics modeling of glass melting furnaces processing multicomponent glasses. Using a dataset with over 3000 viscosity values acquired experimentally for a temperature and composition region of low-activity nuclear waste glasses, we have generated three linear models for viscosity as a function of temperature and composition. Model A quantifies the effects of 20 viscosity-influencing components. Model B achieves a similar prediction accuracy after setting aside volatile components, whose concentrations may vary during glass processing. A parsimonious Model C reduces the number of viscosity-influencing components to a mere seven: Al\textsubscript{2}O\textsubscript{3}, B\textsubscript{2}O\textsubscript{3}, CaO, Li\textsubscript{2}O, Na\textsubscript{2}O, SiO\textsubscript{2}, and Others. In each model, the “Others” component summarizes the fractions of the remaining components. For all three models, the component coefficients are determined with a high confidence (low standard error) and a high coefficient of determination: 0.972 for Model A, 0.970 for Model B, and 0.949 for Model C.

1. Introduction

Glass melting furnaces, whether heated by burning fuel or by dissipating electric power, operate at temperatures at which glass melt viscosity is low, typically 1–10 Pa s, to enhance melt flow for faster melting and to allow efficient homogenization and fining. Below 100 Pa s, glass melt is nearly fully depolymerized, the activation energy of viscous flow is independent of temperature, and the Arrhenius equation adequately represents the viscosity–temperature relationship [1–7]. Because of the constant preexponential factor, the activation energy is then the only composition-dependent parameter, allowing us to express viscosity as a function of temperature and composition with a minimum number of fitting parameters. This is advantageous for both commercial glasses [1,2] and highly multicomponent waste glasses [6].

In this study, we develop Arrhenius models for low-activity waste (LAW) glasses [8] that contain high fractions of alkali oxides, up to 27 mass\% Na\textsubscript{2}O and 5 mass\% Li\textsubscript{2}O, and more than 20 components. These glasses were designed for the Hanford Waste Treatment and Immobilization Plant (WTP) that will vitrify nuclear wastes of a large variety of compositions in Joule-heated melters constraining viscosity to 2–8 Pa s at 1150°C [9].

To guarantee acceptable product quality (chemical durability), to enable easy processing (viscosity in 2–8 Pa s range), and to maximize the fraction of waste components in glass (the waste loading), glass formulation is facilitated by constructing mathematical models that represent property–composition relationship in terms of mathematical functions fitted to a set of experimental data [10]. The models allow formulating glasses that minimize the WTP product volume and shorten the duration of waste cleanup [11]. The viscosity model is also used for simulating the melt flow and temperature fields to facilitate a flawless melter operation and evaluate the effects of melter design features on glass production efficiency [12–14].

Section 2 presents the viscosity approximation function for the Arrhenius model, Section 3 describes the LAW viscosity database, and Section 4 presents the results in terms of component coefficients and component effects, defines linear–nonlinear crossover, and mentions melt structural causes of component effects. Section 5 compares the Arrhenius model with previous approaches to viscosity–composition relationships. Section 6 summarizes major conclusions and outlines an approach to nonlinear models.
2. Theory

Glass melt viscosity, \( \eta \), is a function of glass composition and melt temperature, \( \eta(T, x) \), where \( T \) is the temperature and \( x \) is the composition vector (glass composition as a point in the composition space). It is conveniently displayed as the logarithm of viscosity versus inverse absolute temperature and expressed in the form of the Arrhenius relationship

\[
\ln(\eta) = A + \sum_{i=1}^{N} B_i \frac{x_i}{T},
\]

where \( A = \ln(\eta_\infty) \). Here, \( \ln(\eta) \) is a linear function of the combined composition–temperature variable \( x_i/T \). Eq. (5) is a suitable form for determining the \( A \) and \( B_i \) values by means of regression analysis.

3. Experimental data

The LAW database was created by combining the dataset of 3318 \( x/T \) datapoints for 457 glasses from the Vitreous State Laboratory (VSL) of the Catholic University of America with 569 \( x/T \) datapoints for 97 glasses from the Pacific Northwest National Laboratory (PNNL) [9]. Glass compositions cover the composition region of LAW glasses anticipated for the WTP to support the development of viscosity–composition relationships (Figure 1). Each glass is represented by 1–8 viscosity values [9,17–20]. The temperature range of data in the VSL dataset was 900–1250°C at 50°C steps for most glasses. In the PNNL dataset, 6 viscosity values were measured at 4 temperatures in the order 1150–1050–950–1150–1250–1150°C for most glasses. The repeated measurements at 1150°C were taken to check whether the sample was altered by crystallization or volatilization during the tests.

Table 1 lists and Figure 1 displays the maximum, minimum, and median values of mass fractions of LAW glass components in the PNNL-VSL combined dataset. In Figure 1, the logarithmic scale on the \( y \)-axis was chosen to highlight the compositional data of minor components, which were not statistically designed.

The LAW glasses contain nine major components of median mass fractions larger than 0.01 (\( \text{SiO}_2 \), \( \text{Na}_2\text{O} \), \( \text{B}_2\text{O}_3 \), \( \text{Al}_2\text{O}_3 \), \( \text{CaO} \), \( \text{ZrO}_2 \), \( \text{ZnO} \), \( \text{MgO} \), and \( \text{Fe}_2\text{O}_3 \)) and eight mass fractions at small or trace concentrations. Components present in multiple oxidation states are represented by dominant valence states (\( \text{MnO} \), \( \text{Fe}_{2+} \text{O}_3 \), or \( \text{Cr}_2\text{O}_3 \)), neglecting the change of their redox states with temperature and oxygen partial pressure; typically, 4% Fe is reduced to \( \text{Fe}^{2+} \) and \( \text{Cr}^{3+/6+} \approx 1 \) at 1150°C [21]. For the model development, target glass composition was used except for volatile components \( \text{SO}_3 \) and Cl. Based on data obtained by chemical analysis (not performed for all glasses), the in-glass-retained mass fractions of \( \text{SO}_3 \) and Cl were estimated using the correction functions:

\[
x_{\text{SO}_3} = 0.955x_{\text{Cl},\text{SO}_3} - 0.170x_{\text{SO}_3}^2,
\]

\[
x_{\text{Cl}} = 0.667x_{\text{Cl},\text{SO}_3},
\]

where \( x_{ij} \) is the \( i \)th component target (batched) mass fraction. Eq. (6) is taken from Vienna et al. [9]; Eq. (7) is based on data listed in PNNL reports [17–19] and obtained using linear regression \( (R^2 = 0.962) \). Note that component volatilization is a complex problem, and Cl retention in melts generally differs from the retention measured in crucible tests, e.g. Cl retention 0.544\( x_{\text{Cl}} \) was reported for laboratory-scale melter [22]. After the approximation functions, Equations (6) to (7), were applied, mass fractions of all components were renormalized to sum to one.
Figure 1. Component mass fractions in the PNNL-VSL dataset. Horizontal line represents the median. The box shows region from the first quartile, \( Q_1 \), to the third quartile, \( Q_3 \). The upper whisker corresponds to the largest number smaller than 1.5 IQR above \( Q_3 \) where IQR = \( Q_3 - Q_1 \) is the interquartile region. Similarly, the lower whisker corresponds to the smallest number larger than 1.5 IQR below \( Q_1 \). Individual points show data outside of region delimitated by upper and lower whisker.

Table 1. Maximum, minimum, and median values of component mass fractions of LAW glass components. Components are ordered by median values from largest to smallest. Note that median mass fraction of four components is zero even though their maximum mass fractions are 5–6 mass%.

| Component | min    | median | mean^\[\text{a}\] | max    |
|-----------|--------|--------|-------------------|--------|
| SiO\(_2\) | 0.3355 | 0.4240 | 0.4366            | 0.5225 |
| Na\(_2\)O | 0.0247 | 0.2003 | 0.1776            | 0.2657 |
| B\(_2\)O\(_3\) | 0.0600 | 0.0994 | 0.0909            | 0.1385 |
| Al\(_2\)O\(_3\) | 0.0350 | 0.0701 | 0.0771            | 0.1478 |
| CaO       | 0.0000 | 0.0511 | 0.0416            | 0.1276 |
| ZrO\(_2\) | 0.0000 | 0.0319 | 0.0305            | 0.0676 |
| ZnO       | 0.0100 | 0.0301 | 0.0320            | 0.0581 |
| MgO       | 0.0000 | 0.0115 | 0.0372            | 0.0502 |
| FeO\(_6\) | 0.0000 | 0.0105 | 0.0156            | 0.1201 |
| SO\(_2\)  | 0.0008 | 0.0052 | 0.0094            | 0.0134 |
| K\(_2\)O  | 0.0000 | 0.0050 | 0.0153            | 0.0810 |
| Cl        | 0.0000 | 0.0013 | 0.0044            | 0.0078 |
| P\(_2\)O\(_5\) | 0.0000 | 0.0012 | 0.0024            | 0.0403 |
| Cr\(_2\)O\(_3\) | 0.0000 | 0.0008 | 0.0020            | 0.0063 |
| F         | 0.0000 | 0.0008 | 0.0009            | 0.0131 |
| Others    | 0.0000 | 0.0002 | 0.0031            | 0.0800 |
| Li\(_2\)O | 0.0000 | 0.0000 | 0.0021            | 0.0633 |
| SnO\(_2\) | 0.0000 | 0.0000 | 0.0087            | 0.0505 |
| TiO\(_2\) | 0.0000 | 0.0000 | 0.0085            | 0.0502 |
| V\(_2\)O\(_5\) | 0.0000 | 0.0000 | 0.0043            | 0.0570 |

(a) Component Others combines minor components of marginal effects on the viscosity: CdO, ReO\(_3\), CoO, NiO, Y\(_2\)O\(_3\), Cs\(_2\)O, La\(_2\)O\(_3\), Ba\(_2\)O\(_3\), Bi\(_2\)O\(_3\), SeO\(_2\), BaO, I, PbO, MoO\(_3\), Ga\(_2\)O\(_3\), SnO\(_2\), Ag\(_2\)O, CoO, and WO\(_3\).

(b) Mean composition of all glasses in the dataset, also called centroid. It is used in Section 4.2 as the reference composition.

Figure 2 lists Pearson correlation coefficients between component mass fractions. The largest negative Na\(_2\)O x Li\(_2\)O pairwise correlation (−0.88) is a necessary result of adding Li\(_2\)O to glasses in which the Na\(_2\)O from the waste was in an insufficient fraction for the viscosity constraint of 2–8 Pa s at 1150°C [9]. The effect of this pairwise correlation on the regression analysis is not substantial as seen from small values of standard errors of component coefficients given in Section 4.1. The VSL dataset was not statistically designed to uniformly cover the whole compositional region but consists of viscosity data generated in support of the pilot-scale melter runs. The PNNL dataset was designed to extend the compositional region covered by the VSL database and decrease the correlations between major components. Nevertheless, the combined VSL–PNNL dataset does contain datapoints with a large mass fraction difference from the mean (see individual points in Figure 1).

4. Results

4.1. Model coefficients

The LAW dataset allows us to determine the values of component coefficients only for components that are represented at sufficiently high concentrations. The minor components are grouped into the component Others. The decision which components are included in Others depends on the intention whether to express the effect on viscosity of as many components as possible, or whether to develop a model with as few component coefficients as possible. Below we formulate models with three coefficient sets, two for these extreme aspects and one as a compromise.

To obtain values of coefficients \( A \) and \( B \), Eq. (5) was fitted to data using ordinary least-squares method. The ability of models to predict viscosity of glasses within the LAW composition region was evaluated using a training set consisting of randomly selected 80% of glasses from the whole dataset while the remaining 20% made the testing set. The accuracy metric was defined by the coefficient of determination, \( R^2 \). As stated in Section 2, \( B \) is virtually independent of temperature at \( \eta < 10^7 \) Pa s, where \( z = 2 \). Therefore, 228 datapoints with \( \eta > 100 \) Pa s were removed from both
training and testing set, leaving 2921 datapoints in the training set and 738 in the testing set. The choice of $z$ is explored and justified in Section 4.3.

Table 2 summarizes and Figure 3 displays the values of fitted $B_i$ and their standard errors for three versions of the model. Model A was fitted to the data of glass components with the third quartile of mass fraction $Q_3 \geq 10^{-3}$, presented in Figure 1 and Table 1; the remaining components, considered as minor, are listed in the Table 1 footnote and are treated as a single component called Others. In Model B, components present in low concentrations with the largest standard errors of $B_i$ values (Cl, F, and Cr$_2$O$_3$) were added to Others, reducing the number of parameter values ($A$ and $B_i$) from 21 of Model A to 18 in Model B while the $R^2$ retained its high value of 0.98 (Table 3). Model C results from an attempt to reduce the number of variables to a minimum necessary for predicting viscosity with an $R^2 \geq 0.95$. As in the case of Model B, the extra components were moved to Others. The number of parameters was reduced to 8 (including parameter $A$).

Table 3 summarizes the fitted values of parameter $A$ and the regression statistics. As expected, $R^2$ on the training set decreases with decreasing number of independent parameters. $R^2$ on the testing set is smaller but still close to $R^2$ on the training set for all three models, indicating that the models represent the data well and thus are qualified to estimate melt viscosity of $\eta < 100$ Pa s for other yet untested LAW glasses within the composition region defined in Table 1. The adjusted coefficient of determination, $R^2$, is highest for Model A, implying that the inclusion of F, Cl, and Cr$_2$O$_3$ is beneficial and does not lead to overfitting despite their relatively high standard errors.

Figure 4 plots measured viscosity versus estimated viscosity by Model A. The datapoints with $\eta > 100$ Pa s were excluded from fitting. Most of these data lie outside of the validity range of the Arrhenius relationship with temperature-independent activation energy. This is further discussed in Sections 4.3 and 5. Of
Figure 3. Values of fitted \( B_i \) component coefficients for individual models. Notches display standard error of fitted parameter (note their small values, <6% for most components). Dotted lines display the minimum and maximum estimated values of \( B \), Eq. (4), and the \( B \) value for reference glass, \( B_{ref} \) (defined in Section 4.2), for Model A.

Table 3. Fitted parameter \( A \) and statistics of the fitting.

|                  | Model A | Model B | Model C |
|------------------|---------|---------|---------|
| \( N = \ln(\eta_0/\text{Pas}) \) | 20      | 17      | 7       |
| \( \eta_{\text{ref}} \text{ Pas} \) | 3.79E–06 | 3.75E–06 | 4.07E–06 |
| A Standard Error | 0.0417  | 0.0429  | 0.0571  |
| \( R^2 \) (train) | 0.981   | 0.979   | 0.963   |
| \( R^2 \) (test)  | 0.972   | 0.970   | 0.949   |
| RMSE (train)      | 0.169   | 0.174   | 0.232   |
| RMSE (test)       | 0.199   | 0.204   | 0.267   |

4.2. Component effects

The \( B_i \) coefficients are partial specific activation energies for the composition region of LAW glasses. They are all independent, but the mass fractions are not because \( x_i = 1 - \sum_j x_j \). Therefore, changing \( x_i \) can occur only at the expense of one or more other components. Using this identity, Eq. (4) can be written as

\[
B = B_i x_i + \sum_{j \neq i} B_j x_j = B_i + \sum_{j \neq i} (B_j - B_i) x_j.
\]

Generally, the \( i \)th component effect is the response of the mixture property to the addition of \( i \)th component to the mixture; in the case of the activation energy, \( \beta_i = d\eta/dx_i \). Adding an \( i \)th component to the mixture leaves the proportions of mass fractions of all other components unchanged. The mass balance requires that the \( j \)th component change is \( dx_j/dx_i = -x_j/(1- x_i) \). Using this identity, the above expression for \( B \) and the definition of \( \beta \), we can arrive at the expression

![Figure 4](image-url)

Figure 4. Estimated \( \eta_i \) vs measured \( \eta_{\text{ref}} \) viscosity. Model A was used for viscosity estimation. Viscosity is in Pa s. Datapoints are color-coded by their (a) set label and (b) temperature.
\[ \beta_i = \frac{B_i - B}{1 - x_i}, \]  
(8)

which indicates that components with \( B_i < B \) decrease \( B \) \((dB/dx_i < 0)\) and those with \( B_i > B \) increase \( B \) \((dB/dx_i > 0)\) when added to the glass, and hence, by Eq. (5), decrease or increase melt viscosity regardless of the melt temperature. Moreover, the \( i \)th component has an increasing/decreasing effect on the viscosity of all glasses within the composition region under study if the \( B_i \) value is larger/smaller than the maximum/minimum \( B \) value on the region.

**Figure 5** shows the values of \( \beta_i \) evaluated for the reference composition designated as the average composition of all glasses in the combined dataset. The green dotted line in Fig. 3 represents the reference glass activation energy, \( B_{ref} = 1.99 \times 10^4 \) K, and the maximum and minimum \( B \) values are indicated.

**Figure 5.** Component effect on melt viscosity at the reference composition calculated by Eq. (8).

**Figure 6.** Response trace plots calculated using Eq. (8) with model A values for \( B_i \) values and \( B = B_{ref} \).

---

**Figure 6.** Response trace plots calculated using Eq. (8) with model A values for \( B_i \) values and \( B = B_{ref} \).
4.3. Linear–nonlinear crossover

Recall that the transition from the near-linear to nonlinear branch of the ln(\eta) versus T^{-1} function occurs at the viscosity 10^2 Pa s. At \eta > 10^2 Pa s, the Arrhenius model systematically underpredicts viscosity. Thus, the value of z marks the transition from low-viscosity simple Arrhenian liquid with a constant activation energy to non-Arrhenian glass-forming melt with a progressively increasing activation energy [23,24]. As Fig. 4 shows, the transition is gradual because, as mentioned in Section 4.1, the temperature at which \eta = 10^2 Pa s is different for each glass depending on the composition. Yet for practical purposes – mainly for approximating the ln(\eta) = A + B(x)/T relationship with a minimum number of coefficients – it appears convenient to define a crossover viscosity, \eta_c = 10^2 Pa s, that separates out the data for fitting the Arrhenius model.

Fig. 7 displays signed squared residuals, sgn(\epsilon)\epsilon^2, versus log (\eta_M), where \epsilon = \ln(\eta_M/\eta_e)/\ln(\eta_e/\eta_\infty) is the relative residual, \eta_e is the viscosity estimated by Eq. (5), and \eta_M is the measured viscosity. The value of sgn(\epsilon)\epsilon^2 = a10^b\log(\eta_e), a function fitted to data, where \(a\) and \(b\) are constants, becomes increasingly positive at \eta_M > \eta_c = 10^2 Pa s, which was our original estimate for the Arrhenius model validity limit (the z value in Section 2); at \eta_M = 10^2 Pa s, \epsilon = 1.7 \times 10^{-2}.

Fig. 8 shows that the distribution residuals for \eta_M > \eta_c is visibly shifted relative to points in the training and testing sets. The two peaks overlap, indicating that some data that belong to the linear branch of the ln (eta) = f(T^{-1}) function were deleted from the model dataset, a price for selecting a single value of the crossover viscosity. This conservative choice possibly avoided “outlying” data from influencing values of the component coefficients.

4.4. Molar coefficients

Property models that are intended for application in glass technology are formulated in terms of mass fractions. The reason is that the raw materials are being weighed and the results of chemical analyses are reported in mass percent. Moreover, melter feeds for nuclear waste vitrification are mixtures of radioactive wastes and glassforming and modifying additives, both chemicals and minerals. Wastes and minerals are materials of complex chemistry that is expressed in mass fractions of oxides and elements. To avoid excessive computation in model applications, the component coefficients listed in Table 2 are based on mass fractions rather than mole fractions. However, mole fractions are of interest from the point of view of the glass structure. The ith component mol fraction, \omega_i, can be obtained from the mass fraction using the formula \omega_i = \frac{M_i}{M}, where \(M_i\) is the ith component molar mass and \(M = 1/\sum_{i=1}^{N} \frac{\omega_i}{M_i}\) is the average molar mass. Tables 4 and 5 list the molar coefficients, \(P_i\), and the statistical metrics obtained via regression analysis for the 17-component model (Model B) by fitting Eq. (1) with \(B = \sum_{i=1}^{N} P_i\omega_i\).

![Figure 7](image-url)  
**Figure 7.** Residual of Arrhenius model versus measured viscosity. Red dotted line shows fitted equation sgn(\epsilon)\epsilon^2 = 1.832 \times 10^{-6}10^{0.6\log(\eta_e)}.
4.5. Correlations and causation

As mentioned in Section 4.2, the component coefficients are partial specific or partial molar material properties. Although we call them empirical coefficients or adjustable parameters, they are, in fact, measured properties evaluated by means of regression analysis. They quantify the effects of chemical components on material properties and behavior by means of correlations based on extensive databases from composition variation projects. To predict the material properties of glasses as functions of composition, without a need to design and execute costly and time-consuming composition variations projects, is an objective of fundamental models based on quantum mechanics, thermodynamics (the modified quasichemical model of Pelton and Blander [7,25–28]), or network topology [29–31].

The temperature-dependent topological constraint theory, originally developed by Phillips and Thorpe [32,33] and generalized by Gupta and Mauro [34], successfully predicted glass melt viscosity for simple glasses [35–37]. These fundamental models claim a general validity, free of restrictions on composition regions or approximation functions. Their ultimate goal, once they are developed to the degree at which viscosity can be predicted accurately for multicomponent glasses, is optimizing glass compositions for manufacturing and application. However, matching the empirically determined coefficients is their litmus test, the crucial challenge and measure of success.

The component effects (Fig. 5) reflect the general trends of network formers, which strengthen glass structure, and network modifiers, which weaken the glass structure [38]. Silica, the major network former, increases viscosity, whereas alkali oxides and alkaline earth oxides decrease viscosity by increasing the fraction of nonbridging oxygens, breaking the linkages between silicon tetrahedra. Moreover, Al₂O₃ increases viscosity in high alkali glasses, such as the LAW glasses, by bonding alkali and alkaline earth ions through the charge-compensating effect [39,40]. Various other tetra-valent oxides, such as ZrO₂ [41,42] and SnO₂ [43], increase viscosity by their need to charge compensate their six-coordinated ions.

Both β, and β, values of alkali oxides, and, hence, glass viscosity, increase in the order of the ionic potentials: Li₂O < Na₂O < K₂O [44]. Intriguingly, as observed in a wide range of commercial glasses [2,15,45] and high-level waste glasses [2,5,6], alkaline earth oxides exhibit the opposite trend: CaO decreases viscosity significantly more than MgO. In aluminosilicate melts, the anomalous effect of MgO is being attributed to the effect of Mg⁡²⁺ on aluminum speciation [46,47]. This agrees with Kim et al. [27], according to whom the Gibbs energy of tetrahedrally coordinated charge-compensated Al in the silica network is higher for NaAl⁡³⁺ species than for KAl⁡³⁺ species but lower for MgAl⁡²⁺ species than for CaAl⁡²⁺ species. However, in the alkali-free system CaO–MgO–SiO₂ at high temperatures (>1400°C) at which the melts exhibit Arrhenius behavior, this effect occurs only in melt with less than 55 mass% SiO₂ [26].

In LAW glasses, high-level waste glasses [4–6] and various other glass families [4,15], the predominantly covalent boron weakens the silicate network slightly more than calcium ions when expressed in terms of oxide fractions (see Fig. 6a) [4–6]. In the binary B₂O₃–CaO system [28], viscosity is nearly independent of the CaO/B₂O₃ ratio (within 10 to 30 mol% CaO). In E-glasses, soda-lime glasses, and fiber glasses, B₂O₃ and CaO both decrease high-temperature viscosity, but in various degrees [1].

Fluorine reduces viscosity in LAW glass (Fig. 6b), as well as in other silicate and borosilicate glasses, by replacing oxygen bridges with Si–F bonds [48]. Chlorine and SO₃ tend to decrease viscosity [15] in commercial and simple glasses, but, as Fig. 5 shows, these less soluble components increase the viscosity of high-sodium LAW glasses, possibly by trapping alkali ions in nano-inclusions of alkali salts, which also contain chromate [49] and P₂O₅ [50,51].

Various minor components, Cr₂O₃, Fe₂O₃, MgO, SnO₂, TiO₂, V₂O₅, and ZnO, are added to the LAW glass for various reasons. Chromium oxide saturates

---

Table 4. Component (molar) coefficients, \( P_i \), and their standard errors in 10⁶ K.

| Component | \( P_i \) | St. Err. |
|-----------|------------|----------|
| Li₂O      | -0.444     | 0.026    |
| V₂O₅      | -0.254     | 0.124    |
| Na₂O      | 0.437      | 0.017    |
| B₂O₃      | 0.547      | 0.025    |
| K₂O       | 0.606      | 0.042    |
| CaO       | 0.993      | 0.015    |
| ZnO       | 1.248      | 0.068    |
| TiO₂      | 1.419      | 0.072    |
| Fe₂O₃     | 1.482      | 0.061    |
| MgO       | 1.666      | 0.036    |
| Others    | 1.714      | 0.066    |
| SiO₂      | 2.951      | 0.011    |
| P₂O₅      | 3.294      | 0.183    |
| SnO₂      | 3.634      | 0.095    |
| ZrO₂      | 3.675      | 0.071    |
| SO₂       | 3.939      | 0.210    |
| Al₂O₃     | 4.552      | 0.036    |

Table 5. Fitted parameter A and fitting statistics.

|        | N |        |
|--------|---|--------|
| A = \( \ln(\rho/\text{Pas}) \) | 17 | -12.496 |
| \( \eta \_r \_m \) (Pa s) | 3.74E-06 |
| A Standard Error | 0.0419 |
| \( R^2 \) (train) | 0.980 |
| \( R^2 \) (test) | 0.971 |
| \( R^2 \) (train) | 0.980 |
| \( R^2 \) (test) | 0.970 |
| RMSE (train) | 0.170 |
| RMSE (test) | 0.203 |
5. Discussion

5.1. Nonlinear ln(η) = f(T⁻¹) relationships for interpolation

A range of analytical functions with two or more fitting parameters can be used for interpolation within a narrow temperature interval of η(T) data spread on both sides of the crossover viscosity (see Figures 4 and 7). Whatever approximation function is selected, it faces major problems. First, the number of composition-dependent coefficients increases in proportion to the temperature-dependent parameters. Second, a function fitted to a narrow (10²–10⁴ Pa s) nonlinear segment of the ln(η) versus T⁻¹ relationship does not represent viscosity beyond the temperature interval of data. Thus, nonlinear relationships fitted to the temperature interval form 900°C to 1250°C of the LAW dataset cannot be used for estimating viscosity during melter idling, where temperature may drop as low as 850°C, or for induction-heated melters, where temperature can increase as high as 1450°C.

Following Feng et al. [60], Piepel at al [16,61], used an approximation function

\[ \ln[\eta(T, x)] = A(x) + \frac{B(x)}{T^2}. \] (9)

where the fitting parameters A and B were treated as polynomial functions of composition, A, as a first-order polynomial and B as either a first- or a second-order polynomial. This model with nearly 2 N coefficients for the first-order version (somewhat less than 2 N because some components have zero B, values) is confined to data within 950°C and 1250°C. It is fully adequate for the LAW glass dataset but breaks down outside its temperature range and composition region.

Viscosity temperature relationships that have been developed for the technological viscosity interval spanning 12 orders of magnitude require three or more temperature-independent parameters. The most successful among three-parameter relationships is the Vogel–Tammann–Fulcher (VFT) equation [62–64]:

\[ \eta = \eta_{\text{VFT}} \exp \left( \frac{-B_{\text{VFT}}}{T - T_0} \right). \] (10)

where \( \eta_{\text{VFT}} \), \( B_{\text{VFT}} \), and \( T_0 \) are adjustable coefficients. Alternatively, several authors expressed viscosity as a power-law function of inverse temperature in the form ln(η) = \( A + \left( \frac{T}{T_n} \right)^\alpha \), where A, \( T_n \), and \( \alpha \) are fitting parameters [65–68]. By the VFT equation, viscosity approaches infinity as \( T \to T_0 \) deeply below the glass transition temperature when glass is rheologically a brittle elastic solid. By the power-law relationship, as well as by the MYEGA equation [69], ln(η) = \( A + \left( \frac{L}{T} \right) \exp(C/T) \), where A, C, and L are fitting parameters, viscosity approaches infinity only at the absolute zero temperature. All the above equations converge to the Arrhenius equation, but the convergence is overly slow; none approaches Arrhenius behavior at 100 Pa s. The Douglas equation [70] and several others, such as Doremus [71] and Ojovan [72] equations, converge to Arrhenius relationship at both low and high temperatures, but, inevitably, require more than three parameters.

Any smooth monotonous function can be used for data interpolation. However, fitting a three- or more-parameter equation to a narrow range of data does not improve model performance. Such a model is over-parameterized for the intended application (the formulation of glasses for melters operating at 1150°C and it breaks down outside the experimental region where it is not supported by data. Vienna et al. [9,11] used the VFT equation while focusing on a single temperature, namely 1150°C, the melt operating temperature, \( T_{\text{MO}} \), of WTP melters. The value of \( \eta_{\text{MO}} = \eta(T_{\text{MO}}) \) was obtained through fitting Eq. (10) to data for each glass individually. Polynomial approximation functions were obtained by fitting to \( \eta(T_{\text{MO}}, x) \) data. The linear model

\[ \ln(\eta_{\text{MO}}) = \sum_{i=1}^{N} h_i x_i, \] (11)

where \( h_i \) is the i\textsuperscript{th} component coefficient and N is the number of viscosity-affecting components, estimates the viscosity at a single temperature (\( T_{\text{MO}} \)) using \( N \) fitted coefficients. Unlike the Arrhenius model, Eq. (5), which has \( N + 1 \) fitted coefficients and is based on a subset of data with \( \eta < \eta_C \). Eq. (11) is based on all measured data on both sides of linear–nonlinear crossover.
Table 6 lists and Fig. 9 illustrates the single-temperature coefficients $h_i$ from Vienna et al. [11] denoted as Model V16 and Vienna et al. [9] denoted as Model V21 and compares them with coefficients $h_i = A + B/T_{MO}$ obtained from Models A–C for $T_{MO} = 1423$ K (coefficients $A$ and $B_i$ are listed in Tables 2 and 3). Model V21 was created from the same database as Models A–C, except that it used 534 glasses compared to 554 glasses used in this work. Model V16 used a smaller database using 429 LAW glasses. The Model V16 data were on the linear branch of the $\ln(\eta) = f(T^{-1})$ function, the maximum viscosity in the dataset being 20 Pa s, significantly less than the 100 Pa s crossover.

The difference between Model A and Model V21 in $h_i$ coefficients is the largest for Cl, SO$_2$, and Others, the former two of which are volatile and present in small fractions. The unusually high component coefficient of Others in Model V21 is associated with the exclusion of glasses containing $\geq 0.02$ Others (including glasses

![Figure 8](image-url) Figure 8. Probability histogram of residuals for training, testing, and excluded points for Model A.

![Figure 9](image-url) Figure 9. Comparison of $h_i$ component coefficients for different models; $h_i$ coefficients provide $\ln(\eta_{MO})$ at 1150°C where $\eta_{MO}$ is in Pa s.

| Component | Model V16 | Model V21 | Model A | Model B | Model C |
|-----------|-----------|-----------|---------|---------|---------|
| Li$_2$O   | -32.673   | -32.379   | -35.110 | -35.252 | -30.178 |
| F         | -17.755   | -14.995   |         |         |         |
| Na$_2$O   | -9.308    | -9.506    | -10.195 | -9.950  | -7.963  |
| K$_2$O    | -7.447    | -7.801    | -8.249  | -8.159  | -7.843  |
| Cr$_2$O$_3$ | -11.111  | -8.129    |         |         |         |
| CaO       | -7.605    | -7.657    | -7.517  | -7.630  | -7.685  |
| K$_2$O    | -4.656    | -4.490    | -4.368  | -5.187  |         |
| V$_2$O$_5$ | -2.649    | -3.407    | -3.991  | -4.412  |         |
| TiO$_2$   | -4.933    | -3.285    | -3.226  | -1.770  |         |
| MgO       | -4.263    | -4.033    | -3.181  | -2.384  |         |
| ZnO       | -4.513    | -3.482    | -2.436  | -3.050  |         |
| Fe$_2$O$_3$ | -0.111   | -0.936    | -0.309  | -0.129  |         |
| Others    | 2.740     | 34.736    | 0.794   | -0.347  | -0.669  |
| SnO$_2$   | 4.731     | 4.952     | 6.858   | 6.339   |         |
| P$_2$O$_5$ | 7.941     | 8.787     | 7.395   | 5.342   |         |
| ZrO$_2$   | 6.919     | 6.398     | 8.123   | 7.973   |         |
| SiO$_2$   | 8.881     | 8.915     | 8.957   | 8.881   | 8.311   |
| SO$_3$    | 4.190     | 12.665    | 12.204  |         |         |
| Al$_2$O$_3$ | 11.670   | 12.217    | 12.691  | 12.960  | 13.994  |
| Cl        | 13.899    | 22.922    |         |         |         |

(a) In Ref. [9], viscosity units are dPa s. Accordingly, in Ref. [9], Table 5.3, the $h_i$ values are larger by ln(10).
with \( \geq 0.02 \) Ga\textsubscript{2}O\textsubscript{3}, Y\textsubscript{2}O\textsubscript{3}, La\textsubscript{2}O\textsubscript{3}, and SrO). The remaining fraction of Others was extremely small (<0.0001), thus having little effect regardless of the coefficient value. Also excluded were glasses with \( \geq 0.0091 \) F and 0.06 K\textsubscript{2}O.

Table 7 shows the coefficient of determination for single-temperature models, Eq. (11), applied to the full database of 554 glasses with component coefficients listed in Table 6. Note that the lower \( R^2 \) value of Model V21, which, as argued in Section 5.2, was associated with a lower prediction accuracy of the two-step evaluation. The \( R^2 \) of Model V21 increased to 0.943 after the outliers mentioned above were excluded.

### 5.2. Linear model recovery from a single-temperature model

The linear \( \ln(\eta) = f(T^{-1}) \) relationships, Eq. (5), can be recovered from a single-temperature viscosity model, Eq. (11), provided that the \( A \) value is known, or at least correctly guessed, and that the viscosity value lies within the low-viscosity range of \( \eta < 100 \text{ Pa s} \), which is indeed the case for viscosity at \( T_{MO} = 1423\text{K} \), where \( \eta_{MO} \) varies between 0.47 and 35.4 Pa s for LAW glasses in the database. By Eq. (1),

\[
\ln(\eta_{MO}) = A + \frac{B}{T_{MO}}.
\]

Using Equations (4), (11), and (12), we obtain the component coefficients for the activation energy of low-viscosity range as follows:

\[
B_i = T_{MO}(h_i - A).
\]

Table 8 lists the \( B_i \) values of the Arrhenius model recovered using Eq. (13) with \( A = -12.48 \) and \( h_i \) values listed in Table 6 for Model V16 and Model V21. As in the case of coefficients \( h_i \), the difference between Model A and Model V21 in \( B_i \) coefficients is the largest for Others, Cl, and SO\textsubscript{3}.

Model V16 and Model V21 were created in two steps by fitting Eq. (10) to data for each glass separately and then by fitting polynomial model, Eq. (11), to \( \eta_{MO}(x) \) values. This two-step process avoided overparameterization caused by treating more than one parameter as a function of composition. The values of \( R^2 \) coefficients, listed in Table 9, are close even though Models V16 and V21 used the two-step process, which is generally less favorable than the one-step fitting of temperature- and composition-dependent model.

### 5.3. Extrapolation problem, examples, and resolution

Viscosity–temperature relationships that are designed for application in glass technology from melting to annealing cover viscosity values over 12 orders of magnitude. Although the activation energy is virtually constant for \( \eta < \eta_c \approx 100 \text{ Pa s} \), it may be 10 times higher at the glass transition temperature \( (T_g) \). As Figures 4 and 7 indicate, LAW glass viscosity data cover only 1 order of magnitude of the nonlinear segment of the \( \ln(\eta) \) versus \( T^{-1} \) relationship (between \( 10^2 \) and \( 10^3 \) Pa s). One cannot expect to obtain physically meaningful values of parameters from fitting a function designed to cover 12 orders of magnitude to a 1 order of magnitude interval of data. Experimental errors from even a very precise measurement can thus result in unacceptable errors in extrapolating an otherwise physically well-designed function by several orders of magnitude beyond the experimental range of data. To demonstrate this, we selected, in Table 10, five glasses from the LAW dataset [18], three random (LP2-OL-01-3, LP2-OL-12, and LP2-OL-22) and two borderlines (LP2-OL-13 and LP2-OL-05).

### Table 8. Component coefficients \( B_i \) (10^4 K) for current and literature models.

| Component | Model V16 | Model V21 | Model A | Model B | Model C |
|-----------|-----------|-----------|---------|---------|---------|
| Li\textsubscript{2}O | -2.874 | -2.832 | -3.220 |
| F | -0.751 | -0.357 |
| Na\textsubscript{2}O | 0.451 | 0.423 | 0.326 |
| B\textsubscript{2}O\textsubscript{3} | 0.716 | 0.666 | 0.603 |
| Cr\textsubscript{2}O\textsubscript{3} | 0.195 | 0.620 |
| CaO | 0.694 | 0.686 | 0.707 |
| K\textsubscript{2}O | 1.133 | 1.126 |
| V\textsubscript{2}O\textsubscript{3} | 1.399 | 1.291 | 1.208 |
| TiO\textsubscript{2} | 1.074 | 1.308 | 1.317 |
| MgO | 1.169 | 1.202 | 1.324 |
| ZnO | 1.134 | 1.280 | 1.430 |
| Fe\textsubscript{2}O\textsubscript{3} | 1.760 | 1.643 | 1.732 |
| Others | 2.166 | 1.719 | 1.889 |
| SnO\textsubscript{2} | 2.449 | 2.481 | 2.752 |
| P\textsubscript{2}O\textsubscript{5} | 2.906 | 3.026 | 2.829 |
| ZrO\textsubscript{2} | 2.760 | 2.686 | 2.912 |
| SiO\textsubscript{2} | 3.040 | 3.045 | 3.051 |
| SO\textsubscript{3} | 2.372 | 3.579 |
| Al\textsubscript{2}O\textsubscript{3} | 3.437 | 3.514 | 3.582 |
| Cl | 3.754 | 5.038 |

### Table 9. Accuracy of temperature-dependent models recovered from single-temperature models using Eq. (13) compared to Model A from Section 4.1.

| Component | Model V16 | Model V21 | Model A |
|-----------|-----------|-----------|---------|
| \( R^2 \) (train) | 0.976 | 0.971 | 0.981 |
| \( R^2 \) (test) | 0.967 | 0.903 | 0.979 |

Note that Vienna et al. [9] recommend for application at the WTP a partial quadratic model with 18 linear terms and three quadratic terms, namely Al\textsubscript{2}O\textsubscript{3} × Na\textsubscript{2}O representing the charge compensation effect [73], Li\textsubscript{2}O × Na\textsubscript{2}O for mixed alkali effect [74], and Li\textsubscript{2}O × Li\textsubscript{2}O, a squared term simulating the mutual influence of binary interactions with various oxide components.
Table 10. Viscosities (in Pa s) of five selected LAW glasses [18].

| $T$ (°C) | 950 | 1050 | 1150 | 1150 | 1150 | 1250 |
|----------|-----|------|------|------|------|------|
| LP2-OL-01-3 | 139.00 | 28.70 | 8.53 | 8.59 | 8.61 | 3.24 |
| LP2-OL-05 | 165.87 | 21.20 | 6.77 | 6.84 | 7.00 | 2.77 |
| LP2-OL-12 | 4.87 | 1.76 | 0.80 | 0.80 | 0.81 | 0.42 |
| LP2-OL-13 | 9.10 | 3.19 | 1.32 | 1.33 | 1.35 | 0.64 |
| LP2-OL-22 | 51.58 | 10.60 | 3.20 | 3.24 | 3.22 | 1.27 |

Table 11. Values of Arrhenius and VFT parameters for ln($\eta$/Pa s).

|        | Arrhenius | VFT            |
|--------|-----------|----------------|
|        | Eq. (1)   | Eq. (10)       |
| $A$    | $B$ (K)   | $A_{VFT}$      |
| $B_{VFT}$ (K) | $T_0$ (K)     |
| LP2-OL-01-3 | -13.304 | 22.015 | -7.387 | 8432 | 539 |
| LP2-OL-05 | -12.486 | 20.534 | -3.265 | 2694 | 901 |
| LP2-OL-12 | -10.897 | 15.219 | -6.650 | 5874 | 510 |
| LP2-OL-13 | -11.312 | 16.518 | -8.856 | 10,525 | 272 |
| LP2-OL-22 | -15.081 | 23.176 | -7.298 | 6862 | 613 |

Note that $A$ values are not reasonably close to $-12.5$ ($\eta_\infty = 3.8 \times 10^{-12}$ Pa s) for the Arrhenius relationship, even though the datapoints with $\eta > 100$ Pa s (LP2-OL-05 and 13). These deviations were caused by experimental errors. Fig. 10 displays the Arrhenius plots.

Table 11 shows the coefficient for both Arrhenius and VFT equations fitted to viscosity–temperature data of the five selected glasses. Of the two borderline glasses, LP2-OL-13 has an unusually low value of $T_0$ and a high value of $B_{VFT}$; the other of two, LP2-OL-05, has an unusually high values of $A_{VFT} = \ln(\eta_{VFT})$ and $T_0$.

As for the VFT equation, log($\eta$) versus $T^{\frac{1}{4}}$ does not converge to a linear relationship for $\eta < 100$ Pa s (Fig. 11), where most of the data lie. In fact, the VFT curves are bending far below $\eta = 100$ Pa s. As a result, $A_{VFT} > A$ for each glass (Table 11). Thus, the values of $\eta_\infty$ are substantially higher in the VFT fit than those obtained from the Arrhenius fit. Moreover, neither $A$ nor $A_{VFT}$ coefficients fall near to a common value. Because of a narrow temperature range of data and experimental errors, all three parameter values, those of the $\eta_{VFT}$ (viscosity at infinite temperature), $B_{VFT}$, and $T_0$ (temperature at infinite viscosity), are burdened with high uncertainties. This becomes apparent when the parameters are used to estimate glass transition temperature, $T_g$, i.e. temperature for which $\eta = 10^{12}$ Pa s. For the above five.

Figure 10. Viscosity versus temperature data for selected LAW glasses fitted individually with Arrhenius equation. Lines change from solid to dashed for $\eta > 100$ Pa s, signifying the validity range of the Arrhenius model. Two datapoints with $\eta > 100$ Pa s (LP2-OL-05 and 13) were excluded from fitting.

Figure 11. Viscosity versus temperature data for selected LAW glasses fitted individually with VFT equation.
6. Conclusion

The Arrhenius relationship with temperature-independent activation energy is the simplest possible model representing the glass melt viscosity for $\eta < 100$ Pa s as a function of temperature and glass composition. It is thus suitable for modeling glass melting furnaces in general and electric melters processing nuclear waste glasses in particular.

Using a set containing 3887 viscosity datapoints (3659 for $\eta < 100$ Pa s) measured on 554 glasses, three models were developed, a 20-component model ($R^2 = 0.972$), a 17-component model ($R^2 = 0.970$), and a 7-component model ($R^2 = 0.949$). Out of the major constituents, viscosity is most decreased by Li$_2$O and Na$_2$O and most increased by Al$_2$O$_3$ and SiO$_2$. Out of the minor constituents, F decreases viscosity as expected while SO$_3$ and Cl increase viscosity, likely by bonding alkalis in sulfate–chloride nano-inclusions as discussed in Rong et al. [50,51].

The fraction of LAW viscosity data outside of the validity of the Arrhenius equation (100–3 ×10$^3$ Pa s) is too small, and the temperature range of data is too narrow, for fitting nonlinear approximation functions, such as the VFT equation. This problem could be mitigated if $T_g$ values were available.

Acknowledgments

The authors gratefully acknowledge financial support provided by the U.S. Department of Energy (DOE) Waste Treatment and Immobilization Plant Project. Pacific Northwest National Laboratory is operated by Battelle for DOE under contract DE- AC05- 76RL01830. The authors thank John Vienna for providing LAW viscosity dataset.

Disclosure statement

No potential conflict of interest was reported by the author(s).

Funding

This work was supported by the U.S. Department of Energy [DE-AC05-76RL01830].

ORCID

Pavel Ferkl  http://orcid.org/0000-0003-2844-3199
Albert Kruger  http://orcid.org/0000-0001-8468-0813

References

[1] Hrma P. High-temperature viscosity of commercial glasses. Ceram – Silikáty [Internet]. 2006;50:57–66. Available from http://www.ceramics-silikaty.cz/index.php?page=cs_detail_doI&id=535
[2] Hrma P. Arrhenius model for high-temperature glass-viscosity with a constant pre-exponential factor. J Non Cryst Solids Internet. 2008;354:1962–1968. Available from https://linkinghub.elsevier.com/retrieve/pii/S0022309307013002
[3] Hrma P. Glass viscosity as a function of temperature and composition: a model based on Adam–Gibbs equation. J Non Cryst Solids Internet. 2008;354 (29):3389–3399. Available from https://linkinghub.elsevier.com/retrieve/pii/S002230930800118X
[4] Hrma P, Arrigoni BM, Schweiger MJ. Viscosity of many-component glasses. J Non Cryst Solids Internet. 2009;355(14–15):891–902. Available from https://linkinghub.elsevier.com/retrieve/pii/S0022309309001136
[5] Hrma P, Han -S-S. Effect of glass composition on activation energy of viscosity in glass-melting-temperature range. J Non Cryst Solids Internet. 2012;358(15):1818–1829. Available from https://linkinghub.elsevier.com/retrieve/pii/S0022309312002918
[6] Hrma P, Kruger AA. High-temperature viscosity of many-component glass melts. J Non Cryst Solids Internet. 2016;437:17–25. Available from https://linkinghub.elsevier.com/retrieve/pii/S0022309316300102
[7] Grundy AN, Liu H, Jung J-H, et al. A model to calculate the viscosity of silicate melts. Part I: viscosity of binary SiO2–MeOx systems. Int J Mater Res Internet. 2008;99 (11):1185–1194. Available from https://www.degruyter.com/document/doi/10.3139/146.101752/html
[8] Tilanus S, Bergman L, Lokken R, et al. River protection project system plan. ORP-11242, Rev. 8. Richland: Washington; 2017.
[9] Vienna JD, Heredia-Langner A, Cooley SK, et al. Glass property-composition models for support of hanford WTP LAW Facility Operation. PNNL-30932, Rev. 1. 2021.
[10] Hrma P, Crum JV, Bates DJ, et al. Vitrification and testing of a Hanford high-level waste sample. Part 1: glass fabrication, and chemical and radiochemical analysis. J Nucl Mater Internet. 2005;345(1):19–30. Available from https://linkinghub.elsevier.com/retrieve/pii/S0022311050002461
[11] Vienna JD, Piepel GF, Kim D, et al. Update of hanford glass property models and constraints for use in estimating the glass mass to be produced at hanford by implementing current enhanced glass formulation efforts. PNNL-25855 [Internet]. Richland WA; 2016. Available from https://www.pnnl.gov/main/publications/external/technical_reports/PNNL-25855.pdf
[12] Guillen DP, Abbott AW, Pokorny R, et al. Development of a validation approach for an integrated waste glass melter model. Nucl Technol Internet. 2018;203(3):244–260. Available from https://www.tandfonline.com/doi/full/10.1080/00295450.2018.1458559
[13] Abbott AW, Guillen DP. A methodology to reduce the computational cost of transient multiphysics simulations for waste vitrification. Comput Chem Eng Internet. 2018;115:64–80. Available from https://linkinghub.elsevier.com/retrieve/pii/S098135418302357
[14] Abboud AW, Guilien DP, Pokorny R. Effect of cold cap coverage and emissivity on the plenum temperature in a pilot-scale waste vitrification melter. Int J Appl Glas Sci Int. 2020;110(2):357–368. Available from https://onlinelibrary.wiley.com/doi/abs/10.1111/ijag.15031

[15] Fluegel A. Glass viscosity calculation based on a global statistical modelling approach. Eur J Glass Sci Technol Part A Glas Technol [Internet]. 2007;48:13–30. Available from: http://citeseerx.ist.psu.edu/viewdoc/download?doi=10.1.1.729.4659&rep=rep1&type=pdf

[16] Piepel GF, Heredia-Langner A, Cooley SK. Property-composition-temperature modeling of waste glass melt data subject to a randomization restriction. J Am Ceram Soc Internet. 2008;91(10):3222–3228. Available from: http://doi.wiley.com/10.1111/j.1551-2916.2008.02590.x

[17] Russell R, Jin T, McCarthy B, et al. enhanced hanford low-activity waste glass property data development: phase 1. PNNL-26630 Rev 0 [Internet]. 2017. Available from: http://www.pnl.gov/main/publications/external/technical_reports/PNNL-26630Rev0.pdf

[18] Russell RL, McCarthy BP, Cooley SK, et al. Enhanced hanford low-activity waste glass property data development: phase 2. PNNL-28838 Rev 1 [Internet]. 2019. Available from: https://www.osti.gov/biblio/1631578-enhanced-hanford-low-activity-waste-glass-property-data-development-phase

[19] Lonergan C, George J, Cuthforth D, et al. Enhanced hanford low-activity waste glass property data development: phase 3. PNNL-29847. 2020.

[20] Piepel G, Cooley S, Vienna J, et al. Experimental Design for Hanford Low-Activity Waste Glasses with High Loading. PNNL-24391 [Internet]. 2015. Available from: http://www.pnl.gov/main/publications/external/technical_reports/PNNL-24391.pdf

[21] Schreiber HD, Hockman AL. Redox chemistry in candidate glasses for nuclear waste immobilization. J Am Ceram Soc Internet. 1987;70(8):591–594. Available from http://doi.wiley.com/10.1111/j.1551-2916.1987.tb05712.x

[22] Kim DS, Vienna JD, Kruger AA. Preliminary ILAW formulation algorithm description, 24590 LAW RPT-RT-04-0003, Rev. 1. 2013.

[23] Macedo P, Simmons J, Haller W. Spectrum of relaxation times and fluctuation theory: ultrasonic studies on an alkali-borosilicate melt. Phys Chem Glasses. 1968;9:156–164.

[24] Napolitano A, Macedo PB. Spectrum of relaxation times in GeO2 glass. J Res Natl Bur Stand Sect A Phys Chem [Internet]. 1968;72A(4):425. Available from https://nvlpubs.nist.gov/nistpubs/jres/72A/jresv72A4p425_A1b.pdf

[25] Pelton AD, Blander M. Thermodynamic analysis of ordered liquid solutions by a modified quasichemical approach—Application to silicate slags. Metall Trans B Internet. 1986;17(4):805–815. Available from http://link.springer.com/10.1007/BF02657144

[26] Grundy AN, Jung I-H, Pelton AD, et al. A model to calculate the viscosity of silicate melts. Part II: the NaO0.5-MgO-CaO-ÁO1.5-SiO2 system. Int J Mater Res Internet. 2008;99(11):1195–1209. Available from https://www.degruyter.com/document/doi/10.3139/146.1017535/html

[27] Kim W-Y, Pelton AD, Deckerov SA. A model to calculate the viscosity of silicate melts. Part III: modification for melts containing alkali oxides. Int J Mater Res Internet. 2012;103(3):313–328. Available from https://www.degruyter.com/document/doi/10.3139/146.110637.html

[28] Brosh E, Pelton AD, Deckerov SA. A model to calculate the viscosity of silicate melts. Part V: borosilicate melts containing alkali metals. Int J Mater Res Internet. 2012;103(5):537–550. Available from https://www.degruyter.com/document/doi/10.3139/146.110639/html

[29] Zheng Q, Mauro JC. Viscosity of glass-forming systems. J Am Ceram Soc Internet. 2017;100(1):6–25. Available from http://doi.wiley.com/10.1111/jace.14678

[30] Smedskaer MM, Mauro JC, Sen S, et al. Quantitative design of glasy materials using temperature-dependent constraint theory. Chem Mater Internet. 2010;22(18):5358–5365. Available from https://pubs.acs.org/doi/10.1021/cm101679x

[31] Ndeugoue JL, Ikeda M, Aniya M. A comparison between the bond-strength-coordination number fluctuation model and the random walk model of viscosity. J Therm Anal Calorim Internet. 2010;99(1):33–38. Available from http://link.springer.com/10.1007/s10973-009-0420-x

[32] Phillips JC. Topology of covalent non-crystalline solids I: Short-range order in chalcogenide alloys. J Non Cryst Solids Internet. 1979;34(2):153–181. Available from https://linkinghub.elsevier.com/retrieve/pii/0022309379900334

[33] Phillips JC, Thorpe MF. Constraint theory, vector percolation and glass formation. Solid State Commun Internet. 1985;53(8):699–702 https://linkinghub.elsevier.com/retrieve/pii/0038109885903813

[34] Gupta PK, Mauro JC. Composition dependence of glass transition temperature and fragility. I. A topological model incorporating temperature-dependent constraints. J Chem Phys Internet. 2009;130(9):094503. Available from http://aip.scitation.org/doi/10.1063/1.3077168

[35] Mauro JC, Gupta PK, Loucks RJ. Composition dependence of glass transition temperature and fragility. II. A topological model of alkali borate liquids. J Chem Phys Internet. 2009;130(23):234503. Available from https://aip.scitation.org/doi/10.1063/1.3152432

[36] Smedskaer MM, Mauro JC, Youngman RE, et al. Topological principles of borosilicate glass chemistry. J Phys Chem B Internet. 2011;115(44):12930–12946. Available from https://pubs.acs.org/doi/10.1021/jp208796b

[37] Zeng H, Jiang Q, Liu Z, et al. Unique sodium phosphosilicate glasses designed through extended topological constraint theory. J Phys Chem B Internet. 2014;118(19):5177–5183. Available from https://pubs.acs.org/doi/10.1021/jp5018357

[38] Varshneya A, Mauro J. Fundamentals of Inorganic Glasses [Internet]. Elsevier; 2006. Available from: https://www.elsevier.com/books/fundamentals-of-inorganic-glasses/varshneya/978-0-12-816225-5

[39] Urbain G, Bottinga Y, Richet P. Viscosity of liquid silica, silicates and alumino-silicates. Geochim Cosmochim Acta Internet. 1982;46(6):1061–1072. Available from https://linkinghub.elsevier.com/retrieve/pii/001670378290059X

[40] Nakamoto M, Miyabayashi Y, Holappa L, et al. A model for estimating viscosities of aluminosilicate melts containing alkali oxides. ISIJ Int Internet. 2007;47(10):1409–1415. Available from https://www.jstage.jst.go.jp/article/isijinternational/47/10/47_10_1409/_article
[41] Lu X, Deng L, Du J. Effect of ZrO2 on the structure and properties of soda-lime silicate glasses from molecular dynamics simulations. J Non Cryst Solids Internet. 2018;491:141–150. Available from: https://linkinghub.elsevier.com/retrieve/pii/S002230931830200X

[42] Lu X, Deng L, Kerisit S, et al. Structural role of ZrO2 and its impact on properties of boronoluminosilicate nuclear waste glasses. Npj Mater Degrad Internet. 2018;2(1):19. Available from: http://www.nature.com/articles/s41529-018-0041-6

[43] Ziemath EC, Saggioro BZ, Fossa JS. Physical properties of silicate glasses doped with SnO2. J Non Cryst Solids Internet. 2005;351(52–54):3870–3878. Available from: https://linkinghub.elsevier.com/retrieve/pii/S0022309305007362

[44] Shartsis L, Spinner S, Capps W. Density, expansivity, and viscosity of molten alkali silicates. J Am Ceram Soc Internet. 1952;35(6):155–160. Available from: http://doi.wiley.com/10.1111/j.1151-2916.1952.tb13090.x

[45] Krakner J, Klement R, Liška M. High-temperature viscosity and density of alumino borosilicate glasses as a model system for commercial E-Glass. Ceramics-Silikáty Internet. 2008;52:148–154. Available from: https://www.ceramics-silikaty.cz/index.php?page=cs_detail_doíd=466

[46] Smedskjær MM, Mauro JC, Kjeldsen J, et al. Microscopic origins of compositional trends in aluminosilicate glass properties. rouxel T, editor. J Am Ceram Soc Internet. 2013;96(5):1436–1443. Available from: http://doi.wiley.com/10.1111/jace.12298

[47] Du Z, Zhang X, Yue Y, et al. Effect of MgOON structure and dielectric properties of CaO–Al2O3–B2O3–SiO2 glasses. Surf Rev Lett Internet. 2012;19(6):1250063. Available from: https://www.worldscientific.com/doi/abs/10.1142/S0218625X12500631

[48] Dingwell DB. Effect of fluorine on the viscosity of dioxide liquid. Am Mineral. 1989;74:333–338.

[49] Skidmore CH, Vienna JD, Jin T, et al. Sulfur solubility in low activity waste glass and its correlation to meltter tolerance. Int J Appl Glas Sci Internet. 2019;10 (4):558–568. Available from: https://onlinelibrary.wiley.com/doi/abs/10.1111/jagl.13272

[50] Rong C, Hong L, Hrma PR, et al. Spectroscopic investigation of simulated low-level nuclear waste glass. Ceram Trans. 1996;72:505–512.

[51] Rong C, Wong-Moon KC, Li H, et al. Solid-state NMR investigation of phosphorus in aluminoborosilicate glasses. J Non Cryst Solids Internet. 1998;223(1–2):32–42. Available from: https://linkinghub.elsevier.com/retrieve/pii/S0022309397004365

[52] Mao X, Yuan X, Bridgen CT, et al. Corrosion of inconel in high-temperature borosilicate glass melts containing simulant nuclear waste. 2017; p. 020001. Available from: http://aip.scitation.org/doi/abs/10.1063/1.5005179.

[53] Wing DR, Clare AG, Jones LE. The effects of vanadium additions on the surface tension of soda lime silicate melts. Varner JR, Seward TP, Schaeffer HA, editors. Adv fusion process glas III [Internet]. John Wiley & Sons. 2012; 135–152. Available from: http://doi.wiley.com/10.1002/9781118405949.ch13

[54] Pecoraro GA. How the properties of glass melts influence the dissolution of refractory materials. Pye D, Joseph I, Montenero A, editors. Prop Glass Melts [Internet]. Taylor & Francis. 2005; 340–388. Available from: https://www.taylorfrancis.com/books/mono/10.1201/9781420027310/properties-glass-forming-melts-david-pye-innocent-joseph-angelo-montenero

[55] Hrma P. Dissolution of a solid body governed by surface free convection. Chem Eng Sci Internet. 1970;25:1679–1688. Available from: https://linkinghub.elsevier.com/retrieve/pii/S0009259070800598

[56] Manara D, Grandjean A, Pinet O, et al. Factors influencing the sulphate incorporation in radioactive waste glasses. MRS Proc Internet. 2006;932:84.1. Available from: http://link.springer.com/article/10.1557/PROC-932-84.1

[57] Scholze H. Glass: nature, Structure, Properties [Internet]. New York: Springer New York; 1991. Available from: http://link.springer.com/10.1007/978-1-4613-9069-5

[58] Dingwell DB, Virgo D. The effect of oxidation state on the viscosity of melts in the system Na2O–FeO–Fe2O3–SiO2. Geochim Cosmochim Acta Internet. 1987;51 (2):195–205. Available from: https://linkinghub.elsevier.com/retrieve/pii/0016703787902316

[59] Reddy MR, Reddy MS, Veeraiah N. Physical Properties of PbO-Al2O3-B2O3 glasses doped with Cr2O. Indian J Pure Appl Phys. 2006;44:446–454.

[60] Feng Z, Perez-Cardenas F, Gan H, et al. Summary and recommendations on viscosity and electrical conductivity models of simulated nuclear waste glasses. VSL-03L4480-2, Rev. 1. Washington, DC; 2004.

[61] Piepel G, Cooley S, Muller I, et al. ILAW PCT, VHT, viscosity, and electrical conductivity model development. VSL-07R1230-1, Rev. 0. Washington, D.C.; 2007.

[62] Vogel H. Das Temperatureabhänngigkeitsgesetz der Viskosität von Flüssigkeiten. Phys Zeitschrift. 1921;22:645–646.

[63] Fulcher GS. Analysis of recent measurements of the viscosity of glasses. J Am Ceram Soc Internet. 1925;8 (6):339–355. Available from: http://doi.wiley.com/10.1111/j.1151-2916.1925.tb16731.x

[64] Tammann G, Hesse W. Die Abhängigkeit der Viscosität von der Temperatur bei untersuchten Flüssigkeiten. Zeitschrift für Anorg un Allg Chemie Internet. 1926;156:245–257. Available from: https://doi.wiley.com/10.1002/zaac.1926156012

[65] Walther C. The evaluation of viscosity data. Erdol Teer. 1931;7:382–384.

[66] Bässler H. Viscous flow in supercooled liquids analyzed in terms of transport theory for random media with energetic disorder. Phys Rev Lett Internet. 1987;58:767–770. Available from: https://linkaps.org/doi/10.1103/PhysRevLett.58.767

[67] Avramov I. Viscosity in disordered media. J Non Cryst Solids Internet. 2005;351(40–42):3163–3173. Available from: https://linkinghub.elsevier.com/retrieve/pii/S0022309305006344

[68] Priven AI, New A. Equation for describing the temperature dependence of the viscosity of glass-forming melts. Glas Phys Chem. 1999;25:491–497.

[69] Mauro JC, Yue Y, Ellison AJ, et al. Viscosity of glass-forming liquids. Proc Natl Acad Sci Internet. 2009;106(47):19780–19784. Available from: http://www.pnas.org/cgi/doi/10.1073/pnas.0911705106

[70] Douglas RW. The flow of glass. J Soc Glas Technol. 1949;33:138–162.
[71] Doremus RH. Viscosity of silica. J Appl Phys Internet. 2002;92(12):7619–7629. Available from http://aip.scitation.org/doi/10.1063/1.1515132

[72] Ozhovan MI. Topological characteristics of bonds in SiO2 and GeO2 oxide systems upon a glass-liquid transition. J Exp Theor Phys Internet. 2006;103(5):819–829. Available from http://link.springer.com/10.1134/S1063776106110197

[73] Connelly AJ, Hyatt NC, Travis KP, et al. Predicting the preference for charge compensation in silicate glasses. Phys Chem Glas - Eur J Glas Sci Technol Part B [Internet]. 2011;52:64–67(4). Available from https://www.ingentaconnect.com/content/sgt/egst/2011/00000052/00000002/art00005

[74] Isard JO. The mixed alkali effect in glass. J Non Cryst Solids Internet. 1969;1(3):235–261. Available from https://linkinghub.elsevier.com/retrieve/pii/0022309369900039

[75] Cassar DR, de Carvalho ACPLF, Zanotto ED, et al. Predicting glass transition temperatures using neural networks. Acta Mater Internet. 2018;159:249–256. Available from https://linkinghub.elsevier.com/retrieve/pii/S1359645418306542