Contract No:

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-08SR22470 with the U.S. Department of Energy (DOE) Office of Environmental Management (EM).

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AUGUST 2016

SRNL-STI-2016-00115, Revision 0

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Prepared for
U.S. Department of Energy

SRNL-STI-2016-00115
Revision 0

Keywords: *DWPF, process control, viscosity, Salt Waste Processing Facility, Monosodium Titanate, Crystalline Silicon Titanate*

Retention: *Permanent*

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ACKNOWLEDGEMENTS

The research presented in this document was sponsored by the Savannah River Defense Waste Processing Facility (DWPF) in connection with work done under Contract No. DE-AC09-96SR18500 with the U.S. Department of Energy. The development of the 1991 and 2005 viscosity models was completed and the associated validation data were accumulated from 1988 to present under DOE Contracts No. DE-AC09-89SR18035 with E.I. DuPont deNemours & Co., Contract No. DE-AC09-96SR18500 with Westinghouse Savannah River Co. (WSRC) and Washington Group Inc. (WGI), and Contract No. DE-AC09-08SR22470 with Savannah River Nuclear Solutions (SRNS).

EXECUTIVE SUMMARY

Radioactive high level waste (HLW) at the Savannah River Site (SRS) has successfully been vitrified into borosilicate glass in the Defense Waste Processing Facility (DWPF) since 1996. Vitrification requires stringent product/process (P/P) constraints since the glass cannot be reworked once it is poured into ten foot tall by two foot diameter canisters. A unique "feed forward" statistical *process* control (SPC) was developed for this control rather than statistical *quality* control (SQC). In SPC, the feed composition to the DWPF melter is controlled *prior* to vitrification. In SQC, the glass product would be sampled *after* it is vitrified. Individual glass property-composition models form the basis for the "feed forward" SPC. The models transform constraints on the melt and glass properties into constraints on the feed composition going to the melter in order to guarantee, at the 95% confidence level, that the feed will be processable and that the durability of the resulting waste form will be acceptable to a geologic repository.

The DWPF SPC system is known as the Product Composition Control System (PCCS). One of the process models within the PCCS is the viscosity model which was developed in 1991 with as-batched compositions and revised in 2005 with as-measured compositions which made the model more accurate. The form and terms in the viscosity model did not change between 1991 and 2005, only the fitted coefficients changed. The 2005 model will be referred to as the "historic" PCCS viscosity model throughout this document.

The DWPF viscosity model is based on bond counting of bridging oxygen (BO) and non-bridging oxygen (NBO) bonds and melt temperature. Bridging oxygen bonds polymerize the glass and NBO's depolymerize the glass. A larger NBO term indicates a very fluid melt with a low viscosity while a smaller NBO term indicates a more viscous melt, i.e. one with a higher viscosity. In 2005 it was also shown that the viscosity model did not need a uranium term as the impact of BO's and NBO's around a uranium atom in glass cancel each other out in the model.

The DWPF PCCS modeling approach for each property model, is parsimonious in that the oxide terms in each model are only those which are necessary and sufficient to describe the glass property of interest. This approach excludes composition terms that are unnecessary to the implementation of the DWPF flowsheets and helps to minimize the sources of error in the PCCS models. Another aspect of the PCCS process models, that minimizes the sources of error, is that oxide terms that have a similar impact on the glass property being modeled can be grouped, i.e. Na_2O, Li_2O, K_2O and Cs_2O are grouped in the viscosity model as they each create two NBO bonds per mole of alkali present. These parsimonious models have successfully operated the DWPF vitrification process over the last 20 years.

The DWPF will soon be receiving wastes from the Salt Waste Processing Facility (SWPF) containing increased concentrations of TiO_2, Na_2O, and Cs_2O . The SWPF is being built to pretreat the high-curie fraction of the salt waste to be removed from the HLW tanks in the F- and H-Area Tank Farms at the SRS. The SWPF contains unit operations that remove and concentrate the radioactive cesium (^{137}Cs), strontium (^{90}Sr), and actinides from the bulk salt solution feed. Separation processes planned at SRS include caustic side solvent extraction (CSSX), for ^{137}Cs removal, and ion exchange/sorption of ^{90}Sr and alpha-emitting radionuclides with monosodium titanate (MST which is $NaHTi_2O_5 2.8H_2O$). The predominant alpha-emitting radionuclides in the highly alkaline waste solutions include plutonium isotopes ^{238}Pu, ^{239}Pu and ^{240}Pu. The MST is the source of the TiO_2 and Na_2O enriched wastes while the Cs_2O is derived from the CSSX stream that will be coming to the DWPF from the SWPF.

The SWPF process will replace the current Actinide Removal Process (ARP)/Modular CSSX Unit (MCU) process currently in use. The ARP already sends MST to the DWPF for vitrification but the volume of the ARP product, including the associated MST component, is less than the volume anticipated with the SWPF MST wastes. Currently, the DWPF is operating under a TiO_2 solubility constraint of 2 wt% TiO_2 in the final glass. At the 2.0 wt% solubility concentration, a TiO_2 term was not needed in the PCCS viscosity model and the existing TiO_2 terms in the PCCS durability and liquidus models had not been validated at TiO_2 concentrations greater than 2.0 wt%.

In order to process TiO_2 concentrations >2.0 wt% in the DWPF, new viscosity data were developed over the range of 1.90 to 5.85 wt% TiO_2 (measured compositions for glasses that were considered acceptable for modeling) and evaluated against the 2005 historic viscosity model. The viscosities measured for the SWPF study glasses were designed to cover the anticipated concentrations of TiO_2, Na_2O, and Cs_2O based on the projected volumes of SWPF. These glasses were also designed to cover any gaps in TiO_2 content above the 2.0 wt% solubility limit and the 6.0 wt% maximum TiO_2 anticipated during coupled (sludge + SWPF product) processing at DWPF. At the same time, the adequacy of the Na_2O and Cs_2O viscosity terms were evaluated over the SWPF target range, i.e. 8 to 18 wt% Na_2O and 0.3 to 1.0 wt% Cs_2O since the historic DWPF viscosity model only covers 5.8-15.8 wt% Na_2O and 0-0.33 wt% Cs_2O.

As part of the PCCS durability model and Reduction of Constraints (ROC) TiO_2 assessment, a 4.0 wt% Al_2O_3 restriction had to be placed on the ROC for SWPF high TiO_2 containing glasses. The durability and ROC assessment will be documented in a separate study, but the impact of the change in the ROC meant that several SWPF study glasses were removed from viscosity modeling which altered the ranges for TiO_2 in the glass to 1.9-5.85 wt%. Within measurement error, the 5.85 wt% TiO_2 limit can be rounded up to 6.0 wt% TiO_2, the projected upper limit for the SWPF study, and the mechanistic TiO_2 viscosity model will adequately predict. Conversely, the analyzed high TiO_2 glasses were higher in Na_2O and Cs_2O than the target concentrations giving a range of 8.03-18.14 wt% Na_2O and 0.48-1.62 wt% Cs_2O. It was determined that the Na_2O and Cs_2O terms in the historic viscosity model were adequate up to these high concentrations and that a TiO_2 term was needed in the model to adequately describe the impact of higher TiO_2 concentrations on melt viscosity. This model will be called the SWPF TiO_2-only viscosity model throughout this study.

This study documents the development of a TiO_2 term, as a depolymerizing agent in the glass (creating NBO's), for the historic PCCS viscosity model. The TiO_2-only viscosity model spans from 0.00 to 5.85 wt% TiO_2 since the historic and SWPF datasets were pooled to develop the model and the TiO_2-only viscosity model was validated up to 5.90 wt% TiO_2. At TiO_2 concentrations up to ~6.0 wt%, Ti is octahedral (6-coordinated) and acts as a depolymerizing agent in the glass based on literature studies. Note that validation limits are not model limits and they are not solubility limits.

Several additional SRNL viscosity studies were examined at TiO_2 concentrations up to 8.38 wt%. These studies indicate that TiO_2 acts as a polymerizing agent and is tetrahedrally coordinated (4-coordinated) in waste glasses at these higher concentrations. The literature indicates that the switch in the role of TiO_2 from NBO to BO varies with the complexity of the overall glass composition. The exact TiO_2 concentrations at which TiO_2 switches from a network modifier to a network former lies somewhere between ~6.00 and 8.00 wt% TiO_2 and additional studies would have to be performed to determine this limit. These higher TiO_2 studies are not evaluated in this modeling report as this would change the sign of the TiO_2 term in the viscosity model from a depolymerizing agent (positive term) to a polymerizing agent (negative term).

Therefore the TiO_2-only SWPF viscosity model takes the following form:

$$\log \eta(poise) = -0.606597 + \left(\frac{4587.5797}{T(^oC)}\right) - (1.711755 * NBO)$$

where $$NBO \equiv \frac{2(Na_2O + K_2O + Cs_2O + Li_2O) + 2(Fe_2O_3 - Al_2O_3) + B_2O_3 + TiO_2}{SiO_2}$$

With an adjusted $R^2 = 0.9541$ and a root mean square error of 0.1012 in log (poise) units.

Since the TiO_2-only viscosity model contained glasses with Cs_2O up to 1.62 wt%, the new SWPF data validated the Cs_2O term used in the historic and TiO_2-only DWPF viscosity models. The TiO_2-only model was also shown to be valid up to 4.14 wt% CaO and 2.92 wt% MgO. This means that CaO and/or MgO can be added to frit compositions up to these concentrations since CaO is known to suppress nepheline crystallization and MgO is known to improve glass durability and reduce DWPF refractory corrosion and wear.

An alternate viscosity model is also derived for potential future use, should the DWPF ever need to process other titanate containing ion exchange materials, such as crystalline silicotitanate (CST - $Na_{1.5}Nb_{0.5}Ti_{1.5}O_3SiO_4 \bullet 2H_2O$). The CST viscosity model is not being implemented currently as the DWPF is not processing CST nor does it appear likely that CST will be processed in the near future. The CST contains Nb_2O_5 and Nb would then become an element in the glass that is reportable to the geologic repository. This would require a revision to the DWPF Waste Acceptance Product Specifications (WAPS). In addition, the measurement uncertainty needed to implement an Nb term in PCCS is currently not available. Therefore, the CST viscosity model is being provided for future use should the DWPF have to process CST. When CST processing becomes necessary, the other implementation requirements associated with a CST viscosity model will be addressed. The CST viscosity model takes the following form:

$$\log \eta(poise) = -0.629934 + \left(\frac{4547.3573}{T(^oC)}\right) - (1.622574 * NBO)$$

where

$$NBO \equiv \frac{2\,(Na_2O + K_2O + Cs_2O + Li_2O + Fe_2O_3 + Nb_2O_5 - Al_2O_3) + B_2O_3 + TiO_2 - ZrO_2}{SiO_2}$$

With an adjusted R^2=0.9397 and a RMSE=0.1033 which are somewhat lower and higher, respectively, than the values for the TiO_2-only model.

The CST, also known as IE-911, is remarkable for its ability to separate parts-per-million concentrations of cesium from highly alkaline solutions (pH>14) containing high sodium concentrations (>5M). It is also highly effective for removing cesium from neutral and acidic solutions, and for removing strontium from basic and neutral solutions. Therefore, the DWPF may receive CST generated by an alternate flowsheet if used to pretreat the high-curie fraction of the SRS salt waste. The CST not only contains TiO_2 but also contains Nb_2O_5 and a ZrO_2 binder where TiO_2 and Nb_2O_5 act to depolymerize the glass (create NBO's) and ZrO_2 polymerizes the glass (creates BO's). The MST would still be used for ^{90}Sr removal so this viscosity model would cover future DWPF processing of CST alone or coupled CST-

MST flowsheet additions. When the SWPF model glasses (TiO_2=1.90-5.85 wt%) and the CST model and validation glasses (TiO_2=3.03-6.62, Nb_2O_5=0.03-2.30 wt% and ZrO_2=0.15-2.09 wt%) are combined with the historic DWPF viscosity database (TiO_2=0-1.78 wt%), the MST glass data cover a wider range of TiO_2 than the CST or historic viscosity data. The Nb_2O_5 and ZrO_2 terms are derived solely from the CST data as neither the SWPF viscosity data nor the historic viscosity data contain these species.

While the SWPF TiO_2-only viscosity model has been modeled/validated up to ~ 6 wt% (actual of 5.85 wt% TiO_2) and the CST viscosity model has been modeled/validated up to 6.62 wt% TiO_2. The role of TiO_2 as a network breaker switches to a network former somewhere between 6.62 and 8.38 wt% TiO_2. The exact region at which this switch occurs has not been investigated so the usage of the SWPF TiO_2-only viscosity model is ~6 wt% TiO_2 and the CST model is ~ 6.5 wt% TiO_2.

The ultimate limit on the amount of TiO_2 that can be accommodated from SWPF will be determined by the three PCCS models, the waste composition of a given sludge batch, the waste loading of the sludge batch, and the frit used for vitrification. Once a component like TiO_2 is present at larger concentrations than 1-2 wt%, the interactions of that component with other components in the melter feed must be considered simultaneously, i.e. an individual solubility limit cannot be defined to globally account for the interactions with all the remaining sludge/frit composition variables. It is known that Ti^{4+} competes with Al^{3+} for alkali bonding and it is known that Ti^{4+} and Fe^{3+} have a coupled impact on their joint solubility in a glass.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

AD	Analytic Development
APS	Amorphous Phase Separation
ARP	Actinide Removal Process
ASME	American Society of Mechanical Engineers
ASTM	American Society for Testing and Materials
BO	Bridging Oxygen
CELS	Corning Engineering Laboratory Services
OCF	Owens Corning Fiberglass
CPS	Crystalline Phase Separation
CSSX	Caustic-Side Solvent Extraction
CST	Crystalline SilicoTitanate
DCP	Direct Current Plasma Emission Spectrometry
DOE	Department of Energy
DSS	Dissolved Salt Solution
DWPF	Defense Waste Processing Facility
EPA	Environmental Protection Agency
EPAR	Expected Property Acceptable Region
ES-VSL	Energy Solutions – Vitreous State Laboratory
HLW	High Level Waste
IC	Ion Chromatography
ICP-ES	Inductively Coupled Plasma-Emission Spectroscopy
IDMS	Integrated DWPF Melter System
L95	Lower 95% confidence interval
MAR	Measurement Acceptable Region
MAS NMR	Magic Angle Spinning Nuclear Magnetic Resonance
MCU	Modular CSSX Unit
MST	MonoSodium Titanate
NBO	Non-Bridging Oxygen
NBS	National Bureau of Standards
NQA	Nuclear Quality Assurance
OCF-SS	Owens Corning Fiberglass-Sharp Shurtz
P/P	Product/Process
PAR	Property Acceptable Region
PCCS	Product Composition Control System
PHA	Precipitate Hydrolysis Aqueous
PNNL	Pacific Northwest National Laboratory
PSAL	Process Science Analytic Laboratory
QAP	Quality Assurance Program
RCRA	Resource Conservation and Recovery Act
REDOX	REDuction/OXidation
ROC	Reduction of Constraints
RMSE	Root Mean Square Error
SB	Sludge Batch
SEM	Scanning Electron Microscopy
SG	Study Glasses
SGM	Scale Glass Melter
SME	Slurry Mix Evaporator
SPC	Statistical Process Control

SQC	Statistical Quality Control
SRNL	Savannah River National Laboratory
SRNS	Savannah River Nuclear Solutions
SRS	Savannah River Site
SS	Sharp-Shurtz
SWPF	Salt Waste Processing Facility
TCLP	Toxic Characteristic Leaching Procedure
TEM	Transmission Electron Microscopy
THERMO™	Thermodynamic Hydration Energy Reaction MOdel
TTQAP	Technical Task and Quality Assurance Plan
TTR	Technical Task Request
T_L	Liquidus Temperature
U95	Upper 95% confidence interval
VFT	Vogel-Fulcher-Tammann
V_r	Viscosity ratio
WAPS	Waste Acceptance Product Specifications
WCP	Waste Form Compliance Plan
WGI	Washington Group Inc.
WQR	Waste Qualification Report
WL	Waste Loading
WSRC	Westinghouse Savannah River Co.
XANES	X-ray Absorption Near Edge Spectroscopy
Z/r	Atomic charge/Atomic radius

1.0 Introduction

Borosilicate glasses have been used in the United States and in Europe to immobilize radioactive high level waste (HLW) for ultimate geologic disposal. Waste glass formulations should maximize the concentration of waste in the vitrified waste form so that waste glass volumes and the associated storage and disposal costs are reduced. Moreover, the optimization of HLW glass formulations [1,2,3] must simultaneously balance multiple product/process (P/P) constraints (Table 1).

Table 1. Waste Glass Product and Process (P/P) Constraints

Product Constraints	Process Constraints
chemical durability	melt viscosity/resistivity
glass homogeneity	liquidus
thermal stability	waste solubility
regulatory compliance	melt temperature/corrosivity
mechanical stability	radionuclide volatility
	REDuction/Oxidation (REDOX)*

* controls foaming and thus improves melt rate and controls metal nodule formation and thus improves melter longevity

The chemical durability, which includes glass homogeneity, the melt viscosity, and the liquidus constraints from Table 1 are the only parameters controlled during HLW processing. Thermal and mechanical stability were measured during development of the HLW processing flowsheet.[4] Regulatory compliance using the Toxic Characteristic Leach Test (TCLP) was bounded by using 1X and 10X the Environmental Protection Agency (EPA) Resource Conservation and Recovery Act (RCRA) hazardous constituents anticipated to be in glasses made from the range of wastes found in the Savannah River Site (SRS) tank farm.[5,6] Melt temperature, was balanced against volatilization of radionuclides and materials of construction corrosivity during extensive pilot scale testing at the SRS before the Defense Waste Processing Facility (DWPF) startup. The melt temperature was optimized at 1150°C to minimize radionuclide volatility, afford an adequate viscosity to the melt for convection and at the same time minimize corrosion of melter materials of construction, i.e. Inconel®690 and Monofrax™ K-3 refractory.[7,8,9] Melter REDOX is controlled at an $Fe^{2+}/\Sigma Fe$ target of ~0.2 and in the range of $Fe^{2+}/\Sigma Fe$ = 0.09-0.33.[10,11,12,13,14] Waste solubility is handled in PCCS as limits of the individual species in wt% in the glass.

Radioactive HLW has successfully been vitrified into borosilicate glass during HLW processing at the DWPF since 1996. The DWPF must measure melt/glass acceptability a priori to the melter, since no remediation of the glass composition to ensure durability and processability is possible except in the vessel (i.e., in the Slurry Mix Evaporator (SME) vessel) in which frit and waste are blended. Therefore, the acceptability decision is made on the upstream process (specifically, at the SME), rather than on the downstream *melt* or glass product. That is, it is based on "feed forward" statistical *process* control[†] (SPC) rather than statistical *quality* control (SQC).[††] The DWPF SPC control system is known as the Product Composition Control System (PCCS). Individual property-composition models enable the monitoring and process control strategies embedded in the DWPF PCCS.[15] These models transform constraints on the melt and glass properties such as viscosity, liquidus, and durability into constraints on feed composition.

[†] This controls the slurry feed to the melter *prior* to vitrification.
[††] Which would adjudicate product release by sampling the glass *after* it's been made.

The DWPF property-composition models have been under development and validation since the late 1980's. Since the 1980's, the individual property models for each feed/glass constraint have been developed over wider property ranges than the feeds that were anticipated to be fed to the DWPF. The property models that have been developed are mechanistic[t] in nature and depend on known relationships between glass structure/bonding (viscosity)[16,17], thermodynamics of melt structures and components (durability)[18,19], and quasicrystalline melt species (liquidus).[20,21,22] The P/P models group terms with very similar effects so that each model only contains the terms that are necessary and sufficient (parsimonious) to model the P/P property of interest.

The PCCS historic viscosity model currently in use at DWPF will be assessed in this document against newly generated data covering the future composition region defined by SWPF processing (see Section 3.0 for discussion). Specifically, this document will assess the impact of enriched TiO_2 waste streams from SWPF on viscosity. The TiO_2 and Na_2O enriched waste streams are generated by decontamination of the HLW salt waste stream using MonoSodiumTitanate (MST) to remove ^{90}Sr and ^{137}Cs. If needed, a TiO_2 term will be added to the historic viscosity model. A solubility limit has been placed on TiO_2 additions to DWPF glass, i.e., 2 wt% TiO_2, based on an evaluation of the tendency of TiO_2 to induce crystallization in DWPF glasses.[23] Therefore, a TiO_2 term was not included in the historic viscosity model. While the current assessment of the historic viscosity model is addressing higher concentrations of TiO_2 and the impact on melt viscosity at 1150°C, a revision of the PCCS liquidus model will address the crystallization issue and may limit the amount of SWPF waste that can be added to any one batch of DWPF glass.

In the future, the DWPF may also receive Crystalline SilicoTitanate (CST) that may be used to decontaminate the ^{137}Cs from the salt waste or from tank cleanout. The CST is remarkable for its ability to separate parts-per-million concentrations of cesium from highly alkaline solutions (pH>14) containing high sodium concentrations (>5M). It is also highly effective for removing cesium from neutral and acidic solutions, and for removing strontium from basic and neutral solutions.[24] The CST is comprised primarily of: Na, Si, Ti, and Nb (formerly referred to as proprietary material one, or PM-1) plus an exchangeable monovalent cation. The binder is based on a technology that employs zirconium (formerly PM-2).[25]

1.1 The DWPF PCCS Historical Viscosity Model

The viscosity of a waste glass melt as a function of temperature is one of the most important variables affecting the melt rate,[τ] the pourability of the glass, and the electrical resistivity of the glass, thus inhibiting Joule heating. The viscosity determines the rate of melting of the raw feed, the rate of gas bubble release (foaming and fining), the rate of homogenization, the adequacy of heat transfer, the devitrification rate, and thus, the homogeneity of the final glass product. If the viscosity is too low, excessive convection currents can occur, increasing corrosion/erosion of the melter materials (refractories and electrodes) and making control of the waste glass melter more difficult. The lowest glass viscosities set for the DWPF waste glass melter are, therefore, conservatively set at ~20 poise at T_{melt}. Waste glasses are usually poured continuously into stainless steel canisters for ultimate storage. Glasses with viscosities above 500 poise do not readily pour. Moreover, too high a viscosity can reduce glass quality by causing voids in the final glass. A conservative maximum viscosity of 110 poise at T_{melt},

[t] Mechanistic models can be applied to composition regions outside of the regions for which they were developed. The DWPF mechanistic models allow more flexibility for process control than empirical models which are (1) restricted to the compositional region over which they were developed and (2) require glass formulations near the center of a pre-qualified glass composition region instead of in regions where waste loading can be maximized.

[τ] Melt rate is also related to melt pool resistivity, which is highly correlated to melt pool viscosity: melt rate is also related to the REDOX of the melt pool as an oxidizing melt pool can cause O_2 foaming from manganese oxide reduction, and the foam can form an insulating layer on the melt pool and inhibit heat transfer from the lid heaters; so that neither the fresh batch nor the cold cap melt as efficiently.

was, therefore, established for DWPF production.[26]

The approach taken in the development of the historic viscosity and electrical resistivity process models [2,16,17] was based on glass structural considerations, expressed as a calculated non-bridging oxygen (NBO) parameter. This NBO parameter represents the amount of structural depolymerization in the glass (Equation 1). A larger NBO indicates a very fluid melt while a smaller NBO indicates a more viscous melt, i.e. with a higher viscosity. The same approach is used in this study to incorporate other oxide terms.

Equation 1 $$NBO \equiv \frac{2\,(Na_2O + K_2O + Cs_2O + Li_2O + Fe_2O_3 - Al_2O_3) + B_2O_3}{SiO_2}$$

Oxide species in the DWPF viscosity models are expressed in mole fraction and related to the viscosity-temperature dependence of the Fulcher equation [16,17], also known as the Vogel-Fulcher-Tammann (VFT)[‡] equation. The VFT relates the viscosity (η) of a glass to temperature (Equation 2) for Newtonian fluids. Therefore, non-Newtonian fluids, such as crystallized glasses [27] are not included in the viscosity model or validation data. Phase separated glasses of the glass-in-glass (amorphous phases) type are also not included in the viscosity models or validation data as phase separated glasses give anomalous viscosity vs. temperature plots. [36]

Equation 2 $$\log_{10}\eta = A + \frac{B}{T - T_o}$$

In Equation 2, η is viscosity (poise, P, or Pa•s[*]), T is temperature in °C, and A, B, and T_o are fitted constants. It is well documented that the overall fit of the Fulcher equation is excellent for glasses but that it also overestimates viscosity at lower temperatures in the range of viscosities $>10^{11}$ poise.[28] In addition, viscosities less than 10 poise are not modeled as ASTM C965 [29] indicates that the measurement is not accurate in this low viscosity range.

Calculation of the NBO term from molar compositions was combined with quantitative statistical analyses of response surfaces to express glass viscosity and resistivity as a function of melt temperature and glass composition. The DWPF historic viscosity model was originally developed in 1991 [2,16] based on "as-batched" glass compositions, and the coefficients were revised in 2005 based on "as-measured" glass compositions.[17] The 2005 version of the DWPF viscosity model, referred to in this study as the "historic DWPF viscosity model" is given by:

Equation 3 $$\log\eta(poise) = -0.519571 + \left(\frac{4453.87}{T(^oC)}\right) - (1.690326 * NBO).$$

with an adjusted R^2= 0.966, and a root mean square error (RMSE) of 0.0832. Equation 3 is based on 175 viscosity-temperature data points from 33 different glasses.

‡ Fulcher derived this expression to model viscosity of inorganic glasses in 1925. In 1921, Vogel (Phys. Zeit., 22, 645-646) derived a similar expression for the viscosity of water, mercury, and oils and Tammann and Hesse generated a similar equation for organic liquids in 1926 (Z. Anorg. Allg. Chem. 156, 245-257). So all three are credited with the derivation of the mathematical expression, and it is often referred to as the VFT equation. Throughout this document the VTF equation is noted as the Fulcher equation.

* The unit of viscosity is the dyne second per square centimeter, which is called the poise. The SI unit for viscosity is the Newton second per square meter, or pascal second (Pa.s); one of these units equals 10 poise.

The form of the NBO parameter did not change between 1991 and 2005 but the coefficients to the NBO and 1/T(°C) parameters and intercept were refit. The viscosity model data and the associated validation data comprise the VISCOMP™ database of ~500 HLW glasses. Additional viscosity data have been generated since the 2005 viscosity model was refit, and specifically viscosity and composition data have been developed over the future compositional processing range that DWPF is expected to experience until the end of its mission.

The DWPF viscosity model assumes that a pure SiO_2 glass is fully polymerized; i.e. there are no NBO and 4 bridging oxygen (BO) bonds per silicon atom. Addition of other species known as network modifiers depolymerizes the glass while network formers polymerize the glass. A larger NBO term indicates a very fluid melt with a low viscosity while a smaller NBO term indicates a more viscous melt, i.e. one with a higher viscosity. This approach was a simplification of an NBO term developed by White and Minser [30] to describe the structural features observed in Raman spectroscopy data of complex natural glasses (obsidians and tektites), which had no B_2O_3 and almost all FeO instead of Fe_2O_3. Equation 3 is also consistent with the usage of a viscosity ratio (V_r) to model the viscosity of slags [31]. The V_r is defined as the sum of the Z/r (atomic charge/atomic radius) of the network formers multiplied by the atomic % of the network formers divided by the sum of the Z/r of the network modifiers multiplied by the atomic % of the network modifiers.

In the DWPF historic viscosity model, it is assumed that each mole of alkali oxide added creates two NBO bonds by forming metasilicate ($(Rb,Cs,K,Na,Li)_2SiO_3$) structural units; thus depolymerizing the glass. While the exact number of NBO atoms depends on the molar ratio of all of the species in a waste glass to SiO_2, most DWPF glasses have a O^{2-}/Si^{4+} ratio of 2.6 to 3.3 which implies that disilicate and metasilicate structural units predominate for the alkali species in the waste glasses. Calculation of the O^{2-}/Si^{4+} ratio for DWPF glasses included contributions from Na, K, Li, and Cs alkali species and a Si^{4+} concentration that was depleted by the amount associated with B_2O_3 structural units.

The DWPF historic viscosity model further assumes that each mole of Al_2O_3 creates two BO bonds (polymerizes the glass structure) by creating tetrahedral alumina groups that bond as $(Rb,Cs,K,Na,Li)AlO_2$ structural groups. In Al_2O_3 and/or SiO_2 deficient glasses, Fe_2O_3 can take on a tetrahedral coordination and polymerize a glass by forming $(Rb,Cs,K,Na,Li)FeO_2$ structural groups. However, if sufficient Al_2O_3 and SiO_2 are present in a glass such as DWPF waste glasses that contain >3 wt% Al_2O_3 and >40 wt% SiO_2, then Fe_2O_3 is octahedral and creates two NBO bonds, i.e., it depolymerizes the glass matrix as assumed in the DWPF viscosity model (Equation 3). This is consistent with the work of Mysen [32] who demonstrated that high iron magmas (iron silicate glasses) that contained levels of 10 wt% Fe_2O_3 decreased the melt viscosity. Mysen concluded that $NaFeO_2$ structural groups were not incorporated into the silicate network to the same degree as $NaAlO_2$ structural groups [32]. Therefore, Fe_2O_3 is considered a network modifier (or depolymerizer) in the DWPF viscosity model.

Lastly, the DWPF historic viscosity model assumes that each mole of B_2O_3 creates one NBO bond. This is based on data by Smets and Krol [33], and Konijnendijk [34] who demonstrated that for sodium silicate glasses with low B_2O_3 content the B_2O_3 enters the glass network as BO_4^- tetrahedral. At higher B_2O_3 concentrations, these tetrahedra are converted into planar BO_3^- groups. Tetrahedral BO_4^- contributes no NBO while planar BO_3^- groups contribute one NBO atom.[35]

In 1991, the viscosity model was developed on as-batched compositions [2,16] and revised in 2005 [17] based on analyses of the same non-radioactive glasses and frits (220 viscosity-temperature measurements for 41 glasses). Eight of the 1991 glasses were determined to be phase separated during the development

of the PCCS historic durability model in 1995 (see discussion in Section 2.0). These glasses were removed from the earlier viscosity model during the 2005 revision leaving a data pool of 175 viscosity-temperature measurements for 33 glasses. During the 2005 revision, the model was validated [17] on an additional 200 glasses (radioactive and non-radioactive and 1004 viscosity-temperature pairs). Uranium was shown to have no impact on glass viscosity as U has as many BO's as NBO's and they cancel each other out in the NBO parameter.[17] Likewise, ThO_2 at <1 wt% had no impact on glass viscosity. The viscosity model was developed over wider composition space and temperature regions (873-1491°C), than DWPF operation. This allows for high leverage points during modeling, improves the model fit, and helps ensure that any individual terms are adequately accounted for. The viscosity constraint is applied in PCCS at the DWPF melt temperature of 1150°C.

Equation 3 was implemented in PCCS at the DWPF melt temperature of 1150°C. However, the equation represents a three dimensional plane in composition (NBO), viscosity, and temperature space as shown in Figure 1-1. Therefore, the viscosity model could easily be applied at a variety of glass temperatures in a variety of different melter designs. The historic viscosity model covers temperatures from 873-1491°C but was validated to as low as 808°C. The model covers glasses from 10.2 poise to 122 poise (see Appendix A) but was validated up to 1,100 poise (validation data are given in Reference 17). The composition range over which the 2005 DWPF viscosity model was developed is given in Table 2.

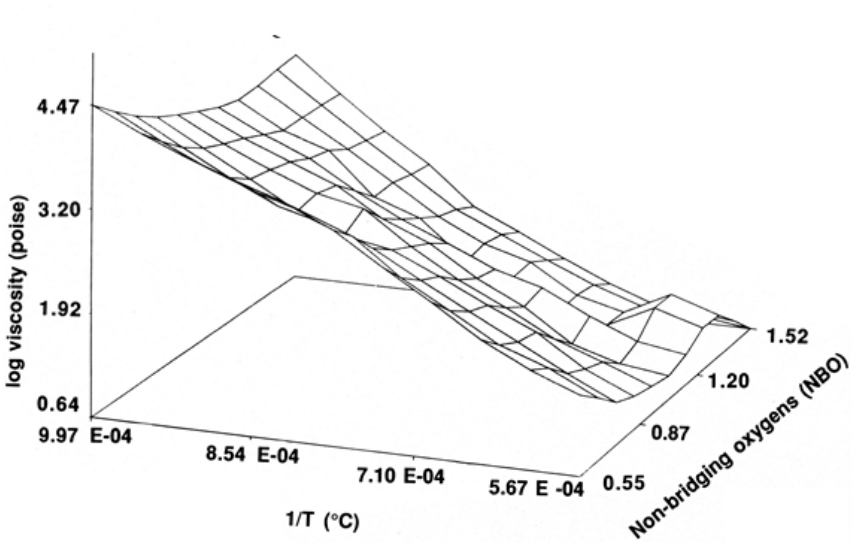


Figure 1-1. DWPF viscosity model showing the relationship between composition (NBO), viscosity and temperature.

Radioactive glasses were not included in the development of the 1991 DWPF viscosity model because the commercial glass laboratories that were performing the measurements could not handle radioactive glasses. The SRNL developed radioactive viscosity measurement capability in 1998. The 1991 viscosity model was re-examined in 2005 [17] to determine whether radioactive components were needed in the model and to determine the impact of having used the as-batched instead of as-measured glass compositions. The following was concluded:

- the 1991 DWPF PCCS viscosity model was found to be biased due to six as-batched glass compositions that were in error and two glasses that were determined to be phase separated: phase separated glasses can give anomalous viscosity response [36]

- the magnitude of the bias in the 1991 DWPF viscosity model based on as-batched glass compositions over the 7-1,000 poise range relative to the non-radioactive as-measured glasses was the same as the bias observed between the as-batched model and radioactive glasses

- the coefficients of the 1991 DWPF viscosity model were revised in 2005 using the as-measured glass compositions and eliminating the inhomogeneous glass responses and this corrected the 1991 model bias

- once the bias in the 1991 DWPF viscosity model was corrected, it was shown that a U^{+6} term was not needed and a Th^{+4} term was not needed as long as the Th^{+4} concentrations in the glass were $\leq$ 1wt%

- a Th^{+4} term may be necessary for DWPF glasses containing Th^{+4} >1 wt% (ThO_2=1.14 wt%) if such concentrations are processed in the future. Subsequently, a study [37] showed that 1.8 wt% ThO_2 could be processed adequately with the historic viscosity model.

Table 2. Composition, Temperature, and Viscosity Range of DWPF Viscosity Model.

Parameter	Viscosity " Model Data" (33 glasses; 175 viscosity-temperature pairs)
	2005 MODEL DATA
Temperature (°C)	873-1491
Viscosity (poise)	10.23-1122.02
$Fe^{+2}/\Sigma Fe$	0.00-0.47
Al_2O_3(wt%)	0.00-13.90
B_2O_3(wt%)	6.41-12.20
BaO(wt%)	0.00-0.20
CaO(wt%)	0.00-1.47
Cr_2O_3(wt%)	0.00-0.09
Cs_2O(wt%)	0.00-0.15
CuO(wt%)	0.00-0.33
Cu_2O(wt%)	0.00-0.30
FeO(wt%)	0.00-7.14
Fe_2O_3(wt%)	0.00-14.20
K_2O(wt%)	0.00-5.73
La_2O_3(wt%)	0.00-0.36
Li_2O(wt%)	2.59-6.96
MgO(wt%)	0.49-2.92
MnO(wt%)	0.00-3.26
Na_2O(wt%)	5.80-15.80
Nb_2O_5 (wt%)	0.00
NiO(wt%)	0.00-2.97
P_2O_5 (wt%)	0.00
SiO_2(wt%)	45.60-77.04
SrO(wt%)	0.00-0.07
ThO_2 (wt%)	0.00
TiO_2(wt%)	0.00-1.78
U_3O_8 (wt%)	0.00
ZnO(wt%)	0.00
ZrO_2(wt%)	0.00-0.99

In the current study, the PCCS viscosity model is assessed against the future composition region of interest to DWPF for the implementation of the fully coupled flowsheet, i.e. when the SWPF comes on line to decontaminate salt solution at much higher throughputs than the current ARP and (MCU) process. This in-depth assessment is presented in Section 5.0 of this study and demonstrates that the PCCS viscosity model requires an additional parameter[f] in order to cover the SWPF composition space.

The assessment of the PCCS viscosity model also examined whether additional species or parameters were needed to encompass any changes in frit formulation that may be necessary, i.e. MgO and/or CaO to prevent nepheline crystallization.[38,39,40] The specific compositional regions assessed in Reference 41 will be the focus of the main body of this document, and this will be discussed in Section 2.0.

[f] Where a parameter can be an individual oxide component or a group of oxides, like the alkali oxides of Cs, Na, K, and Li, that act as a grouped or lumped parameter in a model.

1.2 Quality Assurance

All the model assessments presented in this study were performed in accordance with DOE/RW-0333P and a Quality Assurance Program (QAP) that meets the Quality Assurance criteria specified in DOE O. 414.1, *Quality Assurance*, 10 CFR 830, *Nuclear Safety Management*, Subpart A, "*Quality Assurance Requirements*", paragraph 830.122 and also meets the requirements of ASME Nuclear Quality Assurance (NQA)-1, *Quality Assurance Requirements for Nuclear Facility Applications.*

The customer for this work is DWPF/SALTSTONE Facility Engineering. The point of contact is E.W. Holtzscheiter. The request is detailed in X-TTR-S-00012 and is in accordance with the Task Technical and Quality Assurance Plan (TTQAP) given in Reference 42. This work involved research and development that is considered technical baseline. The TTR requires DOE/RW-0333P to be invoked for specific tasks associated with waste form affecting properties (such as durability). All other scopes do not require RW-0333P procedures.

Requirements for performing reviews of technical reports and the extent of review are established in manual E7 2.60. SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2. All of the viscosity property-composition models presented in this report were conducted using JMP Version 11.1.1 (CMJ), validated using JMP Pro Version 11.2.1 (TBE), and checked by E7 2.60 using JMP Version 11.2.0 (CLT).[43]

2.0 DWPF Process/Product (P/P) Modeling Constraints

2.1 Modeling Constraints Common to PCCS Models

For all the PCCS models and validation data, various constraints are applied on the data. The first requires that the chemical composition of the glass, on an oxide basis, be within 100±5 weight percent (wt%).[44] The "sum of oxides" constraint minimizes the impact of analytic errors during modeling and validation.

Moreover, a given glass must be homogeneous, i.e. not phase separated by liquid-liquid amorphous phase separation (APS). Regions of APS are known to form due to low Al_2O_3 ($\leq$3.00 wt%), high P_2O_5 ($\geq$2.25 wt%), or high B_2O_3 ($\geq$14.00 wt%) concentrations in HLW glasses, and so these compositions are excluded from modeling (see Figure 2-1). Sometimes an XRD of an as-quenched glass will show a double amorphous hump rather than a single amorphous hump which is also an indication of APS. Occasionally, Scanning Electron Microscopy (SEM) or Transmission Electron Microscopy (TEM) is necessary to make the determination of whether a glass is phase separated or not.[18,19] In References 18 and 19, a "homogeneity constraint" based on glass composition was developed to distinguish between homogeneous and phase separated glasses. Likewise, glasses for modeling should not be crystallized because phase separated and/or crystallized glasses can give anomalous durability [18,19,45,46,47], viscosity [36], and liquidus [48] responses.

The glass REDOX, expressed as the $Fe^{2+}/\Sigma Fe$ ratio, must be <0.33, which is the upper limit of processability in the DWPF melter. This is because REDOX values <0.33 have been shown not to impact glass durability [49,50,51], glass viscosity, or glass liquidus values, while higher REDOX ratios (more reducing values) can impact these properties.

The alkali (ΣR_2O where R=Rb, Cs, Na, Li, or K) and alumina (Al_2O_3) constraints shown in Figure 2-1 were developed after the DWPF durability model (THERMO™) was developed to ensure that the durability response of a glass could be modeled. The alkali and alumina constraint replaced the "homogeneity constraint" and became known as the "reduction of constraints (ROC)" as discussed in Appendix B.1. The ROC within PCCS determines whether a glass can be processed in DWPF. The ROC

as shown in Figure 2-1 has worked for DWPF glasses with 0-2.00 wt% TiO_2. Recent investigations [52] have shown that for glasses such as the SWPF glasses with TiO_2>2.00 wt% that the ROC constraint has to be $Al_2O_3 \geq 4.00$ wt% which alters the Figure 2-1 constraints to those shown in Figure 2-2.

The constraints, without the uncertainties factored into the values shown, are summarized graphically in Figure 2-1 and discussed in detail in Appendix B. These constraints are applied to the modeling data (composition and property) so that model accuracy is maximized and model error is minimized by ensuring complete glass analyses and no anomalous property responses.

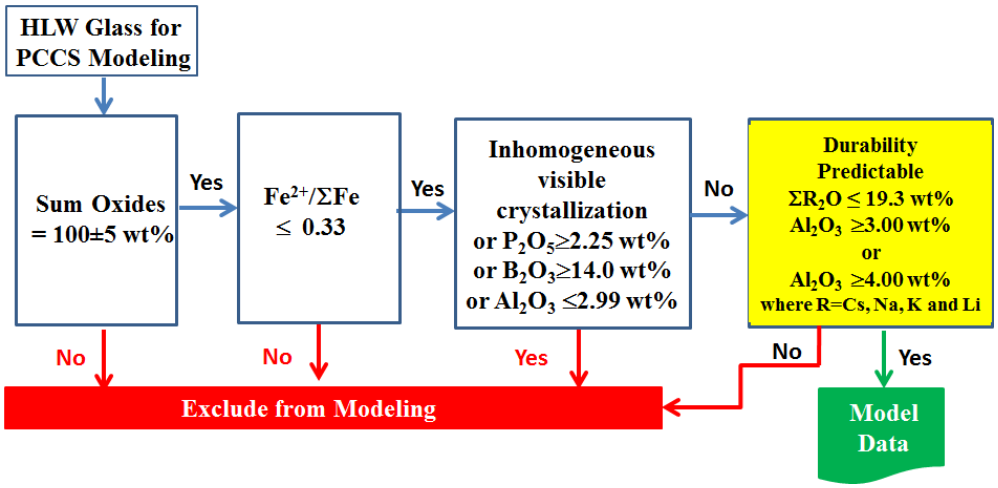


Figure 2-1. Graphical Representation of the Constraints Applied to the Choice of Model and Validation Data for the Durability, Viscosity, and Liquidus P/P Models for glasses with 0-2.00 wt% TiO_2. The Al_2O_3 term in the inhomogeneous by visible crystallization is 2.99 wt% to accommodate the WCP Purex glass which contains 2.99 wt% Al_2O_3.

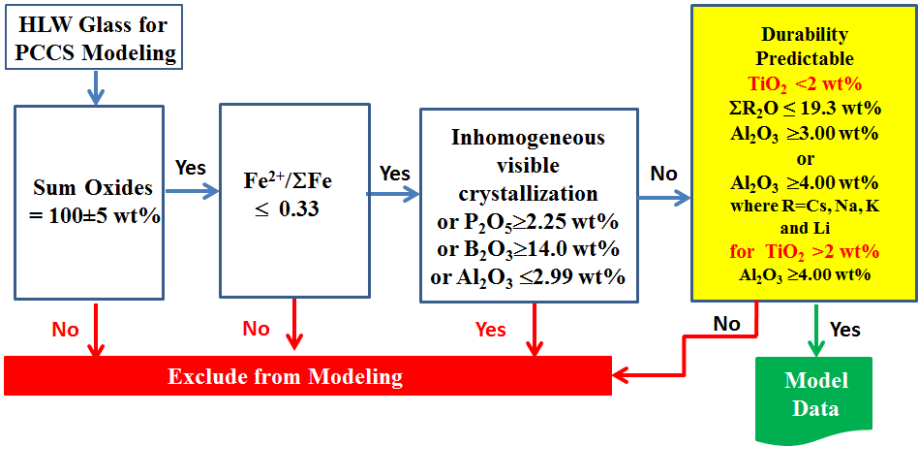


Figure 2-2. Graphical Representation of the Constraints Applied to the Choice of Model and Validation Data for the Durability, Viscosity, and Liquidus P/P Models for glasses with 0-2.00 wt% TiO_2 and glasses with ≥ 2.00 wt% TiO_2. The Al_2O_3 term in the "inhomogeneous by visible crystallization" box is 2.99 wt% to accommodate the WCP Purex glass.

2.2 Modeling Constraints Unique to the PCCS Viscosity Model

Melt viscosity is a unique property and the measurement of this property invokes additional modeling constraints in addition to those discussed in Section 2.1. The unique constraints are:

- no crystallized glasses nor glasses that crystallized during viscosity measurement, i.e. anomalous hysteresis curves, were used as the viscosity of crystallized glasses is non-Newtonian (Note: not all the viscosity measurement vendors provided hysteresis curves. Specifically, OCF and CELS determined that glasses had crystallized during viscosity measurement if there was a sharp break in the viscosity-temperature curves and ES-VSL was not required to perform hysteresis as it is not a requirement in ASTM C965 and it was not specified in the statement of work).

- if the measured temperature was ≤800°C, the data were excluded to avoid bias due to potential non-Newtonian viscosity behavior caused by crystallization of the glass below 800°C (for viscosity measurements where hysteresis curves were not provided by the vendor).

- no viscosities below 10 poise as the ASTM 965 procedure can be inaccurate in this range of viscosity
  - if more than 2 out of 5 measurement points at different temperatures violated the 10 poise criteria then the entire set of glass viscosities was not considered for validation.

3.0 Defining Future DWPF Processing Ranges

With the initiation of the ARP and MCU at SRS in 2008, there was a need to revisit the DWPF homogeneity constraint shown in Figure 2-1 and discussed in Appendix A for coupled operations. This constraint was specifically addressed through the variability study for Sludge Batch 5 (SB5).[53] Table 3 defines the compositional region of interest for coupled operations at DWPF with TiO_2 levels up to 2 wt%.[53]

Table 3. Oxide Intervals for Reduction of Constraints Study for Coupled Operations with ARP and MCU

Oxide	Minimum (wt%)	Maximum (wt%)
Al_2O_3	3.25	18
B_2O_3	4.5	14
CaO	0	4
Cr_2O_3	0	0.2
Fe_2O_3	5	21
Li_2O	4	7
MgO	0	1.5
MnO	0.3	5.5
Na_2O	10	18
NiO	0	2.5
SiO_2	30	55
TiO_2	0.5	2.0
U_3O_8	0	9.5
Others	0	2.0

The information in Table 3 was then used to support an effort to define any potential gaps in the compositional range of the current PCCS models when compared to the compositional region projected for the SWPF flowsheet. In addition to addressing this issue for the PCCS models, the SWPF gap analysis study [41,42,54] extended the reduction of constraints coverage to the glass composition region

anticipated for the DWPF and SWPF coupled flowsheet. From Reference 54, the compositional region of interest is defined by the oxides and wt% intervals given in Table 4. In this table, the shaded oxide rows define the "others" component for this compositional region.

Thus, one may look to the glass regions of Table 3 and Table 4 to define the region of interest for assessing the applicability of the historic viscosity-composition model for SWPF processing. The DWPF viscosity model data [16], augmented by the validation data given in Reference 17, was used to investigate the applicability of the existing viscosity data to the SWPF space defined by Table 3 and Table 4 (see Reference 55). Additional viscosity validation data have been generated at SRNL since Reference 17 was published. The sources of the viscosity model and validation data as a function of measurement temperature and glass composition are discussed in Section 4.1. These additional data were also used to assess how valid the historic DWPF viscosity model is over the future DWPF compositional regions defined by Table 3 and Table 4 (see Reference 55).

Table 4. Oxide Intervals for SWPF Gap Analysis Study

Oxide	Minimum (wt%)	Maximum (wt%)
Al_2O_3	3.5	13
B_2O_3	4.5	10
BaO	0	0.25
CaO	0.2	2
Ce_2O_3	0	0.2
CoO	0	0.1
Cr_2O_3	0	0.2
Cs_2O	0.3	1
CuO	0	0.1
Fe_2O_3	5	16
K_2O	0	0.2
La_2O_3	0	0.1
Li_2O	1	7
MgO	0	2
MnO	0.2	4
Na_2O	8	18
NiO	0	2
PbO	0	0.25
SO_4	0	0.3
SiO_2	40	55
ThO_2	0	1
TiO_2	2	6
U_3O_8	0	6
ZnO	0	0.2
ZrO_2	0	0.25

4.0 Experimental

4.1 Historic Viscosity Model and Validation Databases [from Reference 17]

Forty one glasses of varying, expected extreme DWPF compositions were fabricated between 1984 and 1996. The range of the individual oxides and the sum of oxides is given in Table 5 and the number of

glasses and the studies from which they were derived are given in Table 6. During 1984-1996, viscosity, liquidus temperature (T_L), and replicate chemical analyses were performed on these glasses by commercial glass laboratories such as Corning Engineering Laboratory Services (CELS) and Owen Corning Fiberglass (OCF) analytic division known as Sharp Shurtz (SS). Often duplicate glass compositions were re-made and sent to the laboratories for replicate measurements. Thus, there are two Frit 131 average sludge-only glasses that were made in 1985 (designated AH131AV-1985 and 1985-2) and another Frit 131 average sludge-only glass made in 1988 (designated AH131AV-1988). The laboratory performing >90% of the chemical analyses was CELS as indicated in Appendix A. The viscosity was measured by both OCF-SS and CELS but the data that were used in modeling were the data generated by SS using ASTM C965A which eliminated bias due to unwanted crystallization at the lower temperatures used by CELS during viscosity measurement using ASTM 965B.

Table 5. Temperature, Viscosity and Composition Ranges for the Historical DWPF Viscosity Model (see Appendix A for individual analyses)

Parameter	Maximum Value	Minimum Value
Temperature (°C)	1491	873
Viscosity (poise)	1122.02	10.23
$Fe^{+2}/\Sigma Fe$	0.47	0.00
Al_2O_3(wt%)	13.90	0.00
B_2O_3(wt%)	12.20	6.41
BaO(wt%)	0.20	0.00
CaO(wt%)	1.47	0.00
Cr_2O_3(wt%)	0.09	0.00
Cs_2O(wt%)	0.15	0.00
CuO(wt%)	0.33	0.00
Cu_2O(wt%)	0.30	0.00
FeO(wt%)	7.14	0.00
Fe_2O_3(wt%)	14.20	0.00
K_2O(wt%)	5.73	0.00
La_2O_3(wt%)	0.36	0.00
Li_2O(wt%)	6.96	2.59
MgO(wt%)	2.92	0.49
MnO(wt%)	3.26	0.00
Na_2O(wt%)	15.80	5.80
NiO(wt%)	2.97	0.00
SiO_2(wt%)	77.04	45.60
SrO(wt%)	0.07	0.00
TiO_2(wt%)	1.78	0.00
ZnO(wt%)	0.00	0.00
ZrO_2(wt%)	0.99	0.00
Sum Oxides	100.28	98.23

Table 6. References for Viscosity Model and Validation

Sample Study	Model or Validation	Number of Viscosity-Temperature Measurements	Viscosity Data Year	Reference
Model Data	HISTORIC MODEL – CELS and OCF-SS	160	2005	17
DWPF Startup Frit	HISTORIC MODEL (OCF-SS)	15	2005	17, 56
DWPF Startup Frit	HISTORIC VALIDATION (Round Robin) Standards used in other studies	164 + 40	2005	17, 57, 58
Waste Form Compliance Plan (WCP) Glasses	HISTORIC VALIDATION	129	2005	17, 59, 60, 61, 62, 66, 69, 71
PNNL Studies (Chemical Variability Study; CVS-1 and CVS-2)	HISTORIC VALIDATION	699	2005	63
SRNL Integrated DWPF Melter System (IDMS) glass (Hanford, PX and HM)	HISTORIC VALIDATION	195	2005	17, 62
SRNL SGM	HISTORIC VALIDATION	331	2005	62
SRNL Soper (1982)	HISTORIC VALIDATION	124	2005	17, DPSTN-3345, DPSTN-4025, DPSTN-4416, 64
Crystalline SilicoTitanate (CST) Glasses	HISTORIC U VALIDATION AND CST MODEL	70	2005	17, 65, 66, 67, 68, 69
Precipitate Hydrolysis Aqueous (PHA)	HISTORIC U VALIDATION	74		17, 70, 71, 72, 73, 74
Environmental Assessment (EA) Glass	HISTORIC VALIDATION	7	2005	17, 95,96
West Valley (WVCM and WVUTh, AL,CR,FE,MN, NI,P glasses)	URANIUM-THORIUM VALIDATION	228	2005	17, 75, 76
M-Area	HISTORIC U VALIDATION	80	2005	77
U and U/Th Glasses (RC, RCTH,Tank 40, rchwl, Glass 1-5 and U std)	HISTORIC U and Th VALIDATION	466	2005	17, 58, 61, 78
M-Area (compositions revised in 2014)	HISTORIC U VALIDATION	80	2014	79
PNNL Study Glasses (SG)	VALIDATION NOT USED	60	2014	80
Sulfate Glasses	VALIDATION NOT USED	90	2014	81
High Loaded HLW Glasses	SWPF MODEL VALIDATION	264	2014	82, 83
CST/MST Glasses	CST MODEL AND VALIDATION	587	2014	84, 85, 86, 87
DWPF Non-Rad Startup Glasses (WP-14, 15, 16) as a Function of REDOX	VALIDATION NOT USED	48	2014	88

CELS dissolved the glasses and analyzed the compositions of the AH glasses in quadruplicate[†] by Inductively Coupled Plasma-Emission Spectroscopy (ICP-ES) using ASTM C1463 so that any effects of short term instrument bias on the whole element chemistry would be observable. CELS analyzed the various black frits six to ten times as indicated in Appendix A. All CELS composition analyses are traceable to the NBS 777 standard glass. These data indicate little random or systematic variation for these analyses. The white frits were dissolved and analyzed by SRNL's Analytic Development Directorate (ADD) and analyzed by ICP-ES in duplicate.

The historical model validation data are given in the appendices of Reference 17 and the references cited therein. These studies are summarized in Table 6. Most of the historical validation glasses were measured at SRNL using ASTM C965A. However, the historic validation data also included ~200 replicate viscosity measurements on the DWPF startup frit, a round robin, by six different laboratories [89]. The DWPF startup frit data round robin was performed so that the DWPF startup frit could be used to calibrate viscometers for performing ASTM C965A or B since the SRM711 standard called for in ASTM C965 has a measured viscosity at 1150°C of 4390 poise whereas a typical HLW glass is between 20 and 100 poise at 1150°C. After the DWPF round robin, this startup frit was used to calibrate the SRNL viscometers instead of SRM711. Therefore, there are multiple measurements available for the DWPF startup frit as indicated in Table 6. Additional references with validation data are shown in Table 6 and include ~130 measurements on the Waste Compliance Plan (WCP) glasses by OCF-SS, ~10 measurements of the Environmental Assessment (EA) glass by OCF-SS, ~140 glasses from West Valley measured at Alfred University, ~125 measurements from SRNL testing in the early 1980's, ~700 measurements from Pacific Northwest National Laboratory (PNNL) on two different statistically designed matrices of simulated waste glasses (Composition Variability Study I and II), and ~530 measurements made by OCF-SS on glasses made in the SRNL Integrated DWPF Melter System (IDMS) and the Scale Glass Melter (SGM).

A data set of 192 radioactive viscosity-temperature pairs containing only U^{+6} was also used as validation data for the historical viscosity model. The historic uranium validation data reference is given in Table 6 and can also be found in Reference 17. Uranium appeared to have little to no impact on glass viscosity. An additional 26 glasses for which 98 viscosity-temperature measurements were available indicate disparate roles for ThO_2 depending on the U_3O_8 concentration and the Al_2O_3 concentration of the glasses measured.

In addition, glasses from DWPF Waste Qualification Runs (WQR) WP-14, WP-15, and WP-17 taken from DWPF canisters S00009, S00179, and S00310 [90] were used as validation data. The viscosities of the WQR glasses were measured at the SRNL in 1997 during non-radioactive startup testing of the SRNL radioactive viscometer. The radioactive viscosity measurement capability was set up in SRNL in 1998 with a Harrop viscometer [91, 92]. The ASTM C965A procedure was modified for use at SRNL to use only 6-7 grams of glass compared to the 200-700 grams required by the commercial laboratories. The use of the WQR glasses as historic validation data is given in Reference 17.

In order to constrain the historical validation data to a composition range that overlapped the DWPF composition range but was, in general broader, while not having to develop new composition terms for ZrO_2, CaO, and MgO which are all known to impact glass viscosity strongly, the following boundary conditions were set:

- if the ZrO_2 was ≥ 2.00 wt%, which was twice the ZrO_2 content of the data on which the DWPF model is based (see Table 5), the data were excluded

[†] That is, two dissolutions were performed—one on each day—with each dissolution being analyzed in duplicate.

- if the CaO was ≥ 3.5 wt%, which was more than twice the CaO content of the data on which the DWPF model is based (see Table 5), the data were excluded
- if the MgO was ≥ 6.00 wt%, which was twice the MgO content of the data on which the DWPF model is based (see Table 5), the data were excluded
- if the B_2O_3 was ≥ 14.00 wt%, which was over the B_2O_3 content of the data on which the DWPF model is based (see Table 5) by 2 wt% but clearly in the range of phase separated glasses as defined by Tovena [45], the data were excluded.

Altogether, 1805 waste glass viscosity-temperature pairs and measured glass compositions were used for validation of the historic viscosity model (Table 6). However, the historic validation data from Reference 17 only went to 1.43 w% TiO_2 while the historical model data went to 1.78 wt% TiO_2. The limitation of TiO_2 concentrations in the historic model and validation data is due primarily to the 2 wt% TiO_2 solubility limit that has been imposed for DWPF since 2003 [23] and the previous 1 wt% TiO_2 solubility limit that had been imposed for DWPF between 1990-2003.[93]

4.2 SWPF (TiO_2-only) Viscosity Model Database

The SWPF glasses were made and analyzed by Energy Solutions-Vitreous State Laboratory (ES-VSL). The details of the glass fabrication are given in Reference.94 The chemical compositions were measured by X-ray Fluorescence (XRF) and other methods. Since XRF cannot measure light elements such as B and Li, the glasses were dissolved and analyzed by Direct Current Plasma Emission Spectrometry (DCP) for these two elements. For each glass, two XRF and two DCP preparations were performed and two reads on each were performed on different days. Therefore, each glass had four replicate measurements. A glass standard, the SRNL EA glass was used. The EA glass had been manufactured and analyzed by CELS ten replicate times and the analyses were validated by ten additional analyses by SRNL ADD.[95,96] The details of the SWPF glass measurements and bias correction to the EA glass standards are discussed elsewhere.[97] The biased corrected glass compositions are given in Appendix C.

The SWPF glass viscosities were measured by ES-VSL using ASTM C965A and documented in Reference 98. The relative torque of a rotating spindle immersed in molten glass was measured as a function of rotational velocity (revolutions per minute, rpm) at regular temperature intervals between ≈950°C and ≈1250°C; the melt viscosity was calculated from the torque data versus rpm. Measurements were checked against a NIST traceable standard reference glass (SRM711) since the DWPF startup frit had not been specified as the standard in the scope of work provided to ES-VSL. Among the problems with the SRM711 standard is the fact that there are only two calibration points in the region of viscosity of interest to DWPF processing. Only one SRM711 calibration curve was provided by ES-VSL and there is some deviation from the SRM711 calibration curve where the ES-VSL data are biased low at higher temperatures and biased high at lower temperatures. However, the amount of bias is difficult to quantify since there are only two calibration data points in the DWPF temperature range of interest. Therefore, no statement regarding the bias in the ES-VSL data can be made.

The ES-VSL did not check for the hysteresis of the viscosity curves, i.e. whether the viscosity curves measured during heat up were the same as those measured during cool down. This is not required in ASTM C965A and was not specified in the scope of work provided to ES-VSL. It is a methodology used at SRNL to provide additional data as to whether the samples crystallized during the heat up of the sample for the viscosity measurement as this can be used to screen out viscosity measurements that were impacted by crystallization per the modeling criteria given in Figure 2-1 and Figure 2-2. Viscosity measurements on crystallized glasses can be non-Newtonian in behavior which is undesirable when a Newtonian viscosity model is being developed.

The SWPF viscosity measurements are given in Appendix C. Data that were excluded from modeling is shaded in Appendix C. Data that were excluded from modeling included SWPF-08 which was visually inhomogeneous, SWPF-12 which appears to have crystallized during the viscosity measurement (see Reference 97), SWPF-01 through SWPF-09 which contained TiO_2>2.00 wt% and Al_2O_3<4.00 wt%, and a few viscosity values for other glasses that were 10 poise or less. The individual ES-VSL SWPF glass viscosities are fitted to the Fulcher Equations (see Equation 2) to assess their Newtonian flow behavior in Reference 97. The Fulcher fitting normally does not help determine whether the sample crystallized during the viscosity measurement unless the fit is very non-linear, i.e. SWPF-12, or there is one obvious outlier point. However, the two glasses that gave poor Fulcher fits (SWPF-08 and SWPF-12) were excluded from modeling for other reasons. It is assumed that the remaining glasses used for modeling were not crystallized.

4.3 SWPF (TiO_2-only) Viscosity Validation Database

References 82-83 were studies designed to maximize waste loading in defense waste glasses (see Table 6). These glasses span TiO_2 compositions from 1.25 to 6.76 wt%. These high waste loaded glasses [82-83] are, therefore, used in this study to validate the TiO_2 term in the TiO_2-only viscosity model.

The details of the composition and viscosity measurements for the TiO_2-only validation glasses are given in References 82-83 and include dissolution of the glasses by the Process Science Analytical Laboratory (PSAL) using the methods given in ASTM C1463 for dissolution followed by ICP-ES for cations and Ion Chromatography (IC) for anions. The viscosity measurements were made on the SRNL radioactive Harrop viscometer [91,92]. The TiO_2-only composition-viscosity validation database is given in Appendix D. Glasses that were omitted as TiO_2-only validation data included the following:

- HLW-01 through HLW-06 and FY09EM21-03 which were crystallized
- HLW-15, HLW-18, FY09EM21-05, FY09EM21-08, FY09EM21-11, FY09EM21-14 which contained >2.00 wt% TiO_2 and Al_2O_3<4.00 wt%
- FY09EM21-14 which had over 14 wt% B_2O_3
- Viscosity values for glasses that were 10 poise or less.

4.4 CST Viscosity Model Database

Table 6 lists the CST viscosity study data as having been used to validate the historic viscosity model and document why a uranium term was not needed in the historic viscosity model. In this study, the CST viscosity data from References 65-69 were used to develop a viscosity model with a TiO_2, Nb_2O_5, and ZrO_2 term (all species found in crystalline silicotitanate). Many of the CST glasses failed the old ROC limits (≤2.00 TiO_2 and Al_2O_3<3.00 wt%) and many more failed the higher TiO_2 ROC limits (>2.00 wt% TiO_2 and Al_2O_3<4.00 wt%) from Reference 52 on the CST glass compositions. This left only four glasses from these CST studies to use to develop a CST model. This is an insufficient number of glasses to develop a model.

Half of the 58 glass dataset in References 84-87 was used to supplement the CST study glasses. The KT studies in References 84-87 were designed to maximize the amount of TiO_2 in a glass if the DWPF vitrified combinations of CST and MST. Half of the 58 glasses were selected randomly as CST model data and half were reserved as CST validation data. The glasses given in each data set are shown in Table 7. These glasses span TiO_2 compositions from 3.03 to 6.62 wt% TiO_2 (Table 7 and Appendix E).

The details of the composition and viscosity measurements for the CST model glasses are given in References 65-69 and References 84-87 and include dissolution of the glasses by PSAL using the methods given in ASTM C1463 for dissolution followed by ICP-ES for cations and IC for anions. The

viscosity measurements were made on the SRNL radioactive Harrop viscometer [91,92]. The CST composition-viscosity model database is given in Appendix E.

Table 7. CST Model Data vs. Validation Data Randomly Selected

CST Model Data Sample Identifications	CST Validation Data Sample Identifications
CST 15	KT04-03
CST 20	KT04-04
CST 26	KT04-05
CST 32	KT04-07
KT04-01	KT06-03
KT04-02	KT06-04
KT04-06	KT06-05
KT04-08	KT06-06
KT04-09	KT06-07
KT04-10	KT06-09
KT06-01	KT06-10
KT06-02	KT06-11
KT06-08	KT06-12
KT06-17	KT06-13
KT06-18	KT06-14
KT07-02	KT06-15
KT07-06	KT06-16
KT07-07	KT07-01
KT07-09	KT07-03
KT07-10	KT07-04
KT08-01	KT07-05
KT08-02	KT07-08
KT08-03	KT08-07
KT08-04	KT08-08
KT08-05	KT08-09
KT08-06	KT10-02
KT08-10	KT10-04
KT10-01	KT10-05
KT10-03	KT10-07
KT10-06	
KT10-08	
KT10-09	
KT10-10	
TiO_2 = 3.03-6.62 wt%	TiO_2 = 4.07-6.53 wt%

4.5 CST Viscosity Validation Database

References 84-87 were studies designed to maximize the amount of TiO_2 in a glass if the DWPF vitrified combinations of CST and MST (Table 6). Half of these glasses were randomly selected to be used as validation data for the CST viscosity model (Table 7). These glasses span TiO_2 compositions from 4.07 to 6.53 wt% TiO_2 (Table 7 and Appendix F). These CST-MST glasses [84-87] are, therefore, used in this

study to validate the TiO_2 term in the CST viscosity model. This half of the CST-MST glasses [84-87] is also used to validate the Nb_2O_5 and ZrO_2 terms in the CST viscosity model. Additional glasses, such as the West Valley glasses could not be used to validate the ZrO_2 term as almost all the West Valley glasses contain ThO_2 (1.80-3.60 wt%) in addition to ZrO_2 (0.30-5.50 wt%). While the SWPF validation glasses in Appendix D can also be used to validate the CST model these glasses do not contain Nb_2O_5 and little ZrO_2.

The details of the composition and viscosity measurements for the CST-MST validation glasses are given in References [84-87] and include dissolution of the glasses by PSAL using the methods given in ASTM C1463 for dissolution followed by ICP-ES for cations and IC for anions. The viscosity measurements were made on the SRNL radioactive Harrop viscometer [91,92]. The CST validation composition-viscosity database is given in Appendix F.

5.0 SWPF (TiO_2-only) Viscosity Model

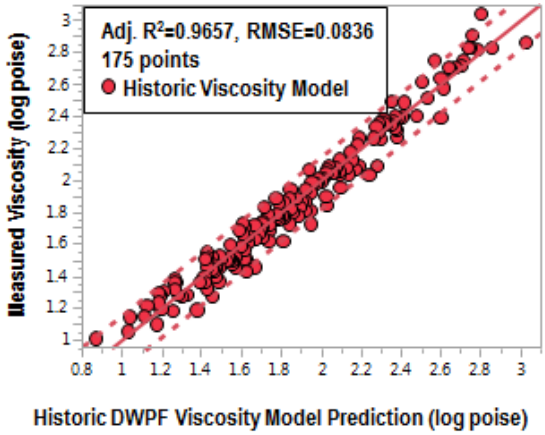
5.1 Evaluation of the SWPF Glasses Against the Historic DWPF Viscosity Model

The fit of the historic DWPF viscosity model (from Equation 1 and Equation 3) is shown in Figure 5-1a. It consists of the 175 data points (temperature-viscosity pairs) from 33 different glasses in the historic model database (Appendix A). The model has an adjusted R^2 of 0.9657 and a RMSE of 0.0836.

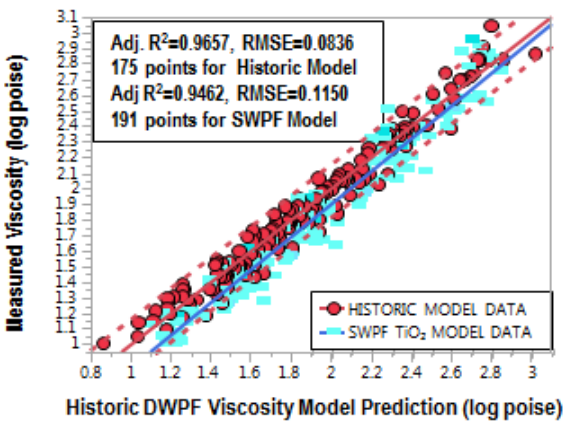
For the SWPF glass viscosity data given in Appendix C (a pool of 198 temperature-viscosity pairs), three temperature-viscosity pairs were excluded from fitting the data. These three data points had viscosities of <10 poise which is one of the exclusion criteria discussed in Section 2.2. Four points from sample SWPF-12 were removed as this sample was visually inhomogeneous.[94] This left an original SWPF TiO_2-only data set of 191 temperature-viscosity pairs. These 191 temperature-viscosity pairs were evaluated against the historic DWPF viscosity model as shown in Figure 5-1b where it can be noted that the SWPF glass viscosities (blue rectangles) do not fit the historic DWPF model. Most of the SWPF TiO_2 rich glasses lie at or below the U95 confidence band of the historic glass model. This indicates that a TiO_2 term is needed in the historic viscosity model.

As modeling progressed, an additional thirty six data points (4 points each for glasses SWPF-01 through SWPF-09) were excluded due to the new ROC requirement that the Al_2O_3 be ≥ 4.0 wt% (see Figure 2-2).[52] However, two of the <10 poise data points were in the SWPF-01 through SWPF-09 dataset. For SWPF-08 and SWPF-12 it was also suspected that these glasses were crystalline before the viscosity measurement was made and this was later confirmed.[f] This left a data modeling pool of 159 temperature-viscosity pairs for 40 of the original 50 glasses which is used in the next section to develop the SWPF TiO_2-only viscosity model.

[f] preliminary liquidus data indicated that these glasses had crystallized Fe_2O_3 and spinel during fabrication,



(a) Historic DWPF viscosity model (from Equations 1 and 3)



(b) Historic DWPF viscosity model (from Equations 1 and 3) and data from SWPF Database Overlain

Figure 5-1. Comparisons of the Historic and SWPF Database Glasses Using the Historic DWPF Viscosity Model (Equations 1 and 3).

5.2 Structural Role of TiO_2 in DWPF Glasses

The historic DWPF viscosity model is a modification of an NBO approach originally developed by White and Minser.[30] While these authors gave mechanistic structural terms for alkali, Fe_2O_3, SiO_2, Al_2O_3 MgO, CaO, and FeO, they did not include +4 charged cations such as TiO_2 or ZrO_2. In the commercial glass industry [99] TiO_2 is known to decrease melt viscosity which implies that its structural role in glass is one of a bond modifier, ie., TiO_2 creates NBOs. Ti acts simultaneously as a network modifier and as a network former because Ti is surrounded by both NBOs and BOs.[100] TiO_4 polyhedra where Ti is 5-coordinated ($^{[5]}$Ti) exist in natural melts and these cause heterogeneities in the melt which can lead to crystallization.[100] TiO_2 is a known crystallizing agent in commercial glasses [99] and HLW defense waste glasses.[101] This is the major reason that a TiO_2 solubility limit exists in DWPF.[23] The DWPF solubility limit will be redefined once the PCCS model applicability for high TiO_2 glasses is assessed.

However, TiO_2 can be tetrahedral ($^{[4]}$Ti) and substitute for SiO_2 at temperatures below the glass transition temperature.[99] In addition, Marumo, et al.[102] noted that tetrahedral $^{[4]}$Ti increases with increasing Ti content and octahedral Ti ($^{[6]}$Ti) is favored at low Ti contents in glass. This is verified in the following sections of this study. For glasses up to ~6 wt% TiO_2 the Ti is predominately $^{[6]}$Ti and acts as a network modifier creating one NBO. It thus is a positive term in the NBO parameter. At concentrations of TiO_2 ≥6 wt% the Ti is predominately $^{[4]}$Ti according to the literature, and the equations developed in the next section for TiO_2 as a network modifier would have to be modified to account for TiO_2 being a network former. Thus the TiO_2 would be a negative term with one BO instead of one NBO. Since this would make the SWPF (TiO_2-only) model non-linear, the equations developed in Section 5.3 and validated in Section 5.5 are only considered valid up to a limit of 5.90 wt% TiO_2 as determined by the validation data in Section 5.5. The exact TiO_2 concentration at which TiO_2 switches from a network modifier to a network former lie somewhere between ~6.00 and 8.00 wt% TiO_2 and additional studies would have to be performed to determine this limit.

5.3 Development of the SWPF (TiO_2-only) Viscosity Model

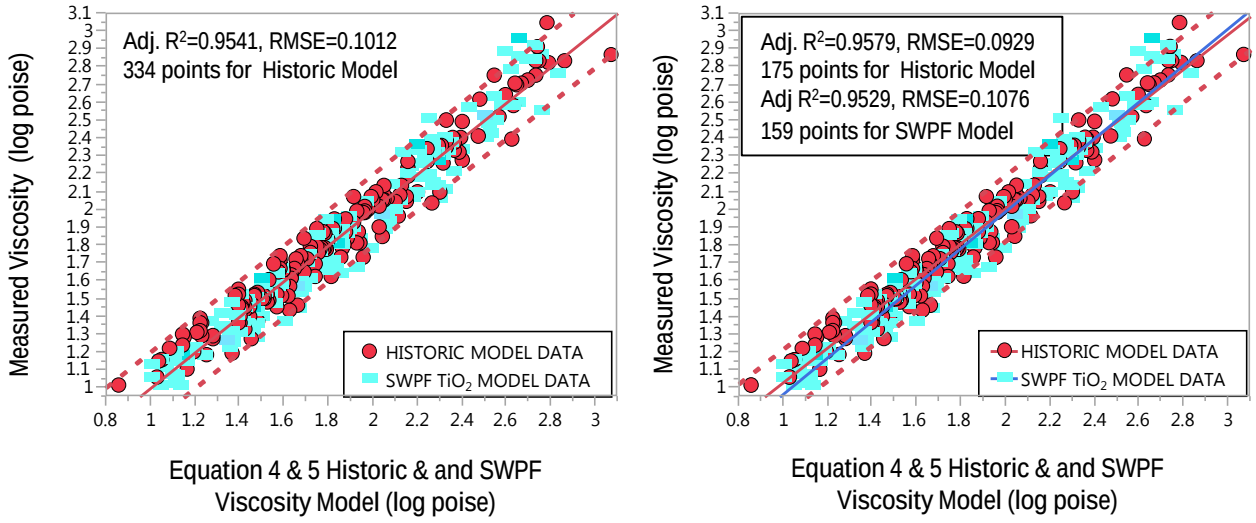
Since TiO_2, in the composition range spanned by the SWPF glass viscosity data, acts as a network modifier, it creates one NBO. Therefore, Equation 1 becomes

Equation 4 $$NBO \equiv \frac{2\,(Na_2O + K_2O + Cs_2O + Li_2O + Fe_2O_3 - Al_2O_3) + B_2O_3 + TiO_2}{SiO_2}$$

Fitting the response surface between log viscosity-1/temperature-NBO for the pooled historic and SWPF databases generates the coefficients given in Equation 5. This response surface has 334 data points (temperature-viscosity pair-NBO combinations) and Equation 3 becomes

Equation 5 $$\log\eta(poise) = -0.606597 + \left(\frac{4587.5797}{T(^oC)}\right) - (1.711755 * NBO)$$

Figure 5-2a shows how the historic and SWPF glasses overlap one another using Equation 4 and Equation 5 which incorporates the bond breaking caused by concentrations of TiO_2 up to 5.85 wt%. Application of Equation 4 and Equation 5 to the pooled viscosity dataset as shown in Figure 5-2a gives an adjusted R^2=0.9541 and a RMSE=0.1012. Figure 5-2b shows how each of the datasets (historic vs. SWPF) fit the revised Equation 4 and Equation 5 when analyzed individually. Figure 5-2b indicates that the SWPF viscosity data give about the same adjusted R^2 as the historic data generated by the two commercial glass laboratories (CELS and OCF-SS) but the RMSE is somewhat larger indicating more scatter in the data. The pooled datasets give an overall good fit and R^2 value since potential bias and crystallization (hysteresis) are not known for the SWPF dataset.



(a) Historic and SWPF viscosity model (from Equations 4 and 5) fitted as a pooled dataset

(b) Historic and SWPF viscosity model (from Equations 4 and 5) fitted as separate datasets

Figure 5-2. New SWPF TiO_2-only Model fit to Pooled SWPF and Historic Databases and Fit Separately.

The analyzed SWPF glasses contained Na_2O and Cs_2O between 8.03-18.14 wt% and 0.48-1.62 wt%, respectively. This allowed validation of the lumped Na_2O and Cs_2O terms in the historic viscosity model up to these high concentrations.

5.4 Property Acceptable Region (PAR) Assessments for the SWPF (TiO_2-only) Viscosity Model

This section provides a closer look at how property-composition models are integrated into DWPF's PCCS, and the information that is necessary to complete that process for the TiO_2-only viscosity model. In the DWPF, radioactive sludge is blended with ground glass (frit) in the SME to produce melter feed

slurry. After the SME, the material then passes to the Melter Feed Tank (MFT), which continuously feeds the melter. The melter vitrifies the feed slurry into a molten glass waste form, which is poured into stainless steel canisters for cooling and ultimate storage.

DWPF personnel cannot wait until the melt or waste glass has been made to assess its acceptability, since by then no further changes to either are possible. Therefore, the acceptability decision is made at the SME. The SME is uniquely positioned in the process — it is both the first control point in the process wherein all necessary constituents are present and the last control point at which any change to them can be effected. Thus, the control strategy involves monitoring the blended SME batch.

The monitoring of the SME is accomplished by sampling its contents. For each SME batch, a set of ($n \geq 4$) samples is taken to initiate an acceptability decision. Each of these samples is vitrified and the chemical compositions of the resulting n glasses are measured. The average of the measured chemical compositions for a minimum of 4 samples is determined, and this average composition serves as the basis for the acceptability decision for the SME batch.

However, the average chemical composition, while necessary, is not sufficient in and of itself, to complete the assessment of the performance of the SME contents against the PCCS constraints. Some of the constraints involve properties (either process or product quality) such as viscosity, liquidus temperature, and durability. These properties cannot be measured in situ, and thus, they must be predicted from models that relate these properties to glass composition. Not only must the model predictions satisfy their corresponding property constraints, but the constraints must also be appropriately met after the applicable modeling uncertainties are introduced into the acceptability decision.

For the constraints involving property-composition models and for most of the other constraints that directly involve composition, the uncertainties associated with the SME samples must also be accounted for as part of the acceptability decision. These uncertainties, the measurement uncertainties, include those related to the collection of the slurry samples in the SME, the preparation of these samples for measurement, and the measurements themselves. Accounting for these uncertainties, while outside of the scope of this effort, is addressed in the technical basis document for PCCS.[103]

A glass composition representing the “average” content of a SME batch is deemed to be within the acceptable operating window for the DWPF if all of the applicable constraints are satisfied, at appropriate confidence levels, after all of the related property modeling and measurement uncertainties are accounted for. Conceptually, there is a layered approach to the acceptability decision. At the first step, the question is, does the average chemical composition representing the SME contents directly or through model predictions satisfy the constraints? If the answer is yes, the composition is said to be within the Expected Property Acceptable Region (EPAR). However, the EPAR does not account for uncertainties in the predicting models. If, after the property model uncertainties are accounted for (to be discussed later), the chemical composition still meets the constraints, then the composition is said to be within the Property Acceptable Region (PAR). Finally, if, after measurement uncertainties are accounted for (to be discussed later), the chemical composition still meets the constraints, then the composition is said to be within the Measurement Acceptable Region (MAR). A composition that is within the MAR for each of the applicable constraints is said to be within the acceptable operating window of the DWPF.

The implementation strategy for integrating the new TiO_2-only model into PCCS is similar to the strategy that was utilized for the historical model (please see SME Acceptability Rev 5.[103]) The TiO_2-only viscosity-composition model may be expressed as given by:

Equation 6 Viscosity:[††] $\log \eta = m_v c_v + b_v$

where

η is viscosity in poise,

m_v is the estimated slope for this regression model (m_v = -1.711755)

b_v is the estimated intercept determined from the fitted three-parameter model evaluated at T=1150 °C (b_v = 3.382603),

$$c_v = \frac{2\left(z_{Fe_2O_3} - z_{Al_2O_3} + z_{Cs_2O} + z_{Li_2O} + z_{K_2O} + z_{Na_2O}\right) + z_{B_2O_3} + z_{TiO_2}}{z_{SiO_2}}, \text{ and}$$

z_{oxide} represents the indicated molar oxide concentration in the glass.

This model can be back-solved (noting the fact that m_v is negative) to translate the viscosity constraints into constraints on the compositional term, c_v, as given by:

Equation 7 High Viscosity:

$$\text{high viscosity} \equiv \eta_{hv} \leq 110 \text{ poise} \qquad \Rightarrow \qquad c_{hv} \geq \left\lceil \frac{\log(\eta_{hv}) - b_v}{m_v} \right\rceil$$

Equation 8 Low Viscosity:

$$\textit{low} \text{ viscosity} \equiv \eta_{lv} \geq 20 \text{ poise} \qquad \Rightarrow \qquad c_{lv} \leq \left\lceil \frac{\log(\eta_{lv}) - b_v}{m_v} \right\rceil$$

The above inequalities describe the region in compositional space where all of the predicted values for viscosity are acceptable. This defines the EPAR for viscosity. The region is denoted as "expected" since it is derived from the fitted line, which is the expected viscosity, based upon the model for a given composition.

The determination of the PAR for this viscosity model is accomplished by accounting for the property model uncertainty in the implementation of the viscosity constraints as was performed in earlier versions of the SME acceptability report for the historic viscosity models. And as before, statistical confidence intervals are used in the determinations of this uncertainty. Specifically, Scheffé simultaneous confidence limits (also called confidence bands [104] and [105]), are used in the development of the PAR's for the constraints associated with the TiO_2-only viscosity model as they were for the historical model.

Since the TiO_2-only viscosity model is of the same form as the historic model, it too includes a linear parameter based upon the inverse temperature (1/T) at which the viscosity (η) is measured. The complete form of the TiO_2-only viscosity model may be expressed as:

[††] Actually the viscosity prediction is a three-parameter model including an inverse temperature term. However, this temperature is fixed at 1150°C for DWPF. This allows the viscosity model to be presented as a two-parameter model with the temperature-dependent term included in the pseudo-constant, b_V.

Equation 9 $$\log(\eta) = m_v c_v + m_T \frac{1}{T(^\circ C)} + b_T .$$

As already indicated in an earlier footnote, for DWPF use, the temperature is fixed at 1150°C. Thus, the predicting relationship for viscosity can be written as:

Equation 10 $$\log(\eta) = m_v c_v + b_v$$

where $b_v \equiv \frac{m_T}{T(^\circ C)} + b_T$ and T(°C) is 1150°C.

However, the additional parameter must be accounted for when defining the confidence limits for viscosity prediction. The approach used to develop the viscosity PAR is the true one-sided, 100(1–α)% Scheffé-type confidence limit. This leads to the following one-sided, 100(1–α)% Scheffé-type confidence limit to determine the PAR for each viscosity constraint:

Equation 11 $$\pi = b_T + \left(\frac{m_T}{T^*}\right) + m_v\left(c^*\right) + s_r\left\{\sqrt{pF_{2\alpha}(p, n-p)}\sqrt{\underline{c}_0\left(\mathbf{X}^T\mathbf{X}\right)^{-1}\underline{c}_0{}^T}\right\}$$

where π represents the EPAR for the corresponding constraint (20 P for low viscosity and 110 P for high viscosity), s_r is the RMSE for the regression fit, $F_{2\alpha}(p,n-p)$ is the upper 2α% tail of the F distribution with p degrees of freedom in the numerator and n-p degrees of freedom in the denominator, T* = 1150ºC, c^* is the compositionally-based term in Equation 6,

$$\underline{c}_0 \equiv \left[1, \frac{1}{T^*}, c^*\right] \text{ and } \mathbf{X} \equiv \begin{bmatrix} 1 & \frac{1}{T_1} & c_1 \\ 1 & \frac{1}{T_2} & c_2 \\ \vdots & \vdots & \vdots \\ 1 & \frac{1}{T_n} & c_n \end{bmatrix}.$$

X is an n×p matrix that contains the data for the independent variables from which the regression model was formulated where p is the number of parameters in the model and n is the number of observations used in the fitting of the TiO_2-only model. Note that the X matrix is different for this model as compared to the matrix that was used for the historical model (i.e., the new matrix had 334 observations while the historical model had 173). Thus, the product moment matrix, X^TX, is different for the two models but of dimension 3x3 for both models. The one-sided, 100(1–α)% Scheffé-type confidence limit to determine the PAR for each viscosity constraint may be written as:

Equation 12

$$\pi = b_T + \left(\frac{m_T}{T^*}\right) + m_v(c^*) + s_r\left\{\sqrt{pF_{2\alpha}(p,n-p)}\sqrt{\begin{bmatrix}1 & (1/T^*) & c^*\end{bmatrix}\begin{bmatrix}c_{0,0} & c_{0,1} & c_{0,2}\\ c_{0,1} & c_{1,1} & c_{1,2}\\ c_{0,2} & c_{1,2} & c_{2,2}\end{bmatrix}\begin{bmatrix}1\\ (1/T^*)\\ c^*\end{bmatrix}}\right\},$$

where the inverse of the $\mathbf{X}^T\mathbf{X}$ matrix is represented by the 3×3 array of c's. Since the (1/T*) term will be constant for DWPF use, the expression given by Equation 12 can be expanded for each viscosity constraint (i.e., low and high) to a quadratic in c* given by $A(c^*)^2 + B(c^*) + C = 0$ with coefficients given by the set of equations:

Equation 13

$$A \equiv m_v{}^2 - c_{2,2}\left[ps_r^2F_{2\alpha}(p,n-p)\right]$$

$$B \equiv -2\left\{m_v(\pi - b_T) + \left(c_{0,2} + \frac{c_{1,2}}{T^*}\right)\left[ps_r^2F_{2\alpha}(p,n-p)\right]\right\}$$

$$C \equiv (\pi - b_T)^2 - \left[c_{0,0} + 2\left(\frac{c_{0,1}}{T^*}\right) + \frac{c_{1,1}}{(T^*)^2}\right]\left[ps_r^2F_{2\alpha}(p,n-p)\right]$$

The information from the fitting of the TiO_2-only viscosity model that is necessary to address its property uncertainty and, thus, to derive its PAR values is provided in Exhibit 1.

Exhibit 1 Information Generated from the Fitting of the TiO_2-Only Viscosity Model

p = 3, n = 334, α = 0.05, m = -1.711755, b_T = 3.382603[1], s_r = 0.101351, and

$$\left(\mathbf{X}^T\mathbf{X}\right) = \begin{bmatrix}334 & 0.299006 & 322.49187\\ 0.299006 & 0.000270798 & 0.2899217\\ 322.49187 & 0.2899217 & 319.71202\end{bmatrix}$$

For the low viscosity constraint, the roots from the quadratic expression are 1.232996 and 1.200566, and selecting the desired root corresponding to the appropriate one-sided simultaneous confidence interval gives 1.200566 as the limit in composition space for the viscosity model, or

Equation 14 $$\eta = 10^{m_v c_v + b_v} = 10^{-1.711755\times 1.200566 + 3.382603} = 10^{1.3275} = 21.26$$

(i.e., 21.26 poise at T* = 1150ºC). Only the SiO_2 coefficient in the low viscosity constraint is impacted; that is, the SiO_2 coefficient in the lower viscosity constraint vector is the root from the quadratic

[1] The new melt viscosity model is a three parameter model where the melt temperature is assumed to be 1150ºC, and thus the intercept provided is $b_v = b_T + (m_T/1150) = -0.606597 + (4587.5797/1150) = 3.382603$.

expression, or $\underline{a}_{\text{low visc},SiO_2}$ = 1.200566, while the coefficients of the other oxides are taken directly from their values in Equation 6. The complete $\underline{a}_{\text{low visc}}$ vector for the TiO_2-only viscosity model is provided in Table 8.

For the upper viscosity constraint the roots are 0.795480 and 0.770608. The desired root corresponding to the appropriate one-sided simultaneous confidence interval becomes 0.795480, or

Equation 15 $$\eta = 10^{m_v c_v + b_v} = 10^{-1.711755 \times 0.795480 + 3.382603} = 10^{2.02093} = 104.94$$

(i.e., 104.94 poise at T* = 1150ºC). Only the SiO_2 coefficient in the high viscosity constraint is impacted; that is, the SiO_2 coefficient in the high viscosity constraint vector is derived from the root from the quadratic expression, or $\underline{a}_{\text{high visc},SiO_2}$ = -0.79548, while the coefficients of the other oxides are taken directly from their values in Equation 6. The complete $\underline{a}_{\text{high visc}}$ vector for the SWPF TiO_2-only viscosity model is provided in Table 8 with the SiO_2 coefficients derived in this section highlighted. The constraints are of the form $z \bullet a^T - \beta \geq 0$ in PCCS (see 103).

Table 8. $\underline{a}$ Vectors and Offsets for the TiO_2–Only Viscosity Model Constraints

	$\underline{z}^T$	Transpose of $\underline{a}$ Vectors for TiO_2–Only Viscosity Model Constraints	
	Average Molar Oxide		
Oxide	Wt Fraction	$\underline{a}^T_{\text{high visc}}$	$\underline{a}^T_{\text{low visc}}$
Al_2O_3	z_{Al2O3}	-2	2
B_2O_3	z_{B2O3}	1	-1
BaO	z_{BaO}	0	0
HCOO	z_{HCOO}	0	0
CaO	z_{CaO}	0	0
Ce_2O_3	z_{Ce2O3}	0	0
NaCl	z_{NaCl}	0	0
Cr_2O_3	z_{Cr2O3}	0	0
Cs_2O	z_{Cs2O}	2	-2
CuO	z_{CuO}	0	0
NaF	z_{NaF}	0	0
Fe_2O_3	z_{Fe2O3}	2	-2
K_2O	z_{K2O}	2	-2
La_2O_3	z_{La2O3}	0	0
Li_2O	z_{Li2O}	2	-2
MgO	z_{MgO}	0	0
MnO	z_{MnO}	0	0
MoO_3	z_{MoO3}	0	0
NO_2	z_{NO2}	0	0
NO_3	z_{NO3}	0	0
Na_2O	z_{Na2O}	2	-2
Na_2SO_4	z_{Na2SO4}	0	0
Nd_2O_3	z_{Nd2O3}	0	0
NiO	z_{NiO}	0	0
P_2O_5	z_{P2O5}	0	0
PbO	z_{PbO}	0	0
SiO_2	z_{SiO2}	-0.79548	1.200566
ThO_2	z_{ThO2}	0	0
TiO_2	z_{TiO2}	1	-1
U_3O_8	z_{U3O8}	0	0
Y_2O_3	z_{Y2O3}	0	0
ZnO	z_{ZnO}	0	0
ZrO_2	z_{ZrO2}	0	0
	Offset (β)	0	0
		$\beta_{\text{high visc}}$	$\beta_{\text{low visc}}$

The MAR assessment of the TiO_2-only viscosity model will follow the same approach as was used for the previous viscosity model in Revision 5 of the SME Acceptability report.[103] Thus, completing the assessment of these constraints for a given composition requires that the measurement uncertainty for each of these constraints be accounted for. Since each of the viscosity constraints involves a linear combination of the $\underline{z}$ vector of component concentrations, the measurement uncertainty can be addressed as described in Appendix B of Reference 103.

The PAR assessment demonstrates that the following operating limits would be imposed on DWPF viscosity using Equation 4 and Equation 5:

20	<	Viscosity	<	110	poise
21.26	<	PAR	<	104.94	poise

5.5 Validation of the SWPF (TiO_2-only) Viscosity Model

References 82-83, two studies which maximized waste loadings in defense waste glasses, (Table 6) were used to validate the SWPF TiO_2-only viscosity model. The acceptable glasses from these studies span TiO_2 compositions from 1.25 to 6.76 wt% TiO_2. The acceptable SWPF TiO_2 data spanned 1.90 to 5.85 wt% TiO_2 (Appendix C) and the historic database (Appendix A and Table 2) spanned 0-1.78 wt% TiO_2. Since the historic and SWPF databases were merged to generate the SWPF (TiO_2-only) viscosity model the range of TiO_2 is 0-5.85 wt%.

The two high waste loading glass databases used for validation of the SWPF (TiO_2-only) model span TiO_2 values of 1.25-5.90 wt% in the absence of Nb_2O_5 and minimal ZrO_2, i.e., 0.01-0.82 wt% ZrO_2 (Appendix D). Other potential datasets listed in Table 6 included glasses with high Nb_2O_5 and/or high ZrO_2, and these were not appropriate validation composition ranges for a model without these oxide components. These high waste loaded glasses [82-83] are, therefore, used in this study to validate the TiO_2 term in the SWPF viscosity model.

Table 6 indicates that the two high level waste loading studies had measured 264 viscosity-temperature pairs. However, 154 viscosity-temperature pairs violated the criteria given in Sections 2.1 or 2.2 and six glasses violated the new ROC requirement of 4.0 wt% Al_2O_3.[52] This left 116 viscosity-temperature pairs and these are tabulated in Appendix D. Figure 5-3 shows how 101 viscosity-temperature-NBO combinations fit within the 95% confidence bands of the SWPF TiO_2-only model generated from Equation 4 and Equation 5. The other five viscosity-temperature-NBO combinations are five viscosity-temperature measurements from the same glass, FY09EM21-15, as identified in Figure 5-3. This glass had only 1.86 wt% TiO_2 but contained 2.27 wt% NiO, 4.35 wt% MnO coupled with 1.34 wt% MgO and 3.33 wt% CaO for a sum of 13.15 wt% XO terms where X=Ni, Mn, Mg, and Ca. Since neither the DWPF historic viscosity model nor the SWPF TiO_2-only model has a +2 cation NBO term, it is believed that the poor fit of this one glass is due to the sum of the divalent cations and not TiO_2.

While the validation data only spans from log 1 or 10 poise to log 2.04 or 110 poise this encompasses the DWPF processing range of 20-110 poise. Therefore, the use of Equation 4 and Equation 5 have shown that the TiO_2 term as a network modifier has been validated up to 5.90 wt% TiO_2 the maximum given in the TiO_2 validation database (Appendix D) while the model development showed that Equation 4 and Equation 5 were valid up to 5.85 wt% TiO_2.

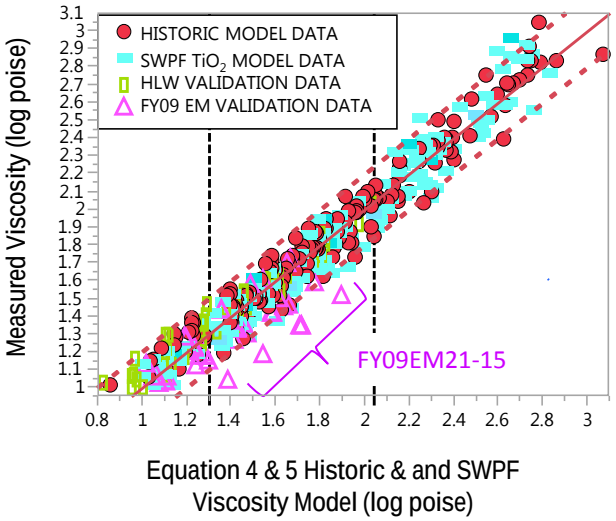


Figure 5-3. Validation Data from Appendix D (116 viscosity-temperature-NBO combinations) overlain on the SWPF (TiO_2-only) model developed from the SWPF and Historic glass Databases in Appendices B and C (334 viscosity-temperature-NBO combinations). Vertical lines indicate DWPF processing limits.

6.0 CST TiO_2-Nb_2O_5-ZrO_2 Viscosity Model

6.1 Evaluation of the CST Model Glasses Against the Historic DWPF Viscosity Model

The DWPF CST glasses not only contain TiO_2 but contain Nb_2O_5 and a ZrO_2 binder. The DWPF validation glasses shown in Table 6 include CST glass viscosity data generated in References 65-69 that are used in this document to generate a CST viscosity model. The CST viscosity model includes the viscosity data from References 65-69 and the SWPF viscosity data generated by ES-VSL which are discussed in Section 5.3, and the historic viscosity data discussed in Section 5.1. Any glasses containing TiO_2 >2.0 wt%, including the CST glasses (TiO_2 up to 6.62 wt% as given in Appendix E) require a TiO_2 term in the DWPF viscosity model as discussed in Section 5.1.

6.2 Structural Role of TiO_2, Nb_2O_5 and ZrO_2 in DWPF Glasses

The role of TiO_2 in glass was discussed in Section 5.2. TiO_2 was shown to act as a network modifier creating NBOs up to about 6.0 wt% TiO_2. ZrO_2 is always octahedrally coordinated ($^{[6]}Zr$ or ZrO_6) and should be a network modifier creating NBO in a similar fashion to TiO_2. However, Zr-Si correlations are observed in melts studied by X-ray Absorption Near Edge Spectroscopy (XANES), i.e. corner sharing of ZrO_6 octahedra and SiO_4 tetrahedra.[99] Zirconium has a large field strength and a directional bond that strengthens glass structures.[99] Thus ZrO_2 acts like a network former rather than a network modifier and is modeled as such in this study.

The element niobium exists as +2, +4 and +5 valence states. It can form niobium monoxide (NbO), niobium dioxide (NbO_2), or niobium pentoxide (Nb_2O_5). While it appears intuitive that NbO_2, which is isostructural with TiO_2, ThO_2, ZrO_2, HfO_2 and other fluorite structured oxides, might be the form of niobium in glass, Volf [99] states that Nb is very difficult to reduce to lower oxidation states in glass and occurs solely in its highest oxidation state as Nb_2O_5. In the chemical formula for CST, $Na_{1.5}Nb_{0.5}Ti_{1.5}O_3SiO_4 \bullet 2H_2O$, the Nb is in the +5 oxidation state as well. So when CST melts into DWPF glass the Nb coordination should remain as a +5 oxidation state.

Niobium is unique in that it shows both ionic and covalent bonding with the covalent bonding being dominant and approaching that of silicon.[99] The coordination number of Nb in glass varies between 6

and 8 and may even be 9. Therefore, it is considered an intermediate glass forming element like other transition elements in the 2nd and 3rd column of the periodic table. Silicon-29 Magic Angle Spinning Nuclear Magnetic Resonance (MAS NMR) spectra suggest that Nb^{5+} ions create cross-links between several oxygen sites, breaking BO bonds to form a range of polyhedra such as $[Nb(OM)_{6-y}(OSi)_y]$ where y varies from 1 to 5 and M can be Na, Ca, or P.[106] Therefore, Nb_2O_5 is considered to create NBOs in this study, i.e.,it is a network modifier.

6.3 Development of the CST (TiO_2-Nb_2O_5-ZrO_2) Viscosity Model

Since TiO_2, in the composition range spanned by the SWPF and CST glass viscosity data, acts as a network modifier, it creates one NBO per mole. Likewise, Nb_2O_5 creates 2 NBO per mole, and ZrO_2 creates one BO per mole. Therefore, Equation 1 becomes

Equation 16 $$NBO \equiv \frac{2\,(Na_2O + K_2O + Cs_2O + Li_2O + Fe_2O_3 + Nb_2O_5 - Al_2O_3) + B_2O_3 + TiO_2 - ZrO_2}{SiO_2}$$

The combined CST and randomly selected KT glass viscosity data used to develop a CST model are given in Appendix E. They consist of a pool of 233 temperature-viscosity pairs. When the 233 CST data points are added to the 159 SWPF glass viscosity data points discussed in Section 5.3, and the 175 historic viscosity-temperature pairs discussed in Section 5.1, the CST model database has 557 log viscosity-1/temperature-NBO combinations.

The response surface between log viscosity-1/temperature-NBO for 557 pooled historic, SWPF, and CST databases generates the CST model, i.e., Equation 17.

Equation 17 $$\log\eta(poise) = -0.629934 + \left(\frac{4547.3573}{T(^oC)}\right) - (1.622574 * NBO)$$

Figure 6-1 shows how the historic, SWPF, and CST glasses overlap one another using Equation 16 and Equation 17 which incorporate the bond breaking caused by TiO_2 and Nb_2O_5 and the bond forming tendencies of ZrO_2. Application of Equation 16 and Equation 17 to the pooled viscosity dataset as shown in Figure 6-1 gives an adjusted R^2=0.9397 and a RMSE=0.1033 somewhat lower than the corresponding values for the combined historic and SWPF TiO_2-only model.

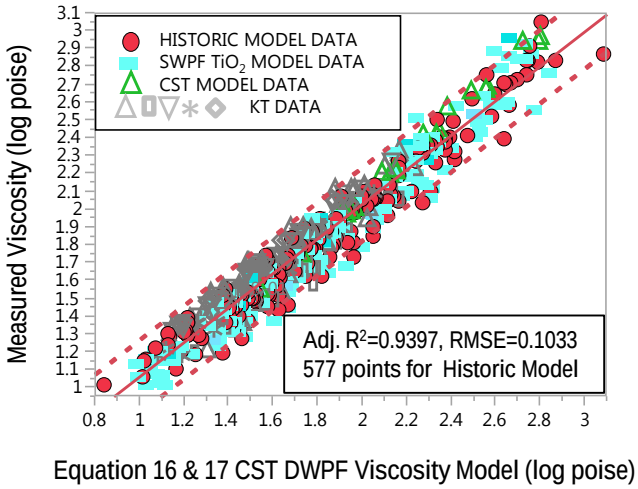


Figure 6-1. CST Viscosity Model with terms for TiO_2, Nb_2O_5, and ZrO_2. Note that there were 5 different KT studies and so there are 5 different symbols on the figure but all the KT studies are shaded gray.

The CST model not only covers the TiO_2 range defined by the CST and randomly selected KT data (TiO_2 = 3.03–6.62 wt%), but covers the combined range of TiO_2 from being merged with the historic and SWPF viscosity databases (Section 5.3, Appendices B and C) for a combined TiO_2 range of 0-6.62 wt% TiO_2. The CST model covers Nb_2O_5 concentrations of 0-1.96 wt% and ZrO_2 concentrations of 0-1.78 wt%.

6.4 Property Acceptable Region (PAR) Assessments for the CST (TiO_2-Nb_2O_5-ZrO_2) Viscosity Model

A major consideration for the introduction of CST into the DWPF flowsheet is that niobium would become a reportable element in PCCS and that means that the measurement error associated with niobium would have to be known. At present, Nb measurement error is not known and Nb is not a reportable element to the geologic repository. Some Waste Acceptance Product Specifications (WAPS) documentation would have to be changed at the point at which CST is introduced into the DWPF. All of the activities necessary to complete this process are not addressed in this document. This section develops only the implementation strategy for integrating the new CST model into the viscosity evaluation conducted by PCCS. This effort follows the strategy that was utilized above for SWFP TiO_2-only viscosity-composition model. The CST viscosity-composition model may be expressed as given by:

Equation 18 Viscosity:[††] $$\log \eta = m_v c_v + b_v$$

where

η is viscosity in poise,

m_v is the estimated slope for this regression model (m_v = -1.763161)

b_v is the estimated intercept determined from the fitted three parameter model evaluated at T=1150 °C (b_v = 3.424645),

[††] Actually the viscosity prediction is a three-parameter model including the inverse temperature term. However, this temperature is fixed at 1150°C for DWPF. This allows the viscosity model to be presented as a two-parameter model with the temperature-dependent term included in the pseudo-constant, b_V.

$$c_v = \frac{2\left(z_{Fe_2O_3} - z_{Al_2O_3} + z_{Cs_2O} + z_{Li_2O} + z_{K_2O} + z_{Na_2O}\right) + z_{B_2O_3} + z_{TiO_2} - z_{ZrO_2}}{z_{SiO_2}}, \text{ and}$$

z_{oxide} represents the indicated molar oxide concentration in the glass.

This model can be back-solved (noting the negative value for m_v) to translate the viscosity constraints into constraints on the compositional term, c_v, as given by:

Equation 19 High Viscosity:

$$\text{high viscosity} \equiv \eta_{hv} \le 110 \text{ poise} \qquad \Rightarrow \qquad c_{hv} \ge \left[\frac{\log(\eta_{hv}) - b_v}{m_v}\right]$$

Equation 20 Low Viscosity:

$$\textit{low}\ \text{viscosity} \equiv \eta_{lv} \ge 20 \text{ poise} \qquad \Rightarrow \qquad c_{lv} \le \left[\frac{\log(\eta_{lv}) - b_v}{m_v}\right]$$

The above inequalities describe the region in compositional space where all of the predicted values for viscosity are acceptable. This defines the EPAR for viscosity. The region is denoted as "expected" since it is derived from the fitted line, which is the expected viscosity, based upon the model for a given composition.

The determination of the PAR for this viscosity model is accomplished by accounting for the property model uncertainty in the implementation of the viscosity constraints. And as before, statistical confidence intervals are used in the determinations of this uncertainty. Specifically, Scheffé simultaneous confidence limits (also called confidence bands [104] and [105]), are used in the development of the PAR's for the constraints associated with the CST viscosity model as they were for the current model.

Since the CST viscosity model is of the same form as the historic model and the SWPF TiO_2-only model, it too includes a linear parameter based upon the inverse temperature (1/T) at which the viscosity (η) is measured. The complete form of the CST viscosity model may be expressed as:

Equation 21 $$\log(\eta) = m_v c_v + m_T \frac{1}{T(°C)} + b_T .$$

As already indicated in an earlier footnote, for DWPF use, the temperature is fixed at 1150°C. Thus, the predicting relationship for viscosity can be written as:

Equation 22 $$\log(\eta) = m_v c_v + b_v$$

where $b_v \equiv \frac{m_T}{T(°C)} + b_T$ and T(°C) is 1150°C.

However, the additional parameter must be accounted for when defining the confidence limits for viscosity prediction. The approach used to develop the viscosity PAR is the true one-sided, 100(1–α)% Scheffé-type confidence limit. This leads to the following one-sided, 100(1–α)% Scheffé-type confidence limit to determine the PAR for each viscosity constraint:

Equation 23

$$\pi = b_T + \left(\frac{m_T}{T^*}\right) + m_v\left(c^*\right) + s_r\left\{\sqrt{pF_{2\alpha}(p,n-p)}\sqrt{\underline{c}_0\left(\mathbf{X}^T\mathbf{X}\right)^{-1}\underline{c}_0{}^T}\right\}$$

where π represents the EPAR for the corresponding constraint (20 P for low viscosity and 110 P for high viscosity), s_r is the RMSE for the regression fit, $F_{2\alpha}(p,n\text{-}p)$ is the upper 2α% tail of the F distribution with p degrees of freedom in the numerator and n-p degrees of freedom in the denominator, T* = 1150ºC, c^* is the compositionally-based term in Equation 18,

$$\underline{c}_0 \equiv \left[1, \frac{1}{T^*}, c^*\right] \text{ and } \mathbf{X} \equiv \begin{bmatrix} 1 & \frac{1}{T_1} & c_1 \\ 1 & \frac{1}{T_2} & c_2 \\ \vdots & \vdots & \vdots \\ 1 & \frac{1}{T_n} & c_n \end{bmatrix}.$$

X is an n×p matrix that contains the data for the independent variables from which the regression model was formulated where p is the number of parameters in the model and n is the number of observations used in the fitting of the CST model. Note that the product moment matrix, X^TX, is different than that for the SWPF TiO_2-Only model but of dimension 3x3. The one-sided, 100(1–α)% Scheffé-type confidence limit to determine the PAR for each viscosity constraint may be written as:

Equation 24

$$\pi = b_T + \left(\frac{m_T}{T*}\right) + m_v(c*) + s_r\left\{\sqrt{pF_{2\alpha}(p,n-p)}\sqrt{\begin{bmatrix}1 & (1/T*) & c^*\end{bmatrix}\begin{bmatrix} c_{0,0} & c_{0,1} & c_{0,2} \\ c_{0,1} & c_{1,1} & c_{1,2} \\ c_{0,2} & c_{1,2} & c_{2,2}\end{bmatrix}\begin{bmatrix}1 \\ (1/T*) \\ c^*\end{bmatrix}}\right\},$$

where the inverse of the X^TX matrix is represented by the 3×3 array of c's. Since the (1/T*) term will be constant for DWPF use, the expression in Equation 24 can be expanded for each viscosity constraint (i.e., low and high) to a quadratic in c* given by $A\left(c^*\right)^2 + B\left(c^*\right) + C = 0$ with coefficients given by the set of equations:

Equation 25

$$\begin{aligned} A &\equiv m_v{}^2 - c_{2,2}\left[ps_r^2F_{2\alpha}(p,n-p)\right] \\ B &\equiv -2\left\{m_v(\pi - b_T) + \left(c_{0,2} + \frac{c_{1,2}}{T*}\right)\left[ps_r^2F_{2\alpha}(p,n-p)\right]\right\} \\ C &\equiv (\pi - b_T)^2 - \left[c_{0,0} + 2\left(\frac{c_{0,1}}{T*}\right) + \frac{c_{1,1}}{(T*)^2}\right]\left[ps_r^2F_{2\alpha}(p,n-p)\right] \end{aligned} \quad (9)$$

The information from the fitting of the CST viscosity model that is necessary to address its property uncertainty and, thus, to derive its PAR values is provided in Exhibit 2.

Exhibit 2 Information Generated from the Fitting of the CST Viscosity Model

p = 3, n = 557, α = 0.05, m = -1.622574, b_T = 3.32429[2], s_r = 0.103304, and

$$\left(\mathbf{X}^T\mathbf{X}\right)=\begin{bmatrix} 557 & 0.494583 & 549.0442 \\ 0.494583 & 0.0004429 & 0.488414 \\ 549.0442 & 0.488414 & 552.1812 \end{bmatrix}$$

For the low viscosity constraint, the roots from the quadratic expression are 1.262267 and 1.232882, and selecting the desired root corresponding to the appropriate one-sided simultaneous confidence interval gives 1.232882 as the limit in composition space for the viscosity model, or

Equation 26 $$\eta = 10^{m_v c_v + b_v} = 10^{-1.622574 \times 1.232882 + 3.32429} = 10^{1.3238} = 21.08$$

(i.e., 21.08 poise at T* = 1150ºC). Only the SiO_2 coefficient in the low viscosity constraint is impacted; that is, the SiO_2 coefficient in the lower viscosity constraint vector is the root from the quadratic expression, or $\underline{a}_{\text{low visc},SiO_2}$ = 1.232882, while the coefficients of the other oxides are taken directly from their values in Equation 18. The complete $\underline{a}_{\text{low visc}}$ vector for the CST viscosity model is provided in Table 9.

For the upper viscosity constraint the roots are 0.801801 and 0.778606. The desired root corresponding to the appropriate one-sided simultaneous confidence interval becomes 0.801801, or

Equation 27 $$\eta = 10^{m_v c_v + b_v} = 10^{-1.622574 \times 0.801801 + 3.32429} = 10^{2.0233} = 105.51$$

(i.e., 105.51 poise at T* = 1150ºC). Only the SiO_2 coefficient in the high viscosity constraint is impacted; that is, the SiO_2 coefficient in the high viscosity constraint vector is derived from the root from the quadratic expression, or $\underline{a}_{\text{high visc},SiO_2}$ = -0.801801, while the coefficients of the other oxides are taken directly from their values in Equation 18. The complete $\underline{a}_{\text{high visc}}$ vector for the CST viscosity model is provided in Table 9 with the SiO_2 coefficients derived in this section highlighted as well as the coefficients for Nb_2O_5 and ZrO_2. The constraints are of the form $z \bullet a^T - \beta \geq 0$ in PCCS (see 103).

[2] The CST viscosity model is a three parameter model where the melt temperature is assumed to be 1150ºC, and thus the intercept provided is $b_v = b_T + (m_T/1150) = -0.629934 + (4547.357/1150) = 3.32429$.

Table 9. a Vectors and Offsets for the CST Viscosity Model Constraints

	$\underline{z}^T$	Transpose of $\underline{a}$ Vectors for CST Viscosity Model Constraints	
	Average		
	Molar Oxide		
Oxide	Wt Fraction	$\underline{a}^T_{\text{high visc}}$	$\underline{a}^T_{\text{low visc}}$
Al_2O_3	z_{Al2O3}	-2	2
B_2O_3	z_{B2O3}	1	-1
BaO	z_{BaO}	0	0
HCOO	z_{HCOO}	0	0
CaO	z_{CaO}	0	0
Ce_2O_3	z_{Ce2O3}	0	0
NaCl	z_{NaCl}	0	0
Cr_2O_3	z_{Cr2O3}	0	0
Cs_2O	z_{Cs2O}	2	-2
CuO	z_{CuO}	0	0
NaF	z_{NaF}	0	0
Fe_2O_3	z_{Fe2O3}	2	-2
K_2O	z_{K2O}	2	-2
La_2O_3	z_{La2O3}	0	0
Li_2O	z_{Li2O}	2	-2
MgO	z_{MgO}	0	0
MnO	z_{MnO}	0	0
MoO_3	z_{MoO3}	0	0
NO_2	z_{NO2}	0	0
NO_3	z_{NO3}	0	0
Na_2O	z_{Na2O}	2	-2
Na_2SO_4	z_{Na2SO4}	0	0
Nb_2O_5	z_{Nb2O5}	2	-2
Nd_2O_3	z_{Nd2O3}	0	0
NiO	z_{NiO}	0	0
P_2O_5	z_{P2O5}	0	0
PbO	z_{PbO}	0	0
SiO_2	z_{SiO2}	-0.801801	1.23288
ThO_2	z_{ThO2}	0	0
TiO_2	z_{TiO2}	1	-1
U_3O_8	z_{U3O8}	0	0
Y_2O_3	z_{Y2O3}	0	0
ZnO	z_{ZnO}	0	0
ZrO_2	z_{ZrO2}	-1	1
	Offset (β)	0	0
		$\beta_{\text{high visc}}$	$\beta_{\text{low visc}}$

Once niobium is introduced into PCCS, the MAR assessment of the CST viscosity model will follow the same approach as was used for the previous viscosity model in Revision 5 of the SME Acceptability report.[103] Thus, completing the assessment of these constraints for a given composition requires that the measurement uncertainty for each of these constraints be accounted for. Since each of the viscosity constraints involves a linear combination of the $\underline{z}$ vector of component concentrations, the measurement uncertainty can be addressed as described in Appendix B of [103].

The PAR assessment demonstrates that the following operating limits would be imposed on DWPF viscosity using Equation 16 and Equation 17:

20	<	Viscosity	<	110	poise
21.08	<	PAR	<	105.51	poise

6.5 Validation of the CST (TiO_2-Nb_2O_5-ZrO_2) Viscosity Model

In References 84-87 combinations of MST and CST in glass were studied (see Table 6). The CST validation data glass studies are randomly selected from studies KT-04, KT-06, KT-07, KT-08, and KT-10. Several of the other KT studies did not measure viscosity. Table 6 indicates that there are 587 viscosity-temperature measurements available for all the KT studies but the randomly selected 29 of 58 glasses provide 201 viscosity-temperature measurements. In the KT studies not used in this report, concentrations of TiO_2 greater than ~6.00 wt% were examined, the TiO_2 in these glasses was acting as a network former and not a network modifier as discussed in Section 5.2. Thus at high TiO_2 concentrations a different term for TiO_2 would be needed with a different sign (negative) which would make the CST viscosity model non-linear and problematic to program into PCCS. The exact TiO_2 concentrations at which TiO_2 switches from a network modifier to a network former lie somewhere between ~6.00 and 8.00 wt% TiO_2, and additional studies would have to be performed to determine this limit.

For the CST Model development 182 viscosity-temperature measurements from studies KT-01 through KT-03 were not used in validation of the CST model. The remaining randomly selected KT-04 through KT-10 data span TiO_2 concentrations from 4.17 to 6.53, Nb_2O_5 concentrations from 0.03 to 2.30, and ZrO_2 concentrations from 0.11 to 2.90. The data are given in Appendix F.

Figure 6-2 shows how the 201 viscosity-temperature-NBO validation combinations fit within the 95% confidence bands of the CST viscosity model generated from Equation 16 and Equation 17. The other seven viscosity-temperature-NBO combinations are viscosity-temperature measurements from the same glass, KT-08-07 as identified in Figure 6-2. This glass had only 4.27 wt% TiO_2, 0.89 wt% Nb_2O_5, and 0.01 wt% ZrO_2. All the other oxides were in ranges studied and/or bracketed by other glasses in the KT-04 through KT-10 studies. Although the Fulcher fit did not indicate hysteresis, this glass did crystallize during canister centerline cooling curve experiments.[87]

Therefore, the use of Equation 16 and Equation 17 has shown that the TiO_2 term as a network modifier has been validated up to 6.53 wt% for the CST model when coupled with Nb_2O_5 and ZrO_2 in a DWPF glass. The value of 6.53 wt% for validation data is less than the 6.62 TiO_2 in the CST model data. Both the CST model and validation data, 6.62 and 6.53 wt% TiO_2 respectively, are higher than the 5.90 wt% TiO_2 validated for the SWPF TiO_2-only model: both the SWPF TiO_2-only and the CST viscosity models are valid up to ~6-6.5 wt% TiO_2.

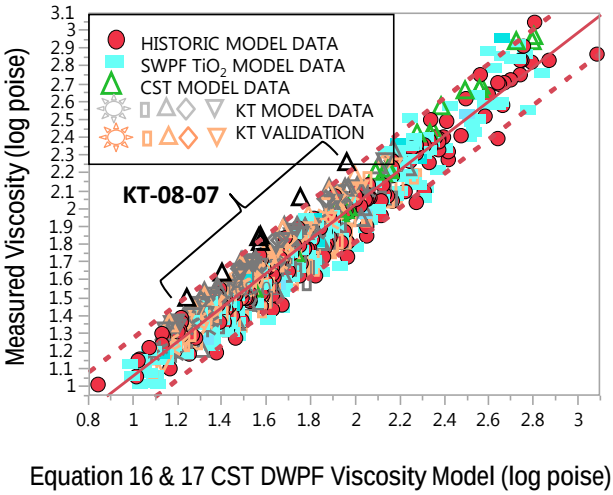


Figure 6-2. Validation Data from Appendix F (201 viscosity-temperature-NBO combinations) overlain on the CST viscosity model developed from the CST, KT (5 different studies shown with 5 different symbols), SWPF, and Historic glass Databases in Appendices B, C, and E (577 viscosity-temperature-NBO combinations).

7.0 Conclusions

The DWPF will soon be receiving increased concentrations of TiO_2 enriched wastes from the SWPF. In order to process TiO_2 concentrations >2.0 wt% in the DWPF, new viscosity data were developed over the range of 1.90 to 6.09 wt% TiO_2 and evaluated against the 2005 viscosity model. The SWPF TiO_2-only model data had to be truncated at 5.85 wt% TiO_2 due to other modeling considerations, i.e. ROC. It was determined that a TiO_2 term was needed in the model to adequately describe the impact of higher TiO_2 concentrations on melt viscosity at 1150°C. Titanium oxide, TiO_2, acts as a depolymerizing agent in the glass (creating NBO's). Therefore, the SWPF TiO_2-only containing viscosity model takes the following form:

$$\log\eta(poise) = -0.606597 + \left(\frac{4587.5797}{T(^{o}C)}\right) - (1.711755 * NBO)$$

where $$NBO \equiv \frac{2(Na_2O + K_2O + Cs_2O + Li_2O) + 2(Fe_2O_3 - Al_2O_3) + B_2O_3 + TiO_2}{SiO_2}$$

With an adjusted R^2 = 0.9541 and a root mean square error of 0.1012.

This SWPF TiO_2-only model covers TiO_2 concentrations up to 5.85 wt% and was validated up to TiO_2 concentrations of 5.90 wt% TiO_2 as determined by the validation data.

The new SWPF data used to develop the TiO_2-only viscosity model (Appendix C) also contained glasses with Cs_2O up to 1.62 wt%. These new data validated the Cs_2O term in the historic and TiO_2-only DWPF viscosity models. The TiO_2-only model was also shown to be valid (see data in Appendices A, C, and D) up to 4.14 wt% CaO and 2.92 wt% MgO. These wide limits on the amount of CaO and/or MgO that can

be added to future frit compositions are beneficial since CaO is known to suppress nepheline crystallization [38,39,40,107,108] and MgO is known to improve glass durability [109] and to reduce DWPF refractory corrosion and wear.

An alternate viscosity model is also derived for potential future use, should the DWPF ever need to process other titanate containing ion exchange materials, such as crystalline silicotitanate (CST - $Na_{1.5}Nb_{0.5}Ti_{1.5}O_3SiO_4 \bullet 2H_2O$). The DWPF may receive CST generated by an alternate flowsheet used to pretreat the high-curie fraction of the SRS salt waste. The CST not only contains TiO_2 but also contains Nb_2O_5 and a ZrO_2 binder where TiO_2 and Nb_2O_5 act to depolymerize the glass (create NBO's) and ZrO_2 polymerizes the glass (creates BO's). The MST would still be used for ^{90}Sr removal so this viscosity model would cover future DWPF processing of CST alone or coupled CST-MST flowsheet additions. Therefore, the CST viscosity model takes the following form:

$$\log\eta(poise) = -0.629934 + \left(\frac{4547.3573}{T(^oC)}\right) - (1.622574 * NBO)$$

where

$$NBO \equiv \frac{2\,(Na_2O + K_2O + Cs_2O + Li_2O + Fe_2O_3 + Nb_2O_5 - Al_2O_3) + B_2O_3 + TiO_2 - ZrO_2}{SiO_2}$$

When the SWPF MST glasses (TiO_2=1.90-5.85 wt%) and the CST glasses (TiO_2=3.03-6.62, Nb_2O_5=0.06-1.96 wt% and ZrO_2=0.15-1.82 wt%) are combined with the historic DWPF viscosity database (TiO_2=0-1.78 wt%), the MST glass data cover a wider range of TiO_2 than the historic viscosity data but the CST glass data are higher in TiO_2 content than either of the other model databases. The Nb_2O_5 and ZrO_2 terms are derived solely from the CST data as neither the SWPF-MST viscosity data nor the historic viscosity data contain these species. The CST viscosity model covers up to 2.28 wt% CaO and 2.92 wt% MgO (Appendices A, C, E, and F) and likely is applicable up to 4.14 wt% CaO (Appendix D) as the CST model was not assessed against the TiO_2 only validation database.

While the TiO_2-only viscosity model has been modeled/validated up to ~ 6 wt% (actual of 5.85 wt% TiO_2) and the CST viscosity model has been modeled/validated up to 6.62 wt% TiO_2, the role of TiO_2 as a network breaker switches to a network former by 8.38 wt% TiO_2. The exact region at which this switch occurs has not been investigated so the usage of the TiO_2-only viscosity model is ~6 wt% TiO_2 and the CST model is ~ 6.5 wt% TiO_2.

The ultimate limit on the amount of TiO_2 that can be accommodated from SWPF will be determined by the three PCCS models, the waste composition of a given sludge batch, the waste loading of the sludge batch, and the frit used for vitrification. Once a component like TiO_2 is present at larger concentrations than 1-2 wt%, the interactions of that component with other components in the melter feed must be considered simultaneously, i.e. an individual solubility limit cannot be defined to globally account for the interactions with all the remaining sludge/frit composition variables. It is known that Ti^{4+} competes with Al^{3+} for alkali bonding and it is known that Ti^{4+} and Fe^{3+} have a coupled impact on their joint solubility in a glass.

8.0 Acknowledgements

The authors would like to acknowledge the assistance of all of the authors of the supporting viscosity composition studies including the ES-VSL.

APPENDIX A. Historic Glass Model Database

Sample ID	Temp (°C)	Visc (poise)	$Fe^{+2}/\Sigma Fe$	Al2O3(v)	B2O3(v)	BaO(v)	CaO(v)	Cr2O3(v)	Cs2O(v)	CuO(v)	FeO(v)	Fe2O3(v)	K2O(v)	La2O3(v)	Li2O(v)	MgO(v)	MnO(v)	Na2O(v)	NiO(v)	SiO2(v)	SrO(v)	TiO2(v)	ZnO(v)	ZrO2(v)	Sum Oxides
AH131AL(1985)	944	562.34	0.02	13.50	10.80	0.00	0.38	0.00	0.00	0.00	0.09	4.57	0.00	0.36	4.09	1.38	2.51	14.10	0.63	46.40	0.00	0.72	0.00	0.34	99.88
	1021	234.42																							
	1098	112.20																							
	1178	58.88																							
	1264	31.62																							
AH131AL(1988)	1020	213.80	0.02	13.50	10.80	0.00	0.38	0.00	0.00	0.00	0.09	4.57	0.00	0.36	4.09	1.38	2.51	14.10	0.63	46.40	0.00	0.72	0.00	0.34	99.88
	1079	120.23																							
	1143	69.18																							
	1200	44.67																							
	1255	30.20																							
	1283	25.12																							
AH165AL(1988)	1079	380.19	0.06	13.40	7.34	0.00	0.51	0.00	0.00	0.00	0.24	4.57	0.00	0.00	4.20	0.66	2.62	10.60	0.67	53.60	0.00	0.00	0.00	0.79	99.23
	1145	208.93																							
	1202	125.89																							
	1259	79.43																							
	1288	64.57																							
AH165AV(1988)	1022	190.55	0.05	5.17	6.57	0.00	1.04	0.00	0.00	0.00	0.47	11.08	0.00	0.00	5.02	0.66	2.57	9.96	1.01	55.30	0.00	0.00	0.00	0.76	99.66
	1082	109.65																							
	1143	64.57																							
	1199	41.69																							
	1255	28.18																							
	1285	23.44																							
AH168AV(1985)	873	741.31	0.06	5.58	10.60	0.00	0.68	0.00	0.00	0.00	0.61	10.51	0.00	0.00	4.24	0.74	2.64	10.10	1.02	51.60	0.00	0.00	0.00	0.69	99.08
	953	245.47																							
	1031	107.15																							
	1107	53.70																							
	1191	28.84																							
AH168AV(1988)	1022	125.89	0.06	5.58	10.60	0.00	0.68	0.00	0.00	0.00	0.61	10.51	0.00	0.00	4.24	0.74	2.64	10.10	1.02	51.60	0.00	0.00	0.00	0.69	99.08
	1084	70.79																							
	1147	41.69																							
	1204	26.92																							
	1260	18.62																							
	1290	15.49																							
AH168FE(1988)	1022	63.10	0.42	2.47	11.40	0.00	1.35	0.00	0.00	0.00	6.22	9.39	0.00	0.00	4.12	0.71	0.98	10.80	2.82	48.30	0.00	0.00	0.00	0.67	99.92
	1082	37.15																							
	1144	22.91																							
	1203	15.85																							
	1259	11.48																							
AH200AL(1988)	1017	812.83	0.02	13.40	10.20	0.00	0.54	0.00	0.00	0.00	0.07	4.39	3.12	0.00	2.65	1.25	2.49	10.60	0.61	48.40	0.00	1.70	0.00	0.03	99.46
	1079	416.87																							
	1143	218.78																							
	1201	134.90																							
	1257	87.10																							
	1286	67.61																							
AH200AV(AH8/1985)	916	660.69	0.04	5.14	10.30	0.00	0.63	0.00	0.00	0.00	0.39	11.47	3.18	0.00	2.68	1.24	2.55	9.77	1.02	49.50	0.00	1.41	0.00	0.02	99.34
	994	251.19																							
	1071	114.82																							
	1148	58.88																							
	1234	31.62																							

Sample ID	Temp (°C)	Visc (poise)	$Fe^{+2}/\Sigma Fe$	Al2O3(v)	B2O3(v)	BaO(v)	CaO(v)	Cr2O3(v)	Cs2O(v)	CuO(v)	FeO(v)	Fe2O3(v)	K2O(v)	La2O3(v)	Li2O(v)	MgO(v)	MnO(v)	Na2O(v)	NiO(v)	SiO2(v)	SrO(v)	TiO2(v)	ZnO(v)	ZrO2(v)	Sum Oxides
AH200AV(1988)	1021	229.09	0.04	5.14	10.30	0.00	0.63	0.00	0.00	0.00	0.39	11.47	3.18	0.00	2.68	1.24	2.55	9.77	1.02	49.50	0.00	1.41	0.00	0.02	99.34
	1084	125.89																							
	1147	74.13																							
	1203	45.71																							
	1259	30.90																							
AH200FE(1988)	1019	85.11	0.40	2.07	10.10	0.00	0.92	0.00	0.00	0.00	5.94	9.80	3.15	0.00	2.59	1.21	0.95	10.60	2.57	47.40	0.00	1.78	0.00	0.02	99.76
	1083	46.77																							
	1143	28.18																							
	1200	19.50																							
	1259	14.45																							
AH202AL(1988)	1050	1122.02	0.02	13.90	7.42	0.00	0.41	0.00	0.00	0.00	0.08	4.31	3.32	0.00	4.18	1.28	2.51	7.34	0.62	52.40	0.00	1.71	0.00	0.03	99.52
	1111	562.34																							
	1173	316.23																							
	1227	186.21																							
	1284	117.49																							
	1344	77.62																							
AH202AV(AH10/1985)	979	512.86	0.03	4.96	7.44	0.00	0.72	0.00	0.00	0.00	0.31	11.56	3.33	0.00	4.27	1.30	2.59	6.55	1.00	54.10	0.00	1.37	0.00	0.03	99.56
	1054	223.87																							
	1129	112.20																							
	1215	57.54																							
	1299	31.62																							
AH202AV(1988)	1037	309.03	0.03	4.96	7.44	0.00	0.72	0.00	0.00	0.00	0.31	11.56	3.33	0.00	4.27	1.30	2.59	6.55	1.00	54.10	0.00	1.37	0.00	0.03	99.56
	1097	169.82																							
	1161	97.72																							
	1217	61.66																							
	1275	44.67																							
AH202FE(1988)	1017	134.90	0.42	1.36	7.08	0.00	0.96	0.00	0.00	0.00	6.28	9.62	3.28	0.00	4.27	1.26	0.95	7.62	2.73	52.55	0.00	1.72	0.00	0.02	100.40
	1078	74.13																							
	1143	42.66																							
	1199	28.18																							
	1253	19.50																							
BLACK FRIT 165-Drain Valve Test Stand-4 (1987)	951	104.71	0.00	3.80	12.20	0.00	1.20	0.00	0.00	0.00	0.00	9.90	0.00	0.00	4.40	0.60	1.79	15.80	0.80	48.39	0.00	0.00	0.00	0.60	99.49
	1016	56.23																							
	1077	33.11																							
	1145	20.42																							
	1198	14.13																							
	1257	10.23																							
DWPF STARTUP 10-26 (1989)	1100	69.18	0.00	4.60	8.51	0.10	1.47	0.09	0.00	0.00	0.00	14.20	2.70	0.00	3.25	0.84	1.93	11.53	1.11	47.90	0.00	1.18	0.00	0.11	99.52
	1130	54.95																							
	1183	35.48																							
	1238	24.55																							
	1266	19.95																							
DWPF STARTUP 10-27a (1989)	1066	87.10																							
	1129	51.29																							
	1184	33.11																							
	1238	22.91																							
	1264	19.05																							
DWPF STARTUP 10-27b(1989)	1068	77.62																							
	1130	46.77																							
	1185	28.84																							
	1239	20.89																							
	1267	17.38																							

Sample ID	Temp (°C)	Visc (poise)	$Fe^{+2}/\Sigma Fe$	Al2O3(v)	B2O3(v)	BaO(v)	CaO(v)	Cr2O3(v)	Cs2O(v)	CuO(v)	FeO(v)	Fe2O3(v)	K2O(v)	La2O3(v)	Li2O(v)	MgO(v)	MnO(v)	Na2O(v)	NiO(v)	SiO2(v)	SrO(v)	TiO2(v)	ZnO(v)	ZrO2(v)	Sum Oxides
	949	512.86																							
	1027	213.80																							
AH4(1985)	1104	104.71	0.00	4.69	7.06	0.00	1.00	0.05	0.06	0.00	0.00	11.00	3.16	0.00	4.10	0.73	2.12	9.89	0.97	53.48	0.05	1.30	0.00	0.01	99.67
	1186	54.95																							
	1270	30.20																							
	957	524.81																							
	1044	229.09																							
AH5(1985)	1119	112.20	0.00	5.48	6.95	0.00	0.66	0.00	0.00	0.00	0.00	11.40	3.16	0.00	3.77	0.60	2.64	9.24	0.96	53.08	0.00	1.31	0.00	0.01	99.26
	1203	57.54																							
	1288	32.36																							
	940	501.19																							
	1017	204.17																							
AH7(1985)	1093	97.72	0.00	6.27	11.50	0.00	0.64	0.00	0.00	0.00	0.00	11.30	3.15	0.00	3.15	0.59	2.62	9.24	0.95	49.00	0.00	1.29	0.00	0.02	99.72
	1173	51.29																							
	1258	28.18																							
	966	436.52																							
	1043	186.21																							
AH9(1985)	1117	95.50	0.00	6.04	8.75	0.00	0.69	0.01	0.06	0.00	0.00	11.60	3.13	0.00	3.47	0.58	2.64	9.20	0.97	50.88	0.05	1.33	0.00	0.01	99.41
	1202	48.98																							
	1288	27.54																							
	926	676.08																							
	1005	257.04																							
AH11(1985)	1082	117.49	0.00	5.70	12.00	0.00	0.65	0.01	0.06	0.00	0.00	11.00	2.99	0.00	3.62	1.11	2.63	6.42	0.93	50.40	0.04	1.29	0.00	0.01	98.86
	1160	60.26																							
	1246	32.36																							
	942	676.08																							
	1023	251.19																							
AH13(1985-HI)	1098	120.23	0.00	6.48	6.41	0.00	1.25	0.01	0.05	0.00	0.00	13.60	3.06	0.00	3.32	0.49	3.25	8.80	1.14	49.00	0.05	1.29	0.00	0.03	98.23
	1177	60.26																							
	1263	32.36																							
	999	229.09																							
	1077	100.00																							
AH15(1985-HI)	1152	52.48	0.00	6.87	9.20	0.00	1.27	0.01	0.05	0.00	0.00	13.60	3.10	0.00	2.80	1.02	3.26	9.41	1.13	45.60	0.06	1.34	0.00	0.01	98.73
	1238	26.92																							
	956	676.08																							
	1035	245.47																							
AH16(1985-HI)	1111	114.82	0.00	6.36	7.20	0.00	1.26	0.08	0.03	0.00	0.00	13.40	3.06	0.00	4.06	1.00	3.22	6.54	1.10	50.20	0.07	1.30	0.00	0.01	98.89
	1191	58.88																							
	1277	30.90																							
	986	331.13																							
	1041	181.97																							
	1095	109.65																							
FRIT 165(1987)	1140	74.13	0.00	0.00	9.32	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	6.96	0.99	0.00	12.16	0.00	68.89	0.00	0.00	0.00	0.99	99.31
	1197	48.98																							
	1255	33.11																							
	1313	22.91																							
	1092	239.88																							
	1137	154.88																							
FRIT 200(1987)	1195	95.50	0.00	0.00	12.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	5.00	2.00	0.00	11.00	0.00	70.00	0.00	0.00	0.00	0.00	100.00
	1253	60.26																							
	1308	40.74																							

Sample ID	Temp (°C)	Visc (poise)	$Fe^{+2}/\Sigma Fe$	Al2O3(v)	B2O3(v)	BaO(v)	CaO(v)	Cr2O3(v)	Cs2O(v)	CuO(v)	FeO(v)	Fe2O3(v)	K2O(v)	La2O3(v)	Li2O(v)	MgO(v)	MnO(v)	Na2O(v)	NiO(v)	SiO2(v)	SrO(v)	TiO2(v)	ZnO(v)	ZrO2(v)	Sum Oxides
FRIT 201(1987)	1353	38.90	0.00	0.00	10.50	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	5.50	1.00	0.00	10.00	0.00	73.00	0.00	0.00	0.00	0.00	100.00
	1382	33.11																							
	1409	28.84																							
	1436	25.12																							
	1491	18.62																							
FRIT 202(1987)	1358	72.44	0.00	0.40	7.81	0.00	0.10	0.00	0.00	0.00	0.00	0.00	0.30	0.00	6.60	1.90	0.00	5.80	0.00	77.04	0.00	0.10	0.00	0.00	100.04
	1384	61.66																							
	1411	52.48																							
	1438	46.77																							
	1466	39.81																							
	1491	33.88																							
FRIT 202PHP(1987)	1091	117.49	0.00	4.30	8.60	0.20	1.22	0.07	0.15	0.66	0.00	10.70	5.73	0.00	3.42	2.92	0.00	9.20	0.70	51.20	0.00	1.24	0.00	0.00	100.31
	1137	77.62																							
	1193	48.98																							
	1249	32.36																							
	1304	22.91																							
	1360	16.60																							
MAX	1491	1122.02	0.47	13.90	12.20	0.20	1.47	0.09	0.15	0.66	7.14	14.20	5.73	0.36	6.96	2.92	3.26	15.80	2.97	77.04	0.07	1.78	0.00	0.99	100.31
MIN	873	10.23	0.00	0.00	6.41	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.59	0.49	0.00	5.80	0.00	45.60	0.00	0.00	0.00	0.00	98.23

APPENDIX B. Modeling Constraints

As stated in Section 2.1, various constraints on the compositions of glasses being considered for inclusion in modeling must be applied. The sum of oxides (100±5 wt%) was mentioned above, as well as the importance that a given glass must be homogeneous, i.e. not phase separated by liquid-liquid amorphous phase separation (APS) due to low Al_2O_3 (≤3.00 wt%), high P_2O_5 (≥2.25 wt%), or high B_2O_3 (≥15.00 wt%) concentrations and not crystallized. The impacts of low Al_2O_3, high P_2O_5, or high B_2O_3 on glass durability are discussed below.

B.1 The Homogeneity and Low Al_2O_3 Constraint

A homogeneity constraint was developed as part of THERMO™ to ensure that DWPF glasses were homogeneous.[18,19] It was noted during the development of THERMO™ that a minimum of 3 wt% Al_2O_3 was necessary in high Fe_2O_3 containing and high Na_2O containing glasses to avoid amorphous phase separation.[18,19,110] Amorphous phase separation in low Al_2O_3 containing glasses is consistent with the known immiscibility gap in the Al_2O_3-Fe_2O_3-Na_2O-SiO_2 quaternary system that defines the melt surface and crystallization of molten basalt magmas.[111] It is also consistent with known phase separation in Na_2O-Al_2O_3-SiO_2 glasses that are known to phase separate when the glasses contain less than ~ 3 wt% Al_2O_3.[112,113]

The homogeneity constraint was implemented in the DWPF PCCS to avoid the possible production of glasses that could be phase separated (liquid-liquid phase separation) and not predictable by the durability models. While the homogeneity constraint was typically an issue at lower waste loadings (WLs), it may impact the operating windows[ξ] for DWPF operations, where the glass forming systems may be limited to lower waste loadings based on fissile or heat load limits. In the Sludge Batch 1b (SB1b) variability study, application of the homogeneity constraint at the MAR limit eliminated much of the potential operating window for DWPF.[114] As a result, Edwards and Brown [115] developed criteria that allowed DWPF to relax the homogeneity constraint from the MAR to the property acceptance region (PAR), which opened up the operating window for DWPF operations. These criteria are defined as:

(1) use the alumina constraint as currently implemented in PCCS ($Al_2O_3 \geq 3$ wt%) and add a sum of alkali constraint with an upper limit of 19.3 wt% ($\sum R_2O < 19.3$ wt%), or

(2) adjust the lower limit on the Al_2O_3 constraint to 4 wt% ($Al_2O_3 \geq 4$ wt%).

where $\sum R_2O$ is the sum of the concentrations of the alkali oxides, i.e. $Cs_2O+K_2O+Li_2O+Na_2O$. The alkali and alumina limits in criterion 1 above are those of the Waste Form Compliance Plan (WCP) Purex glass and the criteria are not only to ensure that glasses are not phase separated but to ensure that the glass durability stays well below that of the benchmark EA glass. Recent studies on the long term durability of high alkali versus low alkali glasses has shown that high alkali glasses return to the undesirable accelerated rate of dissolution preferentially to low alkali glasses.[116, 117] Therefore, the implementation of an alkali/alumina constraint for DWPF glasses was prudent.

Historical glasses of interest to DWPF meeting criteria 1 and 2 above were found to be acceptable using a normalized boron release (NL [B]) of 10 g/L as a benchmark. This value was chosen in order to be certain that the boron releases of the study glasses were 2σ below that of the EA glass with measurement and analytical uncertainty considered. It should be emphasized that this limit was not empirically derived and was only used as a guide to develop the Al_2O_3 and/or sum or alkali criteria. Herman et al. [118] later

[ξ] The WL interval over which a particular glass system is considered to be acceptable based on model predictions.

demonstrated that these criteria could be used to replace the homogeneity constraint for future sludge-only batches.

With the initiation of the ARP and MCU at SRS in 2008, there was a need to revisit the DWPF homogeneity constraint for coupled operations. This constraint was specifically addressed through the variability study for Sludge Batch 5 (SB5).
In addition to variability studies, other studies [119] were conducted to better understand the homogeneity-composition relationship, which is discussed next. Raszewski and Edwards [119] conducted a reduction of constraints (ROC) study for coupled operations (ARP and MCU) and this is discussed in Section 3.0. This constraint was revisited for SWPF coupled operations and the Al_2O_3 content in the ROC was found to be too low in high TiO_2 containing glasses. The higher Al_2O_3 ROC limit will be reported and justified in Reference 52.

B.2 High P_2O_5 Constraint

Glasses were further screened for modeling (see Figure 2-1) and were not modeled if they contained >2.25 wt% P_2O_5 (Figure 2-1) as this had been shown to cause lithium phosphate phase separation and compromise glass durability.[120,121,122] High P_2O_5 (>2.25 wt%) concentration creates crystalline phosphate phases by crystalline phase separation (CPS). In CPS the two phases, one phosphate rich, co-exist as liquid phases in the melt and the glass cannot be quenched rapidly enough to prevent the phosphate rich liquid from crystallizing.[121, 122]

B.3 High B_2O_3 Constraint

In 1994 Tovena, et. al. [45] demonstrated that various glass durability models, whether based on thermodynamics, enthalpy or structural concepts, did not predict waste glass durability accurately when the composition of the waste glass contained >15% B_2O_3 with little or no Al_2O_3. For these glasses, all the models under-predicted the glass durability significantly. Tovena, et. al. [45] attributed the under prediction to phase separation and complete dissolution of a borate rich phase in the glass when the Al_2O_3 content was insufficient. This was confirmed by SRNL researchers in 1995 [18,19,110] and a B_2O_3 constraint of 14 wt% is imposed to be conservative.

APPENDIX C. SWPF (TiO_2-only) Glass Database

Sample ID	Temp (iC)	Measured Visc (poise)	Al2O3(v)	B2O3(v)	BaO(v)	CaO(v)	Ce2O3(v)	CoO(v)	Cr2O3(v)	Cs2O(v)	CuO(v)	Fe2O3(v)	K2O(v)	La2O3(v)	Li2O(v)	MgO(v)	MnO(v)	Na2O(v)	NiO(v)	PbO(v)	RuO2(v)	SO4(v)	SiO2(v)	ThO2(v)	TiO2(v)	U3O8(v)	ZnO(v)	ZrO2(v)	Sum Oxides
SWPF-01	947	391.84	3.90	4.54	0.23	0.23	0.19	0.11	0.19	1.19	0.11	13.27	0.22	0.09	6.95	1.85	0.21	7.78	0.00	0.22	0.11	0.39	55.34	0.95	2.05	0.00	0.18	0.24	100.53
	1047	127.47																											
	1145	51.72																											
	1245	25.27																											
SWPF-02	947	380.20	3.87	4.50	0.00	2.11	0.00	0.00	0.00	0.36	0.00	4.98	0.00	0.00	6.91	0.00	4.20	7.76	2.00	0.00	0.09	0.00	55.49	0.86	1.99	4.97	0.00	0.00	100.09
	1047	120.55																											
	1145	48.54																											
	1245	23.55																											
SWPF-03	947	246.81	3.85	4.55	0.00	2.04	0.00	0.00	0.00	0.45	0.00	7.54	0.00	0.00	6.87	1.85	4.07	7.81	0.00	0.00	0.11	0.00	55.32	0.00	6.03	0.00	0.00	0.00	100.49
	1047	78.72																											
	1145	33.39																											
	1245	16.89																											
SWPF-04	947	438.09	3.86	4.54	0.20	2.11	0.30	0.05	0.19	0.69	0.10	4.96	0.24	0.06	6.84	0.00	0.21	7.75	0.00	0.23	0.11	0.32	55.62	0.00	5.90	5.51	0.19	0.21	100.20
	1047	132.21																											
	1145	52.04																											
	1245	25.21																											
SWPF-05	947	135.55	3.72	10.22	0.21	0.25	0.31	0.05	0.19	0.33	0.12	5.12	0.24	0.05	1.06	1.80	4.14	16.18	2.12	0.23	0.09	0.33	39.90	1.00	6.09	6.23	0.20	0.23	100.41
	1047	41.73																											
	1145	17.69																											
	1245	8.95																											
SWPF-06	947	252.75	3.85	10.03	0.00	0.24	0.00	0.00	0.00	0.38	0.00	5.09	0.00	0.00	6.83	0.00	0.21	9.30	0.00	0.00	0.12	0.00	54.89	0.96	1.99	6.03	0.00	0.00	99.92
	1047	84.14																											
	1145	37.05																											
	1245	19.03																											
SWPF-07	947	135.81	3.86	10.01	0.30	0.22	0.40	0.05	0.18	0.45	0.10	4.89	0.22	0.07	6.84	0.00	4.03	7.56	2.00	0.22	0.13	0.32	52.06	0.00	5.96	0.00	0.18	0.23	100.29
	1047	45.95																											
	1145	20.48																											
	1245	10.76																											
SWPF-08	Not measured		3.92	10.12	0.00	0.24	0.00	0.00	0.00	1.15	0.00	15.34	0.00	0.00	0.98	1.84	0.21	8.07	0.00	0.00	0.13	0.00	45.57	0.97	5.86	6.15	0.00	0.00	100.54
	1145	185.32																											
	1245	61.84																											
SWPF-09	947	99.50	3.75	9.99	0.00	2.00	0.00	0.00	0.00	1.24	0.00	4.84	0.00	0.00	6.81	1.87	0.22	7.96	1.94	0.00	0.10	0.00	47.39	0.00	5.69	5.76	0.00	0.00	99.56
	1047	33.73																											
	1145	14.94																											
	1245	7.83																											
SWPF-10	947	320.89	3.81	10.02	0.20	2.05	0.18	0.08	0.19	1.11	0.12	15.51	0.25	0.07	1.05	0.00	4.06	12.43	0.00	0.22	0.11	0.37	40.00	0.00	1.96	5.94	0.19	0.21	100.12
	1047	87.84																											
	1145	33.48																											
	1245	15.87																											
SWPF-11	947	841.21	5.85	10.31	0.00	0.23	0.00	0.00	0.00	1.62	0.00	4.91	0.00	0.00	1.07	0.00	0.21	18.14	1.99	0.00	0.14	0.00	53.72	0.00	1.90	0.00	0.00	0.00	100.08
	1047	244.55																											
	1145	91.30																											
	1245	43.69																											
SWPF-12	947	790.36	13.63	4.51	0.00	0.23	0.00	0.00	0.00	0.33	0.00	14.94	0.00	0.00	7.13	0.00	0.21	8.42	0.00	0.00	0.12	0.00	40.67	0.00	4.63	5.66	0.00	0.00	100.47
	1047	183.75																											
	1145	39.98																											
	1245	17.45																											
SWPF-13	947	580.58	13.38	4.57	0.21	0.22	0.19	0.05	0.19	1.11	0.11	4.98	0.23	0.12	6.81	1.92	4.08	8.03	0.00	0.23	0.14	0.32	45.15	0.00	1.95	6.24	0.20	0.22	100.65
	1047	162.39																											

Sample ID	Temp (iC)	Measured Visc (poise)	Al2O3(v)	B2O3(v)	BaO(v)	CaO(v)	Ce2O3(v)	CoO(v)	Cr2O3(v)	Cs2O(v)	CuO(v)	Fe2O3(v)	K2O(v)	La2O3(v)	Li2O(v)	MgO(v)	MnO(v)	Na2O(v)	NiO(v)	PbO(v)	RuO2(v)	SO4(v)	SiO2(v)	ThO2(v)	TiO2(v)	U3O8(v)	ZnO(v)	ZrO2(v)	Sum Oxides
	1145	60.14																											
	1245	27.56																											
SWPF-14	947	355.46	13.34	10.21	0.31	1.94	0.42	0.04	0.17	0.48	0.09	4.84	0.22	0.06	6.77	1.94	0.19	8.11	0.00	0.23	0.16	0.33	48.36	0.00	1.93	0.00	0.19	0.24	100.57
	1047	114.44																											
	1145	47.04																											
	1245	23.35																											
SWPF-15	947	130.24	13.35	10.14	0.23	1.98	0.24	0.05	0.19	1.26	0.10	4.83	0.22	0.15	6.76	0.00	3.99	8.18	0.00	0.22	0.11	0.30	40.10	0.95	5.85	0.86	0.19	0.23	100.46
	1047	43.42																											
	1145	19.02																											
	1245	9.54																											
SWPF-16	947	268.76	6.62	7.96	0.11	1.04	0.10	0.06	0.11	0.72	0.07	7.64	0.14	0.06	5.46	0.95	1.96	9.75	0.65	0.11	0.13	0.23	49.30	0.37	3.96	2.92	0.10	0.11	100.64
	1047	85.77																											
	1145	36.02																											
	1245	17.82																											
SWPF-17	947	718.62	6.31	5.93	0.06	0.66	0.06	0.04	0.05	1.09	0.04	7.51	0.09	0.03	2.64	1.41	1.17	14.84	0.51	0.06	0.12	0.16	51.02	0.24	4.90	1.52	0.06	0.06	100.56
	1047	211.47																											
	1145	81.40																											
	1245	38.05																											
SWPF-18	949	151.47	6.24	5.89	0.06	0.65	0.06	0.05	0.05	1.09	0.04	7.49	0.08	0.03	5.68	0.47	1.17	15.42	1.47	0.06	0.12	0.18	48.88	0.71	2.92	1.52	0.05	0.05	100.43
	1049	55.98																											
	1149	25.85																											
	1248	13.45																											
SWPF-19	947	732.25	6.28	5.91	0.18	1.55	0.14	0.06	0.14	0.62	0.09	7.50	0.19	0.04	2.65	0.48	3.08	14.23	0.49	0.16	0.13	0.28	51.12	0.24	2.98	1.52	0.14	0.17	100.37
	1047	209.69																											
	1145	80.10																											
	1245	37.60																											
SWPF-20	951	159.64	6.31	5.79	0.19	1.54	0.15	0.10	0.14	0.66	0.08	12.75	0.17	0.04	5.57	1.40	1.16	10.53	0.50	0.16	0.12	0.34	45.12	0.71	4.96	1.48	0.15	0.17	100.31
	1050	50.68																											
	1150	22.06																											
	1249	11.35																											
SWPF-21	949	254.38	6.18	5.78	0.06	1.56	0.06	0.05	0.05	1.02	0.05	8.09	0.09	0.03	2.57	0.47	3.16	15.39	1.50	0.05	0.13	0.18	43.46	0.71	4.97	4.57	0.05	0.05	100.27
	1049	77.92																											
	1149	32.17																											
	1248	15.62																											
SWPF-22	949	212.17	6.18	7.10	0.06	1.54	0.05	0.04	0.05	1.09	0.04	12.84	0.09	0.03	2.61	0.48	3.10	15.33	0.50	0.06	0.12	0.24	43.67	0.27	3.00	1.52	0.05	0.05	100.12
	1049	71.82																											
	1149	30.17																											
	1248	14.40																											
SWPF-23	949	227.87	6.14	8.35	0.17	0.68	0.11	0.06	0.14	0.54	0.10	7.57	0.19	0.09	2.53	1.26	1.20	15.44	0.50	0.17	0.12	0.28	43.70	0.83	4.90	4.53	0.14	0.17	99.90
	1049	72.40																											
	1149	31.19																											
	1248	15.82																											
SWPF-24	949	897.81	6.25	8.55	0.06	0.67	0.06	0.04	0.05	0.99	0.04	12.80	0.10	0.03	2.56	0.46	1.17	10.48	0.50	0.05	0.13	0.20	46.96	0.80	2.93	4.46	0.06	0.05	100.45
	1049	232.30																											
	1149	87.61																											
	1248	40.71																											
SWPF-25	947	134.77	6.17	8.64	0.06	1.61	0.06	0.04	0.06	0.55	0.03	7.48	0.09	0.03	5.52	0.46	3.11	10.34	0.50	0.06	0.11	0.15	45.36	0.81	4.82	4.43	0.05	0.05	100.60
	1047	45.82																											
	1145	20.21																											
	1245	10.47																											
SWPF-26	947	136.93	6.16	8.66	0.06	1.55	0.06	0.04	0.06	1.02	0.05	7.51	0.09	0.03	5.61	1.40	3.13	10.38	1.47	0.06	0.11	0.17	45.23	0.26	2.93	4.45	0.06	0.05	100.58
	1047	46.33																											
	1145	20.32																											
	1245	10.35																											
SWPF-	949	335.40	10.88	5.74	0.06	0.69	0.07	0.05	0.05	0.59	0.05	7.54	0.10	0.03	5.47	0.49	3.13	10.53	1.45	0.05	0.13	0.17	43.94	0.27	4.86	4.03	0.06	0.05	100.47

Sample ID	Temp (iC)	Measured Visc (poise)	Al2O3(v)	B2O3(v)	BaO(v)	CaO(v)	Ce2O3(v)	CoO(v)	Cr2O3(v)	Cs2O(v)	CuO(v)	Fe2O3(v)	K2O(v)	La2O3(v)	Li2O(v)	MgO(v)	MnO(v)	Na2O(v)	NiO(v)	PbO(v)	RuO2(v)	SO4(v)	SiO2(v)	ThO2(v)	TiO2(v)	U3O8(v)	ZnO(v)	ZrO2(v)	Sum Oxides
27	1049	93.20																											
	1149	36.85																											
	1248	18.51																											
SWPF-28	949	303.41	10.88	5.85	0.06	0.68	0.06	0.04	0.06	1.00	0.04	7.71	0.09	0.03	5.29	1.41	3.17	11.09	0.50	0.05	0.13	0.16	43.76	0.82	2.96	4.59	0.06	0.05	100.53
	1049	91.66																											
	1149	38.21																											
	1248	18.79																											
SWPF-29	949	325.89	10.90	5.69	0.18	1.58	0.17	0.08	0.14	1.00	0.08	7.73	0.18	0.12	5.35	0.47	1.19	10.31	0.51	0.17	0.12	0.29	43.89	0.27	4.91	4.52	0.15	0.16	100.16
	1049	99.94																											
	1149	39.63																											
	1248	19.43																											
SWPF-30	949	698.13	10.96	8.64	0.18	0.67	0.20	0.07	0.14	1.07	0.09	7.49	0.17	0.07	2.61	0.46	3.05	12.43	0.49	0.16	0.13	0.28	43.88	0.82	4.93	1.52	0.15	0.17	100.83
	1049	188.65																											
	1149	70.95																											
	1248	33.45																											
SWPF-31	949	765.07	10.98	8.77	0.06	1.55	0.07	0.04	0.04	0.65	0.03	7.52	0.08	0.03	2.47	1.36	1.17	14.81	1.50	0.05	0.14	0.18	43.72	0.84	3.00	1.53	0.05	0.05	100.69
	1049	211.07																											
	1149	73.80																											
	1248	29.70																											
SWPF-32	951	399.47	6.95	5.90	0.11	1.10	0.10	0.04	0.08	0.89	0.06	7.08	0.13	0.03	5.11	0.80	1.85	10.06	0.96	0.10	0.13	0.22	50.74	0.52	4.68	2.63	0.09	0.10	100.44
	1050	126.06																											
	1150	51.20																											
	1249	25.08																											
SWPF-33	949	218.00	7.67	8.38	0.11	1.07	0.11	0.05	0.09	0.75	0.08	8.52	0.15	0.03	4.88	0.90	1.89	10.30	0.98	0.11	0.12	0.25	44.80	0.53	3.91	4.66	0.10	0.11	100.55
	1049	68.03																											
	1149	29.64																											
	1248	15.15																											
SWPF-34	951	433.62	10.30	6.43	0.10	0.98	0.10	0.05	0.08	0.82	0.06	6.46	0.12	0.06	3.09	1.02	1.92	15.81	0.99	0.10	0.13	0.21	45.65	0.55	3.67	1.58	0.09	0.11	100.48
	1050	139.01																											
	1150	55.70																											
	1249	26.93																											
SWPF-35	951	149.99	7.77	8.87	0.10	1.08	0.11	0.04	0.08	0.83	0.07	10.58	0.12	0.03	5.32	1.08	2.49	10.18	0.90	0.11	0.11	0.25	43.62	0.54	4.31	1.92	0.09	0.10	100.69
	1050	48.13																											
	1150	20.61																											
	1249	10.31																											
SWPF-36	951	384.31	11.34	6.53	0.13	1.10	0.10	0.06	0.08	0.90	0.06	7.00	0.13	0.04	5.37	1.05	2.02	10.37	1.09	0.10	0.13	0.23	46.39	0.56	4.13	1.27	0.11	0.11	100.40
	1050	117.67																											
	1150	46.34																											
	1249	22.89																											
SWPF-37	951	318.06	5.13	7.81	0.11	1.10	0.11	0.05	0.10	0.79	0.07	9.63	0.13	0.04	4.63	0.93	1.84	9.43	1.04	0.11	0.13	0.23	49.68	0.52	3.82	2.78	0.09	0.11	100.41
	1050	99.61																											
	1150	41.02																											
	1249	20.18																											
SWPF-38	951	370.58	5.54	7.63	0.10	1.05	0.10	0.04	0.09	0.75	0.07	11.28	0.13	0.03	2.26	1.00	2.27	13.32	0.99	0.10	0.13	0.25	44.93	0.56	4.02	3.63	0.09	0.09	100.43
	1050	111.17																											
	1150	46.40																											
	1249	23.51																											
SWPF-39	951	213.52	6.04	5.88	0.10	1.07	0.09	0.06	0.09	0.81	0.05	7.03	0.12	0.04	4.95	0.93	1.74	14.24	0.96	0.09	0.12	0.21	49.39	0.52	3.90	1.76	0.08	0.09	100.37
	1050	72.96																											
	1150	32.21																											
	1249	16.51																											
SWPF-40	951	220.34	10.85	7.73	0.13	1.19	0.13	0.04	0.10	0.85	0.07	9.42	0.14	0.03	4.55	1.02	2.72	12.87	0.92	0.11	0.11	0.26	41.65	0.55	3.86	1.40	0.11	0.13	100.96
	1050	68.14																											
	1150	28.51																											
	1249	14.05																											

Sample ID	Temp (iC)	Measured Visc (poise)	Al2O3(v)	B2O3(v)	BaO(v)	CaO(v)	Ce2O3(v)	CoO(v)	Cr2O3(v)	Cs2O(v)	CuO(v)	Fe2O3(v)	K2O(v)	La2O3(v)	Li2O(v)	MgO(v)	MnO(v)	Na2O(v)	NiO(v)	PbO(v)	RuO2(v)	SO4(v)	SiO2(v)	ThO2(v)	TiO2(v)	U3O8(v)	ZnO(v)	ZrO2(v)	Sum Oxides
SWPF-41	951	141.14	5.75	8.36	0.11	1.07	0.10	0.05	0.10	0.86	0.06	6.38	0.12	0.07	5.99	0.95	2.37	11.53	0.99	0.11	0.13	0.22	48.64	0.56	4.06	1.82	0.10	0.11	100.61
	1050	49.83																											
	1150	22.32																											
	1249	11.75																											
SWPF-42	951	696.43	5.91	6.78	0.09	1.00	0.11	0.04	0.08	0.78	0.06	6.21	0.12	0.04	2.26	0.96	1.73	14.48	0.91	0.09	0.13	0.21	50.58	0.58	3.75	3.25	0.09	0.10	100.36
	1050	203.00																											
	1150	77.88																											
	1249	36.88																											
SWPF-43	951	180.07	6.57	5.86	0.09	1.14	0.09	0.05	0.09	0.75	0.06	11.08	0.12	0.06	5.38	1.01	1.97	11.60	0.99	0.10	0.11	0.25	45.68	0.57	3.97	2.68	0.09	0.10	100.46
	1050	58.82																											
	1150	25.42																											
	1249	12.88																											
SWPF-44	951	251.26	6.83	7.24	0.10	1.21	0.11	0.05	0.08	0.76	0.08	6.67	0.13	0.07	5.02	0.96	2.37	10.59	1.01	0.11	0.12	0.23	47.61	0.57	3.98	4.40	0.10	0.11	100.50
	1050	78.34																											
	1150	33.89																											
	1249	16.98																											
SWPF-45	951	616.81	6.67	6.56	0.11	1.09	0.08	0.06	0.08	0.79	0.06	10.26	0.13	0.03	2.35	1.03	1.73	13.83	0.90	0.10	0.13	0.24	48.47	0.49	3.67	1.36	0.09	0.11	100.42
	1050	174.97																											
	1150	67.67																											
	1249	31.71																											
SWPF-46	951	237.69	6.32	6.05	0.10	1.10	0.14	0.06	0.10	0.76	0.08	6.95	0.13	0.05	3.46	0.91	1.81	15.57	1.09	0.11	0.12	0.23	46.22	0.54	3.71	4.52	0.10	0.11	100.34
	1050	79.27																											
	1150	34.27																											
	1249	16.76																											
SWPF-47	951	158.03	7.98	7.80	0.10	1.14	0.10	0.04	0.09	0.76	0.07	6.68	0.13	0.05	4.41	1.14	2.10	13.22	1.09	0.12	0.12	0.23	43.35	0.62	4.76	4.16	0.10	0.11	100.49
	1050	54.28																											
	1150	23.53																											
	1249	11.84																											
SWPF-48	951	377.85	9.28	8.04	0.11	1.13	0.10	0.04	0.06	0.87	0.06	7.18	0.11	0.06	3.75	1.06	2.37	12.47	1.12	0.10	0.13	0.22	46.11	0.59	3.84	1.49	0.09	0.10	100.49
	1050	113.77																											
	1150	46.36																											
	1249	23.17																											
SWPF-49	951	190.48	5.74	8.27	0.13	1.07	0.11	0.06	0.10	0.87	0.06	7.22	0.13	0.04	3.56	0.85	1.75	15.44	0.92	0.12	0.12	0.24	47.29	0.57	3.38	2.10	0.10	0.13	100.37
	1050	64.42																											
	1150	28.30																											
	1249	15.29																											
SWPF-50	951	200.58	11.06	6.23	0.12	1.11	0.09	0.05	0.10	0.76	0.07	6.90	0.14	0.06	5.67	0.97	2.22	12.22	0.89	0.12	0.11	0.24	42.58	0.55	3.66	4.40	0.10	0.11	100.54
	1050	62.92																											
	1150	26.42																											
	1249	13.99																											
MAX*	1249	897.81	13.38	10.31	0.31	2.05	0.42	0.10	0.19	1.62	0.12	15.51	0.25	0.15	6.81	1.94	4.08	18.14	1.99	0.23	0.16	0.37	53.72	0.95	5.85	6.24	0.20	0.24	100.96
MIN*	947	10.31	3.81	4.57	0.00	0.22	0.00	0.00	0.00	0.48	0.00	4.83	0.00	0.00	1.05	0.00	0.19	8.03	0.00	0.00	0.11	0.00	40.00	0.00	1.90	0.00	0.00	0.00	99.90

*Where max and min refer to the glasses used for modeling and not the glasses excluded

APPENDIX D. SWPF (TiO_2-only) Validation Database

Sample ID	Measured Visc (poise)	Temperature (°C)	Al2O3(v)	B2O3(v)	BaO(v)	CaO(v)	CdO(v)	Ce2O3(v)	Cr2O3(v)	Cs2O(v)	Fe2O3(v)	La2O3(v)	Li2O(v)	MgO(v)	MnO(v)	Na2O(v)	NiO(v)	PbO(v)	SO4(v)	SiO2(v)	TiO2(v)	ZnO(v)	ZrO2(v)	Oxide Sum
HWL-01	32.35	1203.00	10.90	7.84	0.09	1.22	0.00	0.23	0.102	0.00	13.74	0.082	5.264	0.187	1.51	10.16	0.45	0.10	0.00	44.12	1.42	0.055	0.22	97.82
	22.01	1258.50																						
	16.39	1301.17																						
	12.03	1352.00																						
	31.73	1203.00																						
	49.93	1149.50																						
	34.35	1201.17																						
HWL-02	23.79	1203.00	12.15	7.11	0.11	1.38	0.00	0.26	0.11	0.00	16.16	0.09	4.66	0.22	1.79	11.27	0.51	0.11	0.00	41.56	1.61	0.062	0.25	99.55
	16.67	1251.00																						
	11.85	1302.50																						
	8.88	1350.83																						
	23.41	1201.17																						
	37.33	1149.00																						
	25.06	1202.50																						
	23.79	1203.00																						
HWL-03	28.09	1201.3	10.83	9.92	0.10	1.21	0.00	0.24	0.10	0.00	13.53	0.09	4.37	0.20	1.49	10.15	0.48	0.10	0.00	42.09	1.47	0.06	0.23	96.79
	20.05	1250.50																						
	14.84	1295.67																						
	10.91	1350.00																						
	28.32	1202.33																						
	43.92	1149.33																						
	30.03	1201.00																						
HWL-04	26.0	1200.50	11.97	9.33	0.11	1.36	0.00	0.26	0.11	0.00	15.28	0.09	4.34	0.21	1.69	11.34	0.49	0.11	0.00	39.10	1.62	0.06	0.25	97.88
	18.21	1250.00																						
	13.31	1299.50																						
	10.16	1348.50																						
	26.77	1201.00																						
	43.04	1148.17																						

Sample ID	Measured Visc (poise)	Temperature (°C)	Al2O3(v)	B2O3(v)	BaO(v)	CaO(v)	CdO(v)	Ce2O3(v)	Cr2O3(v)	Cs2O(v)	Fe2O3(v)	La2O3(v)	Li2O(v)	MgO(v)	MnO(v)	Na2O(v)	NiO(v)	PbO(v)	SO4(v)	SiO2(v)	TiO2(v)	ZnO(v)	ZrO2(v)	Oxide Sum
	29.26	1199.83																						
HWL-05	9.09	1303.50	7.03	7.57	0.12	1.58	0.00	0.25	0.13	0.00	16.05	0.09	5.14	0.22	2.03	10.77	0.49	0.11	0.00	45.46	1.23	0.07	0.27	98.78
	6.89	1352.00																						
	17.01	1203.17																						
	25.41	1150.00																						
	38.77	1099.00																						
	61.09	1049.17																						
	27.32	1150.00																						
HWL-06	19.87	1201.00	7.69	7.30	0.12	1.74	0.00	0.27	0.16	0.00	17.62	0.10	4.77	0.24	2.25	11.68	0.57	0.11	0.00	41.82	1.38	0.08	0.30	98.41
	14.33	1252.00																						
	10.56	1303.83																						
	7.970	1351.00																						
	19.61	1201.83																						
	29.50	1148.00																						
	44.37	1099.33																						
	20.64	1201.17																						
HWL-07	18.92	1204.33	6.92	4.90	0.11	1.53	0.00	0.25	0.15	0.00	16.01	0.09	5.10	0.22	2.02	12.17	0.54	0.11	0.00	46.37	1.25	0.07	0.27	98.24
	13.90	1251.00																						
	10.19	1301.00																						
	7.82	1352.00																						
	19.71	1202.00																						
	29.57	1149.50																						
	44.11	1102.00																						
	72.67	1049.00																						
HWL-08	19.94	1203.00	7.78	4.33	0.13	1.77	0.00	0.27	0.15	0.00	16.98	0.11	4.55	0.24	2.19	13.22	0.57	0.12	0.00	42.73	1.37	0.08	0.29	97.07
	14.75	1249.00																						
	10.72	1298.50																						
	8.10	1348.00																						
	19.87	1200.00																						

Sample ID	Measured Visc (poise)	Temperature (°C)	Al2O3(v)	B2O3(v)	BaO(v)	CaO(v)	CdO(v)	Ce2O3(v)	Cr2O3(v)	Cs2O(v)	Fe2O3(v)	La2O3(v)	Li2O(v)	MgO(v)	MnO(v)	Na2O(v)	NiO(v)	PbO(v)	SO4(v)	SiO2(v)	TiO2(v)	ZnO(v)	ZrO2(v)	Oxide Sum
	29.26	1148.33																						
HWL-09	24.26	1201.00	4.53	11.91	0.07	0.84	0.00	0.18	0.08	0.00	10.37	0.06	5.42	0.13	2.84	8.00	0.60	0.10	0.00	49.36	2.25	0.03	0.72	97.58
	17.85	1249.50																						
	13.36	1298.00																						
	10.19	1347.83																						
	23.75	1201.00																						
	35.47	1146.17																						
	52.12	1100.00																						
	82.43	1049.00																						
HWL-10	22.66	1151.50	5.12	11.12	0.09	0.98	0.00	0.20	0.09	0.00	11.73	0.07	5.18	0.16	3.25	8.99	0.66	0.12	0.00	46.26	2.58	0.04	0.82	97.55
	16.03	1203.00																						
	11.90	1252.00																						
	9.04	13.02																						
	23.10	1150.67																						
	34.78	1099.50																						
	53.51	1052.00																						
	23.89	1150.00																						
HWL-14	25.34	1147.00	5.86	4.46	0.10	1.14	0.00	0.22	0.09	0.00	13.15	0.08	4.68	0.18	3.78	13.88	0.71	0.12	0.00	44.39	2.82	0.04	0.82	96.64
	16.15	1198.00																						
	11.68	1250.00																						
	8.97	1299.00																						
	23.19	1148.17																						
	34.06	1100.00																						
	23.54	1148.00																						
HWL-15	58.94	1150.00	3.91	12.52	0.07	0.87	0.00	0.21	0.06	0.00	10.53	0.07	4.37	0.14	1.94	7.59	0.27	0.10	0.00	51.83	2.57	0.01	0.53	97.65
	39.78	1201.50																						
	28.50	1251.00																						
	20.45	1301.00																						
	58.67	1149.00																						
	89.67	1100.17																						

Sample ID	Measured Visc (poise)	Temperature (°C)	Al2O3(v)	B2O3(v)	BaO(v)	CaO(v)	CdO(v)	Ce2O3(v)	Cr2O3(v)	Cs2O(v)	Fe2O3(v)	La2O3(v)	Li2O(v)	MgO(v)	MnO(v)	Na2O(v)	NiO(v)	PbO(v)	SO4(v)	SiO2(v)	TiO2(v)	ZnO(v)	ZrO2(v)	Oxide Sum
HWL-16	43.05	1150.50	4.45	11.76	0.07	1.00	0.00	0.25	0.08	0.00	11.81	0.08	4.04	0.17	2.19	8.58	0.31	0.12	0.00	48.40	2.92	0.02	0.60	96.94
	28.56	1205.00																						
	20.87	1250.00																						
	14.97	1301.00																						
	42.50	1150.83																						
	64.69	1102.50																						
	107.62	1050.00																						
HWL-17	41.02	1149.50	5.05	10.57	0.09	1.15	0.00	0.28	0.08	0.00	13.61	0.09	3.66	0.19	2.54	9.46	0.36	0.14	0.00	45.73	3.35	0.02	0.70	97.19
	28.43	1200.75																						
	19.60	1247.83																						
	14.30	1297.50																						
	38.75	1149.50																						
	59.53	1099.00																						
	40.01	1148.00																						
HWL-18	39.69	1148.17	3.91	5.55	0.07	0.84	0.00	0.22	0.07	0.00	10.37	0.07	5.72	0.15	1.90	12.36	0.28	0.11	0.00	52.31	2.62	0.02	0.50	97.13
	26.62	1201.00																						
	20.05	1249.50																						
	15.21	1297.50																						
	40.22	1147.83																						
	59.78	1098.00																						
	40.35	1147.67																						
HWL-19	29.14	1150.67	4.48	5.14	0.08	1.01	0.00	0.24	0.09	0.00	11.67	0.08	5.27	0.16	2.23	13.14	0.32	0.12	0.00	49.95	2.93	0.02	0.62	97.65
	20.30	1201.50																						
	14.90	1250.00																						
	11.10	1299.00																						
	28.77	1151.00																						
	42.90	1100.67																						
	66.80	1050.50																						
	29.11	1150.83																						
HWL-	22.93	1153.33	5.08	4.74	0.08	1.16	0.00	0.27	0.10	0.00	13.45	0.09	4.88	0.18	2.53	13.52	0.36	0.13	0.00	46.16	3.28	0.02	0.66	96.81

Sample ID	Measured Visc (poise)	Temperature (°C)	Al2O3(v)	B2O3(v)	BaO(v)	CaO(v)	CdO(v)	Ce2O3(v)	Cr2O3(v)	Cs2O(v)	Fe2O3(v)	La2O3(v)	Li2O(v)	MgO(v)	MnO(v)	Na2O(v)	NiO(v)	PbO(v)	SO4(v)	SiO2(v)	TiO2(v)	ZnO(v)	ZrO2(v)	Oxide Sum
20	15.87	1205.00																						
	11.88	1252.00																						
	8.92	1302.33																						
	23.09	1153.67																						
	34.68	1102.67																						
	23.44	1152.50																						
HLW-21	45.61	1201.00	17.21	8.80	0.09	1.44	0.00	0.09	0.13	0.00	8.77	0.05	4.03	0.19	0.70	14.53	0.14	0.03	0.00	40.22	1.47	0.04	0.22	98.30
	32.45	1249.50																						
	23.42	1299.00																						
	67.43	1151.00																						
	79.36	1100.67																						
	169.30	1050.17																						
	68.69	1150.00																						
HLW-22	70.62	1147.00	18.99	7.90	0.10	1.61	0.00	0.10	0.16	0.00	9.69	0.05	3.72	0.21	0.79	15.70	0.16	0.04	0.00	37.38	1.66	0.05	0.24	98.73
	46.74	1199.00																						
	32.91	1246.50																						
	23.67	1295.00																						
	70.68	1148.00																						
	84.08	1098.00																						
	185.76	1046.33																						
FY09EM21-02	11.99	1151.50	4.11	5.18	0.08	0.01	0.25	0.36	0.01	0.13	20.23	0.09	4.03	1.46	0.26	17.05	0.01	0.18	0.49	40.38	2.06	0.13	0.20	96.70
	8.61	1202.5																						
	12.00	1151.00																						
	17.35	1100.50																						
	12.47	1150.00																						
FY09EM21-03	9.50	1145.00	6.934	4.629	0.006	0.02	0.01	0.01	0.015	0.01	13.22	0.01	6.74	1.415	4.58	14.58	0.01	0.01	0.08	40.11	4.98	0.01	0.01	97.36
	6.91	1197.00																						
	9.50	1146.00																						
	13.21	1095.83																						
	9.50	1146.00																						

Sample ID	Measured Visc (poise)	Temperature (°C)	Al2O3(v)	B2O3(v)	BaO(v)	CaO(v)	CdO(v)	Ce2O3(v)	Cr2O3(v)	Cs2O(v)	Fe2O3(v)	La2O3(v)	Li2O(v)	MgO(v)	MnO(v)	Na2O(v)	NiO(v)	PbO(v)	SO4(v)	SiO2(v)	TiO2(v)	ZnO(v)	ZrO2(v)	Oxide Sum
FY09EM21-05	45.03	1148.50	3.69	4.33	0.01	4.11	0.01	0.01	0.02	0.01	13.35	0.01	3.95	0.01	0.25	9.95	2.29	0.01	0.07	49.74	5.83	0.01	0.01	97.64
	30.74	1199.00																						
	21.20	1251.00																						
	15.04	1304.00																						
	43.57	1150.50																						
FY09EM21-06	10.90	1148.50	4.44	11.48	0.07	0.03	0.25	0.34	0.19	0.13	5.19	0.09	3.85	0.01	4.51	14.80	2.39	0.19	0.43	42.95	5.90	0.01	0.01	97.25
	8.15	1200.25																						
	10.98	1150.00																						
	15.13	1100.00																						
	11.06	1150.00																						
FY09EM21-07	4.70	1150.5	4.814	13.70	0.01	3.97	0.01	0.01	0.01	0.01	16.84	0.01	3.87	1.37	4.43	12.83	0.06	0.01	0.07	33.16	1.99	0.01	0.01	97.16
	3.73	1201.00																						
	4.70	1151.50																						
	6.49	1101.00																						
	4.70	1151.50																						
FY09EM21-08	10.19	1151.50	3.26	4.83	0.01	0.52	0.01	0.01	0.16	0.01	20.16	0.01	6.73	1.38	1.16	9.66	0.02	0.01	0.07	42.73	5.95	0.01	0.01	96.67
	7.53	1201.50																						
	10.03	1151.50																						
	14.18	1101.17																						
	10.11	1151.00																						
FY09EM21-09	15.99	1153.00	12.97	9.54	0.01	3.01	0.01	0.01	0.14	0.01	10.53	0.01	6.79	0.01	1.68	10.08	0.59	0.01	0.07	40.43	2.49	0.01	0.01	98.38
	11.56	1203.00																						
	8.47	1254.67																						
	15.83	1153.00																						
	23.04	1102.50																						
	15.91	1153.00																						
FY09EM21-11	17.49	1150.00	3.23	4.28	0.07	4.03	0.25	0.33	0.02	0.12	5.99	0.08	5.49	1.35	4.41	12.29	0.01	0.18	0.45	47.71	6.76	0.13	0.19	97.37
	12.65	1200.00																						
	9.37	1251.00																						
	17.49	1150.00																						

Sample ID	Measured Visc (poise)	Temperature (°C)	Al2O3(v)	B2O3(v)	BaO(v)	CaO(v)	CdO(v)	Ce2O3(v)	Cr2O3(v)	Cs2O(v)	Fe2O3(v)	La2O3(v)	Li2O(v)	MgO(v)	MnO(v)	Na2O(v)	NiO(v)	PbO(v)	SO4(v)	SiO2(v)	TiO2(v)	ZnO(v)	ZrO2(v)	Oxide Sum
	25.75	1099.00																						
	17.73	1149.00																						
FY09EM21-12	17.08	1154.50	4.57	5.23	0.01	0.01	0.01	0.01	0.02	0.01	15.37	0.01	6.62	0.01	3.81	9.81	1.69	0.01	0.07	46.26	1.99	0.01	0.01	95.50
	12.02	1205.00																						
	8.82	1257.00																						
	16.80	1153.33																						
	24.94	1102.00																						
	17.37	1152.67																						
FY09EM21-14	15.19	1148.83	3.217	14.97	0.08	0.04	0.25	0.34	0.14	0.13	19.62	0.09	4.34	0.01	0.24	9.77	0.01	0.19	0.43	39.42	5.60	0.13	0.19	99.20
	11.02	1199.50																						
	15.13	1150.00																						
	21.95	1099.00																						
	15.29	1149.33																						
FY09EM21-15	22.36	1154.00	5.55	4.60	0.10	3.33	0.21	0.35	0.14	0.13	7.92	0.09	5.89	1.34	4.35	9.94	2.27	0.18	0.44	49.35	1.86	0.13	0.19	98.35
	15.58	1206.00																						
	11.27	1258.00																						
	22.35	1154.83																						
	33.54	1103.00																						
	22.73	1153.50																						
FY09EM21-16	21.57	1148.50	3.74	6.62	0.08	3.84	0.23	0.35	0.15	0.13	8.74	0.09	3.99	1.41	0.25	15.27	2.34	0.19	0.43	48.08	1.97	0.14	0.20	98.21
	15.29	1202.00																						
	10.66	1259.67																						
	21.46	1150.83																						
	32.01	1098.33																						
	21.88	1148.83																						
FY09EM21-17	9.80	1152.33	7.67	4.80	0.09	0.11	0.23	0.37	0.01	0.14	13.81	0.10	7.00	0.01	0.48	15.03	0.01	0.21	0.49	41.29	6.13	0.14	0.21	98.36
	7.14	1204.00																						
	9.79	1154.50																						
	13.62	1103.33																						
	9.79	1154.50																						

Sample ID	Measured Visc (poise)	Temperature (°C)	Al2O3(v)	B2O3(v)	BaO(v)	CaO(v)	CdO(v)	Ce2O3(v)	Cr2O3(v)	Cs2O(v)	Fe2O3(v)	La2O3(v)	Li2O(v)	MgO(v)	MnO(v)	Na2O(v)	NiO(v)	PbO(v)	SO4(v)	SiO2(v)	TiO2(v)	ZnO(v)	ZrO2(v)	Oxide Sum
	9.80	1152.33																						
FY09EM21-18	54.07	1146.00	11.07	4.86	0.08	0.40	0.20	0.35	0.02	0.12	6.67	0.09	5.33	0.01	0.65	16.11	0.01	0.19	0.43	49.74	1.96	0.12	0.20	98.61
	38.27	1199.75																						
	19.17	1296.50																						
	50.57	1151.00																						
FY09EM21-19	26.51	1154.50	5.84	4.58	0.01	4.07	0.01	0.01	0.02	0.01	4.98	0.01	3.97	0.01	0.25	16.72	0.90	0.01	0.07	51.45	5.85	0.01	0.01	98.74
	18.68	1207.00																						
	13.36	1263.33																						
	26.42	1156.17																						
	39.21	1103.33																						
	26.80	1154.00																						
FY09EM21-20	27.67	1152.67	6.16	5.41	0.01	0.01	0.01	0.01	0.16	0.01	11.39	0.01	4.02	1.18	0.24	16.95	2.31	0.01	0.07	47.87	1.98	0.01	0.01	97.79
	19.47	1203.50																						
	13.72	1260.00																						
	27.59	1152.33																						
	40.79	1101.00																						
	27.98	1152.00																						
FY09EM21-21	6.19	1153.00	4.861	8.95	0.08	0.01	0.28	0.36	0.19	0.13	18.84	0.09	6.88	0.01	0.82	14.42	0.01	0.21	0.47	39.15	1.98	0.13	0.20	98.07
	4.76	1204.00																						
	6.22	1154.66																						
	8.52	1103.00																						
	6.35	1154.00																						
FY09EM21-25	29.21	1143.00	6.41	4.98	0.01	4.14	0.01	0.01	0.16	0.01	7.53	0.01	4.01	0.01	4.61	15.40	0.01	0.01	0.07	48.83	2.01	0.01	0.01	98.22
	20.42	1199.00																						
	14.43	1256.00																						
	29.09	1150.00																						
FY09EM21-27	16.06	1154.33	7.29	6.87	0.04	1.79	0.14	0.18	0.09	0.07	12.69	0.05	4.95	0.67	2.20	12.63	1.13	0.10	0.25	43.05	3.89	0.07	0.11	98.25
	11.63	1205.00																						

Sample ID	Measured Visc (poise)	Temperature (°C)	Al2O3(v)	B2O3(v)	BaO(v)	CaO(v)	CdO(v)	Ce2O3(v)	Cr2O3(v)	Cs2O(v)	Fe2O3(v)	La2O3(v)	Li2O(v)	MgO(v)	MnO(v)	Na2O(v)	NiO(v)	PbO(v)	SO4(v)	SiO2(v)	TiO2(v)	ZnO(v)	ZrO2(v)	Oxide Sum
	16.17	1154.00																						
	23.83	1103.00																						
	16.45	1154.00																						
MAX*	107.62	1347.83	12.97	11.91	0.13	4.14	0.25	0.36	0.19	0.13	20.23	0.11	6.79	1.46	4.61	17.05	2.39	0.19	0.49	51.45	5.90	0.14	0.82	98.74
MIN*	10.19	1049.00	3.74	4.33	0.01	0.01	0.00	0.01	0.01	0.00	4.98	0.01	3.66	0.01	0.24	8.00	0.01	0.01	0.00	40.38	1.25	0.01	0.01	95.50

*Where max and min refer to the glasses used for modeling and not the glasses excluded

APPENDIX E. CST (TiO_2-Nb_2O_5-ZrO_2) Glass Model Database

Sample ID	Temp (iC)	Measured Visc (poise)	Al_2O_3(v)	B_2O_3(v)	BaO (v)	CaO(v)	Ce_2O_3(v)	Cr_2O_3(v)	CuO(v)	Fe_2O_3(v)	K_2O(v)	La_2O_3(v)	Li_2O(v)	MgO(v)	MnO(v)	Na_2O(v)	Nb_2O_5(v)	NiO(v)	PbO(v)	SO_4 (v)	SiO_2(v)	ThO_2 (v)	TiO_2(v)	U_3O_8(v)	ZnO (v)	ZrO_2(v)	Oxide Sum
CST 01	1197.00	48.88	2.74	8.25	0.00	0.91	0.00	0.14	0.08	9.72	0.19	0.00	4.71	0.06	1.83	8.87	0.66	0.85	0.00	0.00	55.39	0.00	2.03	2.02	0.00	0.41	98.85
	1141.00	75.70																									
	1088.00	121.82																									
	1035.00	211.70																									
	982.00	391.25																									
CST 07	1195.50	50.34	2.94	7.79	0.00	0.98	0.00	0.13	0.07	11.25	0.09	0.00	4.05	0.09	1.93	8.97	0.70	0.88	0.00	0.00	53.43	0.00	1.81	2.86	0.00	0.64	98.61
	1140.00	78.05																									
	1087.00	126.73																									
	1034.00	217.55																									
	980.50	401.17																									
CST 08	1192.50	45.31	2.96	7.24	0.00	0.93	0.00	0.12	0.08	11.14	0.09	0.00	4.17	0.09	1.89	8.45	1.28	0.87	0.00	0.00	52.27	0.00	2.68	3.04	0.00	1.14	98.43
	1138.50	70.75																									
	1085.50	115.38																									
	1032.00	200.04																									
	979.50	370.70																									
CST 09	1197.00	38.98	2.83	7.10	0.00	0.99	0.00	0.13	0.08	11.98	0.12	0.00	3.72	0.09	1.91	8.73	1.92	0.89	0.00	0.00	50.40	0.00	3.81	2.51	0.00	1.66	98.88
	1142.50	60.12																									
	1088.50	99.37																									
	1035.50	173.61																									
	982.00	324.34																									
CST 10	1199.00	42.20	2.82	7.33	0.00	0.97	0.00	0.12	0.07	10.48	0.09	0.00	4.26	0.09	1.96	9.05	0.74	0.87	0.00	0.00	52.45	0.00	2.43	3.65	0.00	0.64	98.01
	1146.00	64.62																									
	1094.00	103.29																									
	1036.50	177.95																									
	983.00	323.51																									
CST 11	1198.50	37.11	2.89	7.71	0.00	1.01	0.00	0.12	0.06	11.91	0.09	0.00	3.98	0.09	2.00	9.05	1.41	0.93	0.00	0.00	52.49	0.00	3.53	2.50	0.00	1.17	100.94
	1145.00	57.32																									
	1089.00	92.77																									
	1035.50	160.56																									
	982.50	295.24																									
CST 12	1197.50	33.97	3.00	7.53	0.00	1.02	0.00	0.14	0.09	11.70	0.09	0.00	3.91	0.10	1.87	8.66	2.03	0.92	0.00	0.00	49.47	0.00	4.50	2.65	0.00	1.64	99.32

Sample ID	Temp (iC)	Measured Visc (poise)	Al_2O_3(v)	B_2O_3(v)	BaO (v)	CaO(v)	Ce_2O_3 (v)	Cr_2O_3(v)	CuO(v)	Fe_2O_3(v)	K_2O(v)	La_2O_3 (v)	Li_2O(v)	MgO(v)	MnO(v)	Na_2O(v)	Nb_2O_5(v)	NiO(v)	PbO(v)	SO_4 (v)	SiO_2(v)	ThO_2 (v)	TiO_2(v)	U_3O_8(v)	ZnO (v)	ZrO_2(v)	Oxide Sum
	1145.00	52.92																									
	1088.50	86.87																									
	1035.50	150.16																									
	982.50	283.45																									
	1199.00	42.81																									
	1143.50	66.59																									
CST 06	1089.00	108.50	2.60	7.53	0.00	0.88	0.00	0.17	0.10	10.46	0.21	0.00	4.22	0.07	1.64	8.67	1.92	0.82	0.00	0.00	51.73	0.00	5.08	2.16	0.00	1.06	99.33
	1035.50	188.65																									
	983.00	353.10																									
	1197.00	35.82																									
	1142.50	55.08																									
CST 14	1088.50	90.10	3.90	7.40	0.00	1.21	0.00	0.15	0.09	13.87	0.18	0.00	4.01	0.08	2.30	9.65	1.32	1.08	0.00	0.00	50.58	0.00	2.91	3.22	0.00	1.26	103.22
	1036.00	156.54																									
	983.00	293.59																									
	1198.00	36.61																									
	1142.00	57.62																									
CST 15	1088.50	95.92	4.00	6.58	0.00	1.22	0.00	0.15	0.09	13.19	0.17	0.00	3.97	0.07	2.49	9.53	1.96	1.13	0.00	0.00	49.59	0.00	3.94	2.84	0.00	1.78	102.70
	1035.50	169.18																									
	983.00	379.17																									
	1200.00	34.54																									
	1144.00	53.57																									
CST 12c	1091.00	87.94	3.01	6.60	0.00	0.92	0.00	0.17	0.10	11.23	0.19	0.00	3.89	0.07	2.06	8.75	1.89	0.96	0.00	0.00	48.19	0.00	5.05	2.32	0.00	1.33	96.73
	1037.50	152.89																									
	984.00	286.43																									
	1200.00	102.49																									
	1148.00	162.38																									
CST 20	1096.00	268.02	6.28	8.54	0.00	0.54	0.00	0.10	0.05	7.16	0.18	0.00	4.40	0.15	1.95	8.76	1.27	0.32	0.00	0.00	55.85	0.00	3.08	0.72	0.00	0.93	100.28
	1043.00	471.58																									
	991.00	894.41																									
	1200.00	100.55																									
	1147.00	161.21																									
CST 26	1090.50	267.88	6.82	7.68	0.00	0.52	0.00	0.12	0.04	7.84	0.18	0.00	4.19	0.15	2.16	8.64	1.27	0.35	0.00	0.00	54.76	0.00	3.03	0.61	0.00	0.94	99.29
	1037.00	474.04																									

Sample ID	Temp (iC)	Measured Visc (poise)	Al_2O_3(v)	B_2O_3(v)	BaO (v)	CaO(v)	Ce_2O_3 (v)	Cr_2O_3(v)	CuO(v)	Fe_2O_3(v)	K_2O(v)	La_2O_3 (v)	Li_2O(v)	MgO(v)	MnO(v)	Na_2O(v)	Nb_2O_5(v)	NiO(v)	PbO(v)	SO_4 (v)	SiO_2(v)	ThO_2 (v)	TiO_2(v)	U_3O_8(v)	ZnO (v)	ZrO_2(v)	Oxide Sum
	984.00	892.81																									
	1200.50	104.09																									
	1145.00	166.82																									
CST 32	1092.00	279.30	8.01	6.95	0.00	0.54	0.00	0.12	0.06	8.44	0.21	0.00	3.98	0.18	2.63	8.73	1.28	0.42	0.00	0.00	52.57	0.00	3.10	1.04	0.00	0.97	99.22
	1039.00	498.98																									
	986.00	950.84																									
	1145.67	54.96																									
	1200.00	36.20																									
	1252.50	25.06																									
KT04-01	1147.50	52.38	6.03	5.91	0.07	0.98	0.27	0.07	0.06	11.71	0.04	0.09	3.52	0.15	1.93	13.03	0.95	0.33	0.13	0.00	47.90	0.00	4.48	0.00	0.01	0.83	98.51
	1097.00	79.48																									
	1046.00	129.80																									
	1146.50	53.16																									
	1148.00	45.28																									
	1203.00	30.55																									
	1254.00	21.78																									
KT04-02	1149.33	45.61	5.46	5.87	0.07	0.99	0.28	0.08	0.05	11.34	0.04	0.06	3.57	0.16	1.73	14.07	1.05	0.19	0.11	0.00	48.65	0.00	4.61	0.00	0.04	0.94	99.37
	1099.00	69.54																									
	1048.00	113.58																									
	1148.00	46.38																									
	1147.50	72.29																									
	1202.33	47.53																									
	1254.50	32.92																									
KT04-06	1150.00	71.41	7.65	5.99	0.07	1.05	0.10	0.08	0.07	8.97	0.17	0.03	3.55	0.10	1.19	13.68	0.95	0.15	0.06	0.00	49.45	0.00	4.51	0.00	0.08	0.88	98.75
	1100.00	110.09																									
	1048.50	183.10																									
	1149.83	72.94																									
	1148.00	45.60																									
	1201.17	31.48																									
	1254.00	22.75																									
KT04-08	1148.00	45.44	5.38	5.95	0.08	0.87	0.08	0.10	0.05	9.23	0.12	0.03	3.54	0.11	0.96	15.43	1.26	0.59	0.06	0.00	49.66	0.00	5.13	0.00	0.04	1.05	99.73
	1099.00	67.60																									
	1048.00	107.94																									
	1148.83	45.13																									

Sample ID	Temp (iC)	Measured Visc (poise)	Al_2O_3(v)	B_2O_3(v)	BaO (v)	CaO(v)	Ce_2O_3 (v)	Cr_2O_3(v)	CuO(v)	Fe_2O_3(v)	K_2O(v)	La_2O_3 (v)	Li_2O(v)	MgO(v)	MnO(v)	Na_2O(v)	Nb_2O_5(v)	NiO(v)	PbO(v)	SO_4 (v)	SiO_2(v)	ThO_2 (v)	TiO_2(v)	U_3O_8(v)	ZnO (v)	ZrO_2(v)	Oxide Sum
KT04-09	1149.83	43.32	5.96	5.99	0.07	1.04	0.19	0.07	0.07	12.35	0.13	0.07	3.52	0.11	0.55	14.21	0.82	0.48	0.12	0.00	48.30	0.00	5.03	0.00	0.05	0.74	99.86
	1205.50	29.00																									
	1257.17	20.80																									
	1152.50	43.58																									
	1102.00	66.35																									
	1050.67	107.86																									
	1151.33	44.66																									
KT04-10	1146.00	48.57	5.93	5.91	0.08	1.01	0.25	0.08	0.05	13.31	0.05	0.08	3.53	0.12	0.35	13.37	0.77	0.48	0.13	0.00	47.95	0.00	4.74	0.00	0.04	0.73	98.96
	1200.00	32.81																									
	1252.00	23.09																									
	1147.83	48.47																									
	1097.00	74.69																									
	1046.00	122.52																									
	1146.83	50.28																									
KT06-01	1150.00	32.46	5.81	8.27	0.04	I	0.20	0.10	0.04	8.94	0.13	0.06	3.55	0.10	1.33	12.56	0.59	0.59	0.10	0.15	47.57	0.00	6.05	0.00	0.05	0.61	98.05
	1201.00	22.15																									
	1247.00	15.98																									
	1149.00	32.58																									
	1107.00	46.24																									
	1050.83	77.87																									
	1151.00	32.43																									
KT06-02	1147.33	46.78	9.79	8.29	0.02	1.82	0.10	0.05	0.05	7.15	0.06	0.03	**3.51**	0.04	1.09	12.50	0.06	1.13	0.05	0.15	46.88	0.00	6.08	0.00	0.04	0.15	99.04
	1198.83	31.53																									
	1246.00	22.48																									
	1145.00	47.68																									
	1103.67	67.59																									
	1047.50	114.80																									
	1147.33	38.46																									
KT06-08	1148.33	54.14	7.35	4.84	0.02	1.11	0.11	0.06	0.03	11.04	0.06	0.03	5.38	0.05	1.27	10.07	0.54	0.44	0.06	0.15	50.51	0.00	6.28	0.00	0.03	0.61	100.04
	1200.33	41.84																									
	1246.67	25.25																									
	1148.00	53.80																									
	1107.00	77.29																									
	1051.00	132.45																									

Sample ID	Temp (iC)	Measured Visc (poise)	Al_2O_3(v)	B_2O_3(v)	BaO (v)	CaO(v)	Ce_2O_3 (v)	Cr_2O_3(v)	CuO(v)	Fe_2O_3(v)	K_2O(v)	La_2O_3 (v)	Li_2O(v)	MgO(v)	MnO(v)	Na_2O(v)	Nb_2O_5(v)	NiO(v)	PbO(v)	SO_4 (v)	SiO_2(v)	ThO_2 (v)	TiO_2(v)	U_3O_8(v)	ZnO (v)	ZrO_2(v)	Oxide Sum
	1149.33	54.41																									
KT06-14	1149.00	45.89	12.13	8.25	0.03	2.17	0.12	0.06	0.02	8.36	0.06	0.03	5.43	0.06	0.46	9.45	0.10	0.14	0.06	0.15	44.91	0.00	6.20	0.00	0.02	1.84	100.05
	1200.00	30.35																									
	1246.00	21.40																									
	1146.00	46.51																									
	1106.67	66.33																									
	1049.50	115.94																									
	1148.00	46.21																									
KT06-17	1148.00	54.08	12.05	4.80	0.02	2.28	0.11	0.06	0.03	8.64	0.08	0.03	6.60	0.08	0.43	9.43	0.07	0.13	0.06	0.15	47.40	0.00	6.06	0.00	0.02	1.71	100.23
	1200.00	35.41																									
	1246.00	25.23																									
	1147.00	54.35																									
	1107.00	77.75																									
	1048.67	135.54																									
	1148.00	54.00																									
KT07-02	1144.67	46.83	5.36	6.13	0.06	0.98	0.28	0.10	0.05	11.21	0.03	0.06	3.47	0.15	1.71	14.15	1.01	0.18	0.11	0.37	48.51	0.00	4.29	0.00	0.03	0.95	99.18
	1197.67	31.03																									
	1245.00	21.98																									
	1145.00	46.83																									
	1105.00	66.49																									
	1048.00	110.34																									
	1148.33	46.10																									
KT07-06	1147.50	73.92	7.39	5.74	0.06	1.00	0.11	0.14	0.05	9.10	0.12	0.03	3.29	0.10	1.19	13.48	0.95	0.15	0.06	0.37	48.94	0.00	4.27	0.00	0.07	0.91	97.51
	1199.00	48.95																									
	1244.00	34.65																									
	1143.50	75.92																									
	1103.83	108.03																									
	1047.17	189.33																									
	1146.83	74.13																									
KT07-07	1146.00	50.55	5.67	5.87	0.07	0.93	0.08	0.15	0.05	9.32	0.08	0.03	3.40	0.11	0.72	14.02	1.13	0.62	0.07	0.39	48.94	0.00	4.77	0.00	0.08	1.03	97.53
	1198.00	33.57																									
	1245.00	26.73																									
	1145.00	51.51																									
	1104.33	73.06																									

Sample ID	Temp (iC)	Measured Visc (poise)	Al_2O_3(v)	B_2O_3(v)	BaO (v)	CaO(v)	Ce_2O_3 (v)	Cr_2O_3(v)	CuO(v)	Fe_2O_3(v)	K_2O(v)	La_2O_3 (v)	Li_2O(v)	MgO(v)	MnO(v)	Na_2O(v)	Nb_2O_5(v)	NiO(v)	PbO(v)	SO_4 (v)	SiO_2(v)	ThO_2 (v)	TiO_2(v)	U_3O_8(v)	ZnO (v)	ZrO_2(v)	Oxide Sum
	1047.50	125.99																									
	1147.33	50.45																									
	1146.50	47.24																									
	1197.50	31.56																									
	1244.50	22.32																									
KT07-09	1144.00	47.32	5.51	5.98	0.07	1.00	0.19	0.11	0.04	12.05	0.08	0.06	3.41	0.11	0.56	13.67	0.72	0.49	0.12	0.36	46.90	0.00	4.75	0.00	0.04	0.74	96.97
	1104.00	66.62																									
	1047.17	113.60																									
	1147.00	46.87																									
	1148.00	46.64																									
	1199.33	30.85																									
	1246.00	21.65																									
KT07-10	1146.00	46.48	5.76	6.12	0.07	1.05	0.24	0.11	0.05	13.35	0.04	0.07	3.48	0.11	0.39	13.53	0.73	0.46	0.13	0.36	47.06	0.00	4.45	0.00	0.04	0.74	98.34
	1105.00	67.00																									
	1048.00	115.91																									
	1148.00	46.75																									
	1151.00	51.71																									
	1202.50	34.65																									
	1253.83	23.89																									
KT08-01	1152.50	51.18	6.06	6.01	0.07	0.98	0.29	0.09	0.08	11.82	0.21	0.09	3.53	0.15	1.88	13.32	0.86	0.34	0.21	0.26	45.92	0.17	4.12	0.60	0.01	0.82	97.89
	1100.50	80.27																									
	1049.00	133.08																									
	1151.50	52.01																									
	1148.50	52.37																									
	1199.50	35.44																									
	1250.50	24.91																									
KT08-02	1149.50	51.59	5.36	5.98	0.07	0.98	0.30	0.09	0.05	11.03	0.23	0.06	3.51	0.14	1.62	13.92	0.92	0.20	0.12	0.26	48.49	0.62	4.16	0.44	0.04	0.81	99.41
	1097.50	80.62																									
	1045.50	133.68																									
	1148.50	52.22																									
	1151.50	35.51																									
	1204.17	23.73																									
KT08-03	1255.00	16.60	4.66	6.01	0.07	0.96	0.27	0.08	0.05	10.85	0.23	0.06	3.47	0.15	1.74	14.19	0.97	0.32	0.12	0.26	52.09	0.89	4.13	0.63	0.04	0.82	103.08
	1153.00	35.25																									

Sample ID	Temp (iC)	Measured Visc (poise)	Al_2O_3(v)	B_2O_3(v)	BaO (v)	CaO(v)	Ce_2O_3 (v)	Cr_2O_3(v)	CuO(v)	Fe_2O_3(v)	K_2O(v)	La_2O_3 (v)	Li_2O(v)	MgO(v)	MnO(v)	Na_2O(v)	Nb_2O_5(v)	NiO(v)	PbO(v)	SO_4 (v)	SiO_2(v)	ThO_2 (v)	TiO_2(v)	U_3O_8(v)	ZnO (v)	ZrO_2(v)	Oxide Sum
	1101.00	54.88																									
	1049.83	89.54																									
	1152.50	35.40																									
	1150.50	55.20																									
	1201.50	38.48																									
	1253.00	27.50																									
KT08-04	1151.00	55.25	5.28	5.98	0.07	0.92	0.24	0.09	0.05	11.79	0.22	0.07	3.44	0.14	1.04	13.88	0.92	0.19	0.09	0.26	50.81	0.24	4.26	0.24	0.08	0.74	101.03
	1099.50	85.12																									
	1048.50	139.77																									
	1150.50	55.97																									
	1151.00	76.37																									
	1202.50	51.29																									
	1253.17	38.00																									
KT08-05	1151.50	79.13	7.22	6.01	0.07	0.98	0.17	0.13	0.05	9.65	0.24	0.07	3.46	0.15	1.02	13.99	0.98	0.14	0.12	0.26	51.93	0.02	4.35	0.49	0.04	0.91	102.45
	1099.50	132.61																									
	1048.00	216.09																									
	1151.00	79.94																									
	1152.50	66.19																									
	1203.83	43.96																									
	1255.50	30.26																									
KT08-06	1153.00	65.42	7.60	6.01	0.07	1.04	0.13	0.13	0.05	8.94	0.27	0.04	3.43	0.11	1.17	13.75	0.94	0.17	0.12	0.26	52.52	.0.02	4.21	0.77	0.08	0.86	102.68
	1101.50	103.69																									
	1049.50	174.40																									
	1149.33	65.28																									
	1200.50	47.04																									
	1251.00	37.05																									
KT08-10	1150.00	66.96	5.34	5.98	0.07	0.93	0.23	0.09	0.04	12.11	0.22	0.07	3.45	0.11	0.36	12.60	0.64	0.46	0.16	0.27	50.70	0.02	3.93	4.54	0.05	0.62	102.98
	1097.67	107.54																									
	1046.33	176.99																									
	1149.50	69.89																									
	1147.67	36.14																									
	1200.33	24.25																									
KT10-01	1247.00	17.56	5.50	4.98	0.06	0.88	0.25	0.09	0.04	10.91	0.04	0.08	5.39	0.14	1.78	11.29	1.35	0.30	0.13	0.00	48.24	0.00	5.98	0.00	0.01	1.17	98.59
	1146.50	36.94																									

Sample ID	Temp (iC)	Measured Visc (poise)	Al_2O_3(v)	B_2O_3(v)	BaO (v)	CaO(v)	Ce_2O_3 (v)	Cr_2O_3(v)	CuO(v)	Fe_2O_3(v)	K_2O(v)	La_2O_3 (v)	Li_2O(v)	MgO(v)	MnO(v)	Na_2O(v)	Nb_2O_5(v)	NiO(v)	PbO(v)	SO_4 (v)	SiO_2(v)	ThO_2 (v)	TiO_2(v)	U_3O_8(v)	ZnO (v)	ZrO_2(v)	Oxide Sum
	1106.00	51.74																									
	1049.00	87.24																									
	1149.17	36.08																									
	1142.00	31.94																									
	1195.00	21.33																									
	1242.00	15.27																									
KT10-03	1142.00	31.60	4.25	4.82	0.06	0.85	0.23	0.09	0.04	10.40	0.04	0.06	5.39	0.14	1.67	12.28	1.51	0.27	0.11	0.00	49.31	0.00	6.06	0.00	0.04	1.28	98.89
	1101.00	44.36																									
	1044.33	75.02																									
	1145.00	30.85																									
	1143.00	50.77																									
	1195.17	33.31																									
	1242.33	23.38																									
KT10-06	1142.00	50.75	6.95	4.68	0.06	0.86	0.10	0.13	0.04	8.36	0.11	0.03	5.42	0.09	1.11	11.83	1.34	0.13	0.05	0.00	51.13	0.00	6.13	0.00	0.07	1.14	99.76
	1101.00	72.56																									
	1044.67	124.90																									
	1144.00	49.86																									
	1142.67	31.71																									
	1195.00	21.25																									
	1241.33	15.14																									
KT10-08	1140.00	32.37	4.68	4.72	0.07	0.73	0.07	0.10	0.04	8.20	0.08	0.03	5.30	0.10	0.86	13.09	1.73	0.51	0.06	0.00	51.40	0.00	6.58	0.00	0.04	1.41	99.78
	1099.00	45.99																									
	1041.00	79.43																									
	1143.00	31.26																									
	1148.00	34.19																									
	1200.33	23.07																									
	1247.17	16.62																									
KT10-09	1147.00	34.34	5.21	4.68	0.07	0.85	0.18	0.10	0.05	11.25	0.08	0.06	5.36	0.10	0.52	12.09	1.17	0.44	0.12	0.00	49.95	0.00	6.62	0.00	0.04	1.02	99.96
	1107.67	48.26																									
	1051.00	81.42																									
	1150.00	34.77																									
	1143.00	34.56																									
KT10-10	1195.33	22.87	5.29	4.98	0.07	0.92	0.22	0.10	0.04	12.23	0.04	0.06	5.38	0.11	0.34	11.59	1.08	0.42	0.13	0.00	48.94	0.00	6.26	0.00	0.04	0.99	99.22
	1243.00	16.08																									

Sample ID	Temp (iC)	Measured Visc (poise)	Al_2O_3(v)	B_2O_3(v)	BaO (v)	CaO(v)	Ce_2O_3 (v)	Cr_2O_3(v)	CuO(v)	Fe_2O_3(v)	K_2O(v)	La_2O_3 (v)	Li_2O(v)	MgO(v)	MnO(v)	Na_2O(v)	Nb_2O_5(v)	NiO(v)	PbO(v)	SO_4 (v)	SiO_2(v)	ThO_2 (v)	TiO_2(v)	U_3O_8(v)	ZnO (v)	ZrO_2(v)	Oxide Sum
	1141.83	34.17																									
	1102.00	48.02																									
	1045.67	81.75																									
	1145.00	33.76																									
MAX	1257.17	950.84	12.13	8.54	0.08	2.28	0.30	0.15	0.09	13.35	0.27	0.09	6.60	0.18	2.63	15.43	1.96	1.13	0.21	0.39	55.85	0.89	6.62	4.54	0.08	1.84	103.08
MIN	983.00	15.14	4.00	4.68	0.00	0.52	0.00	0.05	0.02	7.15	0.03	0.00	3.29	0.04	0.34	8.64	0.06	0.13	0.00	0.00	45.91	0.00	3.03	0.00	0.00	0.15	96.97

*Where max and min refer to the glasses used for modeling and not the glasses excluded

APPENDIX F. CST Glass Validation Database (KT-04 to KT-10 Studies)

Sample ID	Temp (iC)	Measured Visc (poise)	Al2O3(v)	B2O3(v)	BaO(v)	CaO(v)	Ce2O3(v)	Cr2O3(v)	CuO(v)	Fe2O3(v)	K2O(v)	La2O3(v)	Li2O(v)	MgO(v)	MnO(v)	Na2O(v)	Nb2O5(v)	NiO(v)	PbO(v)	SO4(v)	SiO2(v)	ThO2(v)	TiO2(v)	U3O8(v)	ZnO(v)	ZrO2(v)	Oxide SUM
KT04-03	1151.00	32.99	4.79	5.93	0.07	1.03	0.24	0.08	0.05	11.60	0.05	0.06	3.55	0.15	1.84	14.44	1.04	0.29	0.11	0.00	48.90	0.00	4.47	0.00	0.04	0.92	99.66
	1205.67	20.65																									
	1258.50	13.57																									
	1150.50	32.85																									
	1099.00	51.88																									
	1048.00	85.53																									
	1150.50	33.08																									
KT04-04	1148.00	48.92	5.21	5.87	0.06	0.92	0.19	0.08	0.06	11.75	0.05	0.06	3.53	0.15	1.03	13.71	0.97	0.15	0.08	0.00	49.51	0.00	4.53	0.00	0.07	0.83	98.83
	1203.00	32.87																									
	1256.00	23.11																									
	1149.50	49.08																									
	1097.67	75.39																									
	1045.00	124.32																									
	1147.33	51.04																									
KT04-05	1142.50	70.46	7.19	6.00	0.07	0.96	0.14	0.15	0.06	9.44	0.09	0.06	3.53	0.16	1.00	13.42	1.02	0.12	0.06	0.00	49.99	0.00	4.58	0.00	0.04	0.94	99.01
	1196.50	45.34																									
	1249.50	31.88																									
	1144.00	68.65																									
	1093.00	107.88																									
	1041.00	173.75																									
	1142.00	71.55																									
KT04-07	1145.00	52.04	5.96	5.93	0.07	0.93	0.08	0.11	0.04	9.40	0.11	0.03	3.55	0.11	0.71	14.28	1.12	0.62	0.06	0.00	49.28	0.00	5.00	0.00	0.08	0.99	98.48
	1199.00	35.29																									
	1251.00	25.21																									
	1145.67	52.17																									
	1093.83	79.37																									
	1041.17	129.90																									
	1142.00	53.58																									
KT06-03	1150.00	37.34	5.70	4.76	0.05	1.23	0.20	0.10	0.04	9.15	0.13	0.06	4.74	0.10	1.33	12.48	0.58	0.59	0.10	0.15	50.68	0.00	6.14	0.00	0.05	0.73	99.09
	1201.33	25.31																									
	1249.00	18.06																									
	1148.00	37.52																									
	1108.00	52.43																									
	1052.00	88.03																									

Sample ID	Temp (iC)	Measured Visc (poise)	Al2O3(v)	B2O3(v)	BaO(v)	CaO(v)	Ce2O3(v)	Cr2O3(v)	CuO(v)	Fe2O3(v)	K2O(v)	La2O3(v)	Li2O(v)	MgO(v)	MnO(v)	Na2O(v)	Nb2O5(v)	NiO(v)	PbO(v)	SO4(v)	SiO2(v)	ThO2(v)	TiO2(v)	U3O8(v)	ZnO(v)	ZrO2(v)	Oxide SUM
	1150.00	37.23																									
	1148.50	61.95																									
	1201.17	40.71																									
	1247.00	28.97																									
KT06-04	1147.00	61.97	10.02	4.91	0.02	1.84	0.09	0.05	0.04	7.39	0.07	0.02	4.78	0.04	1.12	11.22	0.08	1.13	0.05	0.15	50.24	0.00	6.21	0.00	0.04	0.19	99.68
	1107.00	88.20																									
	1050.00	152.60																									
	1150.00	61.26																									
	1148.00	49.40																									
	1201.00	32.72																									
	1247.00	23.31																									
KT06-05	1147.50	49.26	7.46	8.44	0.02	1.18	0.11	0.06	0.02	11.46	0.07	0.03	4.22	0.07	1.21	9.99	0.51	0.40	0.05	0.15	47.68	0.00	6.06	0.00	0.03	0.59	99.81
	1107.67	69.78																									
	1051.33	119.43																									
	1149.00	49.19																									
	1148.17	41.61																									
	1200.00	27.83																									
	1247.00	19.81																									
KT06-06	1147.00	41.31	5.72	8.58	0.02	1.10	0.11	0.06	0.03	12.93	0.06	0.03	4.22	0.05	1.31	9.93	0.54	0.45	0.06	0.15	49.00	0.00	6.28	0.00	0.02	0.61	101.28
	1107.00	58.12																									
	1050.50	99.17																									
	1149.00	41.64																									
	1149.00	58.53																									
	1201.00	38.39																									
	1247.00	27.22																									
KT06-07	1149.00	60.00	9.77	8.14	0.05	0.74	0.23	0.10	0.03	6.93	0.11	0.07	4.17	0.12	3.53	10.02	0.09	0.12	0.11	0.15	47.05	0.00	6.18	0.00	0.05	1.54	99.30
	1108.00	87.25																									
	1052.00	153.58																									
	1150.00	60.33																									
	1149.33	37.91																									
	1201.33	25.50																									
	1247.00	17.56																									
KT06-09	1148.00	36.56	5.71	4.86	0.02	1.11	0.11	0.05	0.02	12.28	0.07	0.03	5.42	0.05	1.24	10.54	0.51	0.40	0.05	0.15	49.96	0.00	6.17	0.00	0.02	0.58	99.35
	1108.00	51.35																									
	1049.50	88.52																									

Sample ID	Temp (iC)	Measured Visc (poise)	Al2O3(v)	B2O3(v)	BaO(v)	CaO(v)	Ce2O3(v)	Cr2O3(v)	CuO(v)	Fe2O3(v)	K2O(v)	La2O3(v)	Li2O(v)	MgO(v)	MnO(v)	Na2O(v)	Nb2O5(v)	NiO(v)	PbO(v)	SO4(v)	SiO2(v)	ThO2(v)	TiO2(v)	U3O8(v)	ZnO(v)	ZrO2(v)	Oxide SUM
	1149.00	36.81																									
KT06-10	1149.00	52.92	9.89	4.99	0.05	0.76	0.21	0.10	0.06	7.37	0.13	0.06	5.31	0.11	3.59	10.77	0.08	0.11	0.11	0.15	48.73	0.00	6.23	0.00	0.07	1.45	100.32
	1200.00	34.99																									
	1247.00	24.47																									
	1147.00	53.50																									
	1106.67	76.30																									
	1049.83	132.53																									
	1149.17	52.69																									
KT06-11	1149.00	40.31	5.57	8.39	0.02	1.09	0.10	0.05	0.04	14.62	0.07	0.03	4.16	0.05	1.24	9.14	0.48	0.39	0.05	0.15	47.54	0.00	6.20	0.00	0.03	0.55	99.98
	1200.00	27.02																									
	1246.00	19.09																									
	1146.00	40.30																									
	1106.00	57.08																									
	1050.00	97.55																									
	1149.00	40.53																									
KT06-12	1150.83	26.23	6.50	8.31	0.10	1.21	0.42	0.18	0.07	10.38	0.27	0.13	5.30	0.25	0.52	9.22	2.22	0.15	0.21	0.15	44.85	0.00	6.11	0.00	0.11	2.09	98.72
	1201.33	17.59																									
	1247.17	12.49																									
	1147.00	26.67																									
	1107.00	37.84																									
	1048.67	66.42																									
	1150.00	26.09																									
KT06-13	1147.00	46.70	9.98	8.56	0.07	0.74	0.29	0.14	0.04	7.44	0.17	0.09	5.36	0.15	3.47	9.08	0.03	0.11	0.14	0.15	49.00	0.00	6.08	0.00	0.07	0.11	101.28
	1199.17	31.22																									
	1245.00	22.40																									
	1145.83	46.91																									
	1106.00	66.05																									
	1049.00	111.85																									
	1148.00	47.45																									
KT06-15	1147.00	32.56	6.56	4.77	0.11	1.07	0.43	0.17	0.09	10.54	0.24	0.13	6.57	0.23	0.53	9.76	2.30	0.16	0.22	0.15	47.45	0.00	5.95	0.00	0.12	2.06	99.62
	1200.00	21.31																									
	1246.00	15.15																									
	1145.00	32.01																									
	1106.00	45.88																									
	1050.50	78.79																									

Sample ID	Temp (iC)	Measured Visc (poise)	Al2O3(v)	B2O3(v)	BaO(v)	CaO(v)	Ce2O3(v)	Cr2O3(v)	CuO(v)	Fe2O3(v)	K2O(v)	La2O3(v)	Li2O(v)	MgO(v)	MnO(v)	Na2O(v)	Nb2O5(v)	NiO(v)	PbO(v)	SO4(v)	SiO2(v)	ThO2(v)	TiO2(v)	U3O8(v)	ZnO(v)	ZrO2(v)	Oxide SUM
	1148.00	32.13																									
KT06-16	1149.00	46.37	10.04	4.87	0.07	0.75	0.28	0.12	0.05	7.34	0.17	0.08	6.61	0.15	3.53	9.49	0.08	0.10	0.14	0.15	50.79	0.00	6.20	0.00	0.08	0.18	101.28
	1201.00	30.70																									
	1246.00	22.31																									
	1146.00	47.07																									
	1107.00	65.62																									
	1049.33	112.76																									
	1149.83	45.86																									
KT06-18	1148.00	58.91	5.68	4.89	0.02	1.12	0.10	0.05	0.05	14.65	0.08	0.03	4.80	0.05	1.17	9.40	0.49	0.39	0.05	0.15	50.72	0.00	6.08	0.00	0.03	0.56	100.55
	1199.00	38.77																									
	1245.00	27.15																									
	1145.00	58.60																									
	1106.00	83.36																									
	1048.00	147.66																									
KT07-01	1144.00	49.12	5.77	5.97	0.06	1.01	0.28	0.10	0.06	11.68	0.03	0.09	3.47	0.15	1.93	13.01	0.90	0.33	0.15	0.37	45.99	0.00	4.17	0.00	0.01	0.83	96.37
	1196.33	32.32																									
	1244.00	22.74																									
	1143.83	48.59																									
	1104.00	68.89																									
	1046.50	119.06																									
	1145.00	48.69																									
KT07-03	1146.00	41.23	4.53	6.00	0.06	1.02	0.25	0.12	0.05	11.21	0.03	0.06	3.45	0.15	1.81	13.85	1.04	0.31	0.12	0.38	48.29	0.00	4.20	0.00	0.03	0.97	97.94
	1199.00	27.30																									
	1246.00	19.59																									
	1144.00	41.61																									
	1104.00	58.66																									
	1046.67	100.33																									
	1147.67	40.71																									
KT07-04	1148.00	48.50	5.19	5.98	0.06	0.91	0.22	0.09	0.05	11.84	0.03	0.06	3.49	0.15	1.07	13.79	0.93	0.15	0.09	0.38	48.40	0.00	4.36	0.00	0.07	0.87	98.19
	1199.67	32.03																									
	1246.00	22.73																									
	1146.00	48.68																									
	1105.50	69.07																									
	1048.83	119.68																									
	1148.50	48.44																									

Sample ID	Temp (iC)	Measured Visc (poise)	Al2O3(v)	B2O3(v)	BaO(v)	CaO(v)	Ce2O3(v)	Cr2O3(v)	CuO(v)	Fe2O3(v)	K2O(v)	La2O3(v)	Li2O(v)	MgO(v)	MnO(v)	Na2O(v)	Nb2O5(v)	NiO(v)	PbO(v)	SO4(v)	SiO2(v)	ThO2(v)	TiO2(v)	U3O8(v)	ZnO(v)	ZrO2(v)	Oxide SUM
	1148.00	70.84																									
	1198.50	47.08																									
	1244.00	33.15																									
KT07-05	1144.00	72.61	7.02	6.14	0.06	1.10	0.15	0.14	0.05	9.56	0.07	0.06	3.47	0.16	1.03	13.62	1.04	0.11	0.06	0.37	49.95	0.00	4.32	0.00	0.06	0.99	99.54
	1103.17	104.60																									
	1047.00	184.81																									
	1146.17	72.87																									
	1147.00	41.45																									
	1198.00	27.95																									
	1244.33	19.99																									
KT07-08	1143.67	42.32	5.09	6.07	0.07	0.90	0.08	0.11	0.04	9.13	0.07	0.03	3.44	0.11	0.96	14.93	1.28	0.59	0.07	0.38	48.51	0.00	4.89	0.00	0.04	1.11	97.89
	1103.67	59.57																									
	1047.00	101.61																									
	1146.67	41.48																									
	1150.50	66.11																									
	1201.50	44.71																									
	1252.83	31.89																									
KT08-07	1151.50	69.74	5.35	6.06	0.07	0.84	0.11	0.13	0.04	8.32	0.27	0.04	3.55	0.10	0.65	13.75	0.89	0.57	0.06	0.26	47.21	0.02	4.27	3.73	0.07	0.77	97.13
	1099.50	118.53																									
	1048.50	184.55																									
	1150.50	71.45																									
	1150.00	55.75																									
	1201.00	38.28																									
	1252.50	27.25																									
KT08-08	1150.83	58.87	4.59	5.89	0.06	0.74	0.10	0.09	0.05	7.94	0.25	0.03	3.47	0.09	0.82	14.02	1.11	0.51	0.12	0.26	48.67	0.02	4.18	5.22	0.04	0.90	99.16
	1099.50	93.69																									
	1048.00	157.42																									
	1150.50	60.23																									
	1153.00	49.77																									
	1204.00	32.97																									
	1255.67	22.95																									
KT08-09	1153.50	49.30	5.21	6.02	0.07	0.92	0.20	0.09	0.04	10.73	0.28	0.07	3.51	0.10	0.50	13.01	0.65	0.45	0.13	0.26	45.67	0.02	4.20	4.86	0.04	0.57	97.59
	1101.50	77.38																									
	1050.00	128.26																									
	1153.00	49.72																									

Sample ID	Temp (iC)	Measured Visc (poise)	Al2O3(v)	B2O3(v)	BaO(v)	CaO(v)	Ce2O3(v)	Cr2O3(v)	CuO(v)	Fe2O3(v)	K2O(v)	La2O3(v)	Li2O(v)	MgO(v)	MnO(v)	Na2O(v)	Nb2O5(v)	NiO(v)	PbO(v)	SO4(v)	SiO2(v)	ThO2(v)	TiO2(v)	U3O8(v)	ZnO(v)	ZrO2(v)	Oxide SUM
	1141.17	34.46																									
	1194.00	23.10																									
	1241.00	16.33																									
KT10-02	1139.67	34.50	4.93	4.89	0.06	0.89	0.26	0.08	0.03	10.35	0.04	0.05	5.34	0.14	1.55	11.95	1.30	0.17	0.10	0.00	49.90	0.00	5.95	0.00	0.03	1.14	99.16
	1099.00	48.89																									
	1041.83	83.29																									
	1142.67	33.89																									
	1148.00	36.06																									
	1201.00	24.24																									
	1247.50	17.48																									
KT10-04	1148.00	36.06	4.66	4.97	0.05	0.81	0.19	0.09	0.04	10.78	0.03	0.05	5.40	0.14	0.98	11.60	1.41	0.14	0.08	0.00	49.90	0.00	5.96	0.00	0.07	1.20	98.56
	1108.00	50.47																									
	1051.00	85.40																									
	1150.50	35.53																									
	1148.00	48.58																									
	1200.17	32.39																									
	1247.00	23.17																									
KT10-05	1147.00	48.93	6.44	4.81	0.05	0.87	0.13	0.13	0.03	8.74	0.07	0.05	5.39	0.14	0.92	11.70	1.47	0.10	0.05	0.00	50.27	0.00	6.10	0.00	0.03	1.30	98.79
	1106.33	69.69																									
	1050.00	119.45																									
	1148.67	48.69																									
	1152.67	37.97																									
	1204.33	25.71																									
	1250.00	18.64																									
KT10-07	1149.00	38.84	5.37	4.83	0.06	0.83	0.07	0.14	0.05	8.59	0.08	0.03	5.34	0.11	0.67	12.43	1.60	0.54	0.06	0.00	50.06	0.00	6.53	0.00	0.08	1.32	98.79
	1109.00	54.35																									
	1052.00	92.90																									
	1152.00	38.23																									
MAX*	1258.50	184.81	10.04	8.58	0.11	1.84	0.43	0.18	0.09	14.62	0.28	0.13	6.61	0.25	3.59	14.93	2.30	1.13	0.22	0.38	50.79	0.02	6.53	5.22	0.12	2.09	101.28
MIN*	1041.00	12.49	4.53	4.76	0.02	0.74	0.07	0.05	0.02	6.93	0.03	0.02	3.44	0.04	0.50	9.08	0.03	0.10	0.05	0.00	44.85	0.00	4.17	0.00	0.01	0.11	96.37

*Where max and min refer to the glasses used for modeling and not the glasses excluded

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