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Summary Report on Potential Impacts of Small Column Ion Exchange on DWPF Glass Formulation

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EXECUTIVE SUMMARY

This report summarizes a large amount of experimental work completed to identify the potential impacts of material from Small Column Ion Exchange (SCIX) on glass formulation at the Defense Waste Processing Facility (DWPF). The results show no significant issues with the predicted values of chemical durability and viscosity using the current Product Composition Control System (PCCS) models when the SCIX components are added to projected DWPF glass compositions. No modifications to the viscosity and durability models appear to be necessary at this time in order to incorporate the SCIX streams at DWPF. It is recommended that the Savannah River National Laboratory (SRNL) continue to verify the durability and viscosity models as the projected compositions for DWPF processing evolve. It is also recommended that the data generated thus far be reviewed and a determination be made as to how best to extend the validation ranges of the durability and viscosity models.

The liquidus temperatures for the experimental glasses are also reported and discussed in this report. The results show that the measured or estimated (based on measured data) liquidus temperature values for the glasses with SCIX components added are consistently higher than those predicted by the current model. Therefore, the PCCS liquidus temperature model will need to be modified in order to incorporate the SCIX streams at DWPF. It is recommended that SRNL carry out full measurements of the liquidus temperatures for those KT-series glasses where estimates have been made. These data should then be used to support an evaluation of whether a refitting of the liquidus temperature model coefficients will be sufficient to correctly predict the liquidus temperature of glasses containing the SCIX components (particularly higher TiO_2 concentrations), or whether additional modifications to the model are required.

While there are prediction issues with the current liquidus temperature model, they are not at this time expected to hamper the incorporation of SCIX streams at DWPF. The estimated liquidus temperatures, while higher than the model predicted values, remain below the current DWPF limit of 1050 °C for most of the study glasses. Note that the properties and performance of the glasses in this study are highly dependent on glass composition. Therefore, should significant changes be made to the projected compositions or processing rates for SCIX or DWPF, many of the assessments and experiments may have to be revisited.

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LIST OF ABBREVIATIONS

CCC	Canister Centerline Cooled
CST	Crystalline Silicotitanate
DWPF	Defense Waste Processing Facility
EA	Environmental Assessment
HLW	High Level Waste
ICP-AES	Inductively Coupled Plasma – Atomic Emission Spectroscopy
MAR	Measurement Acceptability Region
M&TE	Measurement and Test Equipment
MST	Mono Sodium Titanate
PCCS	Product Composition Control System
PCT	Product Consistency Test
RMF	Rotary Micro Filter
SCIX	Small Column Ion Exchange
SRNL	Savannah River National Laboratory
SRS	Savannah River Site
SWPF	Salt Waste Processing Facility
T _L	Liquidus Temperature
TTT	Time-Temperature-Transformation
XRD	X-ray Diffraction

1.0 Outline

This report is intended to summarize a large amount of experimental work completed in support of the Small Column Ion Exchange (SCIX) Program at the Savannah River Site (SRS). The work was performed to identify the potential impacts of material from SCIX on glass formulation at the Defense Waste Processing Facility (DWPF). This summary report is divided into sections, as follows: Section 2.0 provides brief background information on the SCIX program and its potential impacts to DWPF glass formulation. Section 3.0 details the liquidus temperature experiments that have been performed in support of this study. These data require a significant amount of time to collect; therefore, they could not be included in the previous technical reports. Section 4.0 provides a summary and review of all of the studies completed to date, including paper studies using model predicted properties and experimental glasses fabricated and characterized in the laboratory. Section 5.0 presents an overall summary of the study and provides recommendations for continued work.

All of the work discussed in this report was initiated by a DWPF Technical Task Request¹ and was performed following a Task Technical and Quality Assurance Plan.²

2.0 Background

The SRS Liquid Waste contractor will begin a process referred to as SCIX to disposition salt solution in fiscal year 2014. In the first step of the process, salt solution retrieved from various waste tanks will be struck with Monosodium Titanate (MST) to remove key actinides and Sr. The salt solution will then be processed using Rotary Micro Filtration (RMF) to remove the MST and any insoluble solids. The MST and insoluble solids will accumulate on the bottom of Tank 41. The filtrate from RMF will be fed to ion exchange columns, also in Tank 41, to remove the ¹³⁷Cs using Crystalline Silicotitanate (CST) resin. The decontaminated salt solution from SCIX will be sent to the Saltstone Facility for immobilization in grout. The ¹³⁷Cs-laden CST resin will be sluiced and ground for particle size reduction, then sent to the DWPF for immobilization in glass. These processes mirror the current disposition paths for streams associated with the Salt Waste Processing Facility (SWPF), which is under construction and will run concurrently with SCIX.

The MST and insoluble solids from Tank 41 will periodically be transferred to a sludge batch preparation tank (e.g., Tank 42 or Tank 51) as part of the High Level Waste (HLW) sludge batch preparation process for DWPF. The ground, ¹³⁷Cs-laden CST material (hereafter referred to simply as CST) from SCIX will be periodically transferred to Tank 40 prior to being processed at DWPF. Periodic additions of CST to Tank 40 would result in a changing composition of each sludge batch as it is processed since Tank 40 serves as the feed tank for the DWPF. Work is currently in progress to determine the feasibility of depositing the ground CST in Tank 41. If ground CST can be deposited in Tank 41 (depending on heat loading issues, among others), the CST would be sent to Tank 42 or Tank 51 using an existing transfer line. Therefore, the studies of SCIX impacts on DWPF glass formulation have encompassed scenarios where the CST is sent to either Tank 40 or to a sludge batch preparation tank. MST from the SWPF was also considered in the study.

The MST and CST from the SCIX process will significantly increase the concentrations of Nb₂O₅, TiO₂, and ZrO₂ in the DWPF feed. Other constituents of MST and CST – Na₂O and SiO₂ – are already present in high concentrations in DWPF glass; thus their influences are well understood. The increased concentrations of Nb₂O₅, TiO₂, and ZrO₂ will likely have some impact on the properties and performance of the DWPF glass product. Properties such as the liquidus

temperature, viscosity, and rate of melting of the glass may be impacted. The performance of the glass, particularly its chemical durability as it pertains to repository acceptance requirements, may also be impacted. The DWPF uses a set of semi-empirical and first-principles models referred to as the Product Composition Control System (PCCS)³ to predict the properties and performance of a glass based on its composition, since it is not possible to measure these attributes during processing. The objective of this study was to evaluate the impacts of the SCIX streams on the properties and performance of the DWPF glass product and on the applicability of the current process control models.^a Any anticipated issues with model applicability or performance of the glass product were to be identified, and recommendations were to be made for addressing these issues.

3.0 Liquidus Temperature Studies

The liquidus temperatures (T_L)^b of select study glasses were determined using the isothermal heat treatment method.⁵ The temperature profiles of the furnaces were carefully determined and periodically verified.⁶ All thermocouples and temperature measurement devices were calibrated and periodically verified by the Savannah River National Laboratory (SRNL) Measurement and Test Equipment (M&TE) program. A standard glass composition was incorporated periodically into the test glass matrix as a method of verifying the measured data.^c Polished samples of each quenched glass were observed via optical microscopy prior to T_L measurement to determine whether any preexisting spinel crystals were present. Quenched glasses that were found to contain spinel crystals were excluded from testing. The study glasses were ground and heat treated for 24 hours in platinum-alloy boats with tight fitting lids following the procedure.⁵ The glasses were air quenched after being removed from the furnace, then sectioned and polished for microscopy.⁷ Any bulk crystallization (as opposed to surface or interface crystallization) that occurred during the isothermal heat treatments was identified by optical microscopy. The procedure was repeated over various temperatures to determine the T_L to within a narrow range of tolerance (typically +/- 5 °C).

Observations of crystallization within all of the study glasses during the T_L evaluations via optical and scanning electron microscopy indicated that the primary crystalline phases forming were spinels, including $TiFe_2O_4$.

Liquidus temperatures were determined for the KT01-series glasses only.^d In the interest of reducing the time necessary for further measurements, the T_L values for the KT03, KT04, KT06, KT07, and KT10-series glasses were estimated. The isothermal heat treatment method described above was continued, although a smaller number of heat treatments were performed in order to estimate the T_L for each glass over a broader range of temperature while supporting comparisons with the model predicted T_L values. The temperature range for each composition was chosen to fall within the 95% confidence interval of the model predicted T_L value for that composition (based on measured composition data).

^a Fox and Edwards provide a more detailed discussion of the potential impacts of SCIX material on PCCS model predictions.⁴

^b Note that for DWPF-type glasses, T_L is defined as the spinel liquidus temperature, or the maximum temperature at which the molten glass and the spinel crystalline phase are at equilibrium.

^c See B. J. Riley et al., "International Round-Robin Study on Liquidus Temperature," *submitted for publication in International Journal of Applied Glass Science* (2011). Measurements of the standard glass, referred to as ARG-1, consistently fell within the reported T_L range of 1024-1046 °C for this composition.

^d The T_L data for the KT01-series glasses have been reported previously,⁴ but will be repeated here to provide a comprehensive summary.

Liquidus temperatures for the KT02-series glasses were not measured due to their unrealistically high TiO_2 concentrations. These compositions were selected to meet other objectives, as will be described in Section 4.2.1. Liquidus temperatures were not measured for the KT05 and KT09-series glasses since they were expected to form crystalline phases at or near the melt temperature. Liquidus temperatures were not measured for the KT08-series glasses since they contained uranium and thorium, and a T_L measurement capability for radioactive glasses is not currently available at SRNL.

The results of the T_L measurements for the KT01-series glasses are shown graphically in Figure 3-1. The predicted and measured T_L values for each KT01-series glass are also included in Table A-1 in Appendix A. A review of Figure 3-1 shows that seven of the KT01-series glasses had measured T_L values that fell within the 95% confidence intervals of the model predicted values. Note that crystals were present in the quenched version of glass KT01-HK; therefore, a T_L value could not be measured for this composition. The remaining four glasses had measured T_L values that were higher than the upper 95% confidence interval bound. Overall, the model under predicted the T_L for all of these glasses with elevated TiO_2 concentrations (target values of 8 wt % TiO_2), although the trends between the measured and model predicted data appeared to be consistent and several of the measured T_L values fell within the 95% confidence bands. One must keep in mind that these TiO_2 concentrations were well above the region of applicability defined for the current T_L model of 0-1.8549 wt % TiO_2 ; therefore, this prediction bias is not necessarily unexpected.⁸

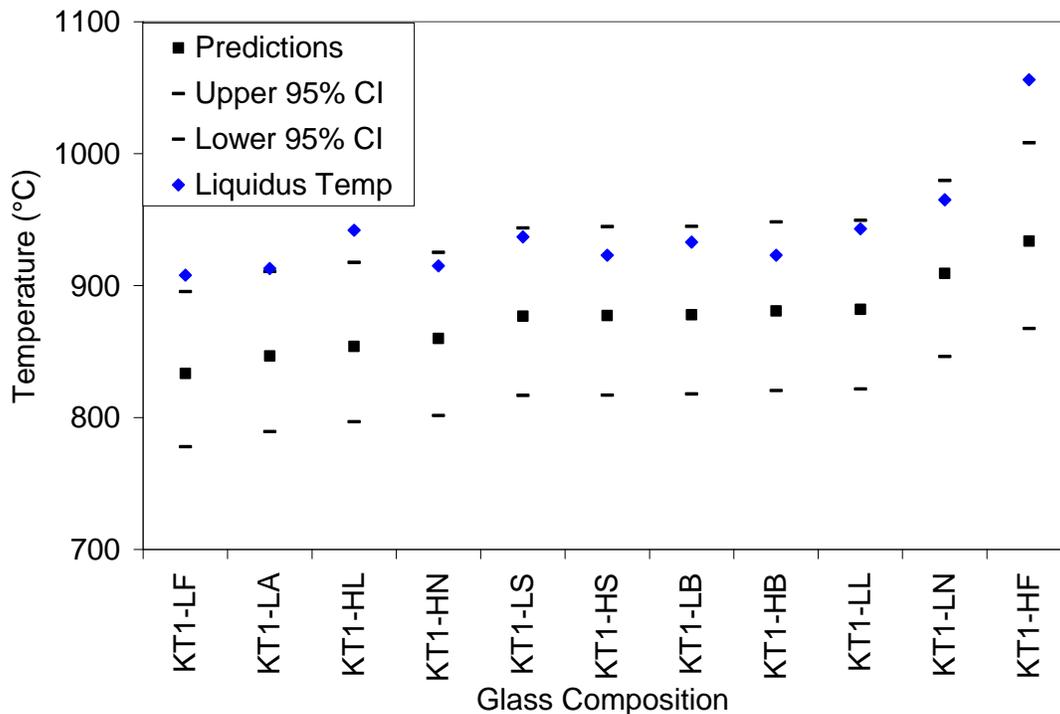


Figure 3-1. Liquidus Temperature Measurements for the KT01-Series Glasses.

The estimated T_L values for the KT03-series glasses are shown graphically in Figure 3-2. The predicted and estimated T_L values for each KT03-series glass are also included in Table A-2 in Appendix A. A review of Figure 3-2 shows that most of the estimated T_L values (between the temperature of the blue data point where no crystals were present and the temperature of the red

data point where crystallization had occurred) fall within the 95% confidence interval of the model predicted values. Composition KT03-HL, a high Li₂O concentration glass, has a T_L that is very close the upper 95% confidence interval bound for the predicted T_L. All of the KT03-series glasses had crystals present at or above the predicted T_L values, again indicating that the current model is under predicting the T_L of glasses with high TiO₂ concentrations (8 wt % TiO₂ for the KT03-series). Note that the T_L could not be estimated for compositions KT03-HK and KT03-MK since crystals were visible via optical microscopy in the quenched versions of these glasses.^a

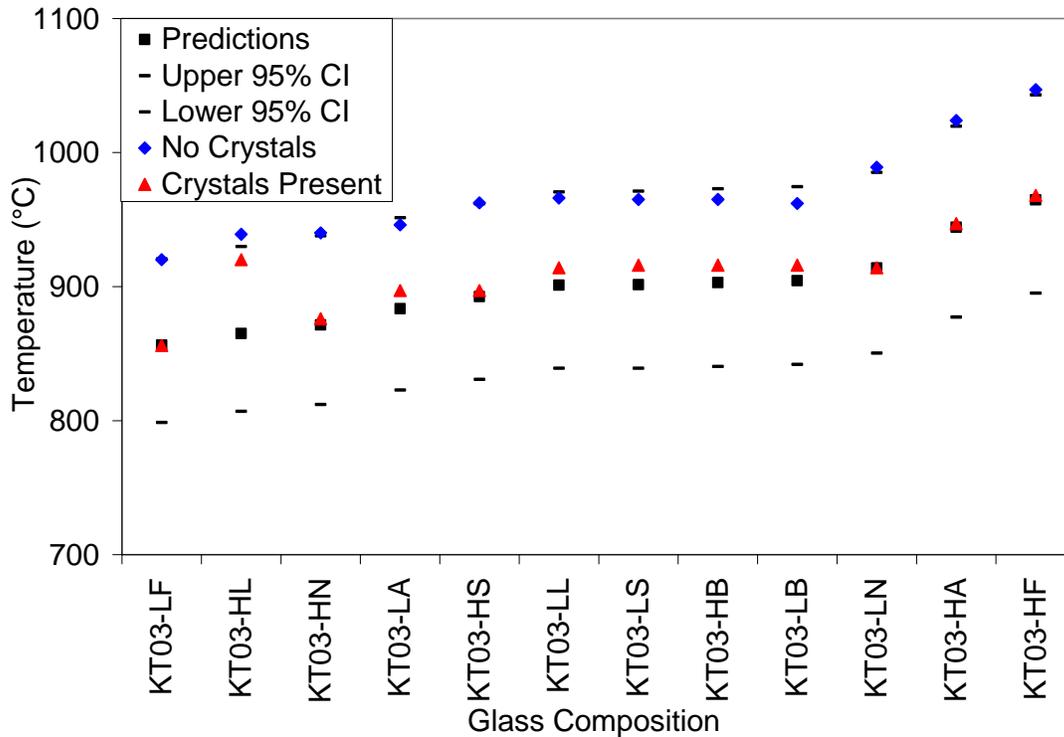


Figure 3-2. Liquidus Temperature Estimates for the KT03-Series Glasses.

The estimated T_L values for the KT04-series glasses are shown graphically in Figure 3-3. The predicted and estimated T_L values for each KT04-series glass are also included in Table A-2 in Appendix A. A review of Figure 3-3 and comparison with Figure 3-2 shows that the results are quite similar to those for the KT03-series glasses. Most of the estimated T_L values for the KT04-series glasses fall within the 95% confidence interval of the model predicted values, although all of the KT04-series glasses had crystals present at or above the predicted T_L values. These data continue to show a bias in the current model predicted T_L values for glasses with high TiO₂ concentrations (4-5 wt % TiO₂ for the KT04-series).

^a As will be discussed in Section 4.2.1, these glass compositions were selected to determine the impact of high potassium concentrations on titanium incorporation and are very unlikely for actual DWPF processing.

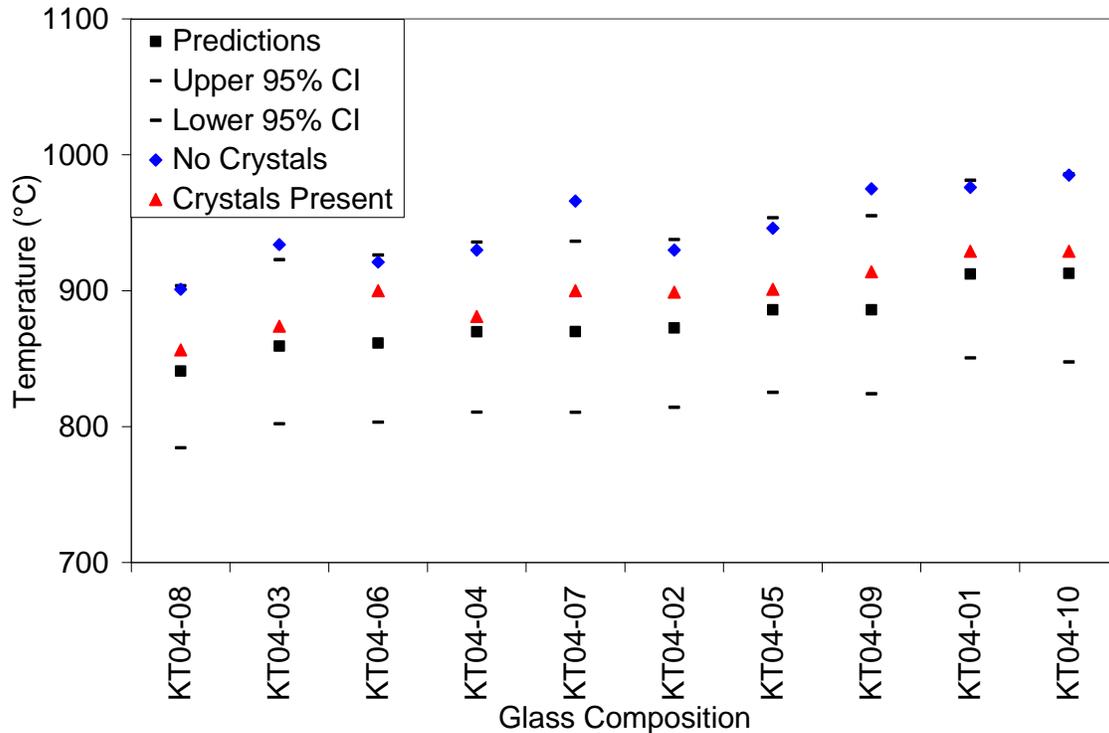


Figure 3-3. Liquidus Temperature Estimates for the KT04-Series Glasses.

The estimated T_L values for the KT06-series glasses are shown graphically in Figure 3-4. The predicted and estimated T_L values for each KT06-series glass are also included in Table A-2 in Appendix A. A review of Figure 3-4 shows that the estimated T_L values for most of the KT06-series glasses fall within the 95% confidence interval for the model predicted values. Compositions KT06-04, -13, and -16 had crystals present at or very close to the upper 95% confidence interval bound for the predicted T_L . This indicates that the current model under predicts the T_L for these three compositions. Composition KT06-12 was free of crystallization at a temperature of 20 °C above the predicted T_L , indicating that there may not be an issue with under prediction for this particular composition. All of the other KT06-series glasses had crystals present at or above the predicted T_L values, again indicating that the current model is under predicting the T_L of glasses with high TiO_2 concentrations (6 wt % TiO_2 for the KT06-series).

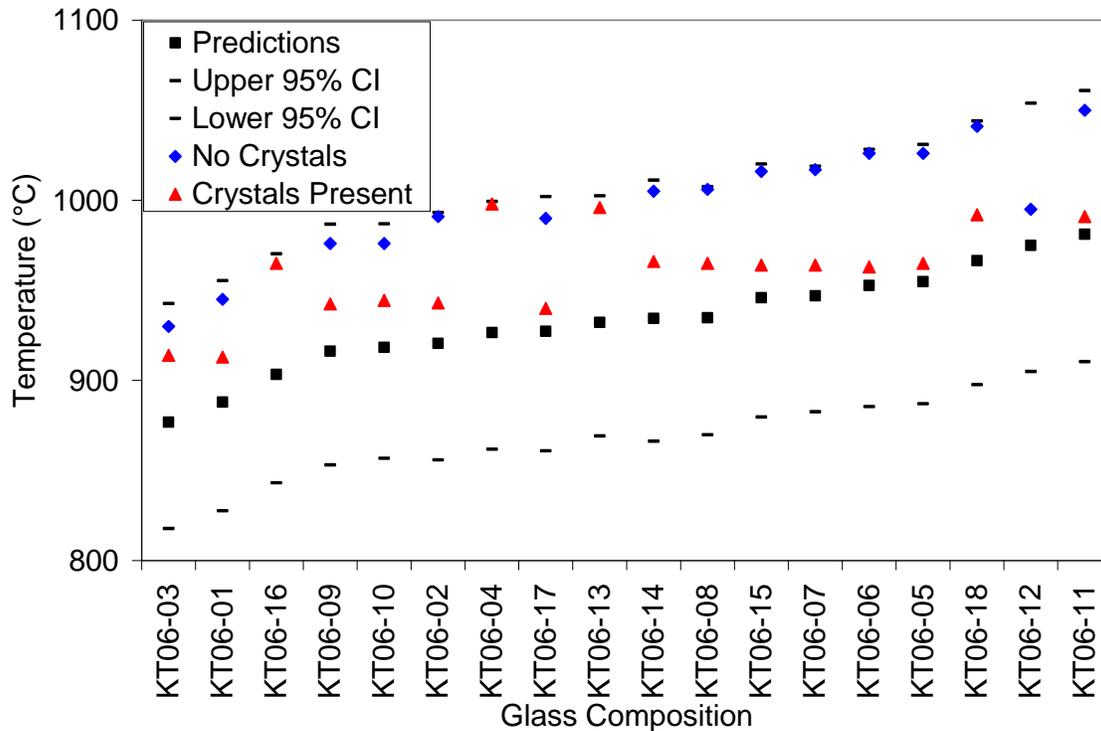


Figure 3-4. Liquidus Temperature Estimates for the KT06-Series Glasses.

The estimated T_L values for the KT07-series glasses are shown graphically in Figure 3-5. The predicted and estimated T_L values for each KT07-series glass are also included in Table A-2 in Appendix A. A review of Figure 3-5 shows that all of the glasses had crystals present at temperatures that were at or very close to the upper bound of the 95% confidence interval of the model predicted T_L value. A major difference between the KT07-series and the earlier KT-series glasses is the inclusion of noble metals in the KT07-series.^a At first glance, it may appear that the addition of noble metals to these glasses has increased their T_L values as compared to the earlier glasses that did not contain noble metals. However, previous work in developing Time-Temperature-Transformation (TTT) diagrams for SRS waste glass has shown a strong kinetic effect of noble metals, particularly RuO_2 , on the crystallization of spinels and acmite.^b The inclusion of noble metals does not change the liquidus temperature, but significantly reduces the time necessary for crystallization to occur in a given composition at a given temperature. Thus, the implication is that the heat treatment time of 24 hours used in the liquidus temperature estimates where noble metals were not present may not have been sufficient to allow crystallization to occur. When noble metals were included, the time necessary for crystallization was less than 24 hours, giving the results shown in Figure 3-5.^c

^a The KT07-series glasses used the same target compositions as the KT04-series glasses, except that sulfur and the noble metals Ag, Pd, Rh, and Ru were added to the KT07-series glasses.⁹

^b C. M. Jantzen and D. F. Bickford, TTT Diagrams of SRL 165 Waste Glasses, unpublished results.

^c As a further example, compare the data for composition KT04-10 in Figure 3-3 (no crystals present after 24 hours at 985 °C) with the data for composition KT07-10 in Figure 3-5 (spinel crystals present after 24 hours at 999 °C). The noble metals in composition KT07-10 may have reduced the time necessary for spinel crystallization in this composition to less than 24 hours in this temperature range. Heat treating KT04-10 at this temperature for a period longer than 24 hours may therefore lead to spinel crystallization.

Additional heat treatments were performed for glasses KT07-02, -03, -04, -06, -07, and -08 at higher temperatures to ensure that a crystal-free temperature could be identified for some of the KT07 compositions. As shown by the blue data points in Figure 3-5, the heat treatments at higher temperatures did produce crystal-free glasses for these compositions where noble metals are included. The estimates for these compositions indicate that the actual liquidus temperatures of these glasses may still fall below the current DWPF limit (without uncertainties applied) of 1050 °C. The results for all of the KT07-series glasses indicate that the measured ranges of the T_L values are well above the model predicted values for these glass compositions (4-5 wt % TiO_2 for the KT-07 series).

Overall, the result of these T_L estimates is the same as seen in the previous KT-series glasses: the model predicted T_L values are lower than the estimated T_L values (based on measured data) for the high TiO_2 concentration glasses. The amount of bias in the predicted values is likely to be larger than was apparent with the glasses that did not include noble metals, since the heat treatment time for the earlier series of glasses may have been too short.

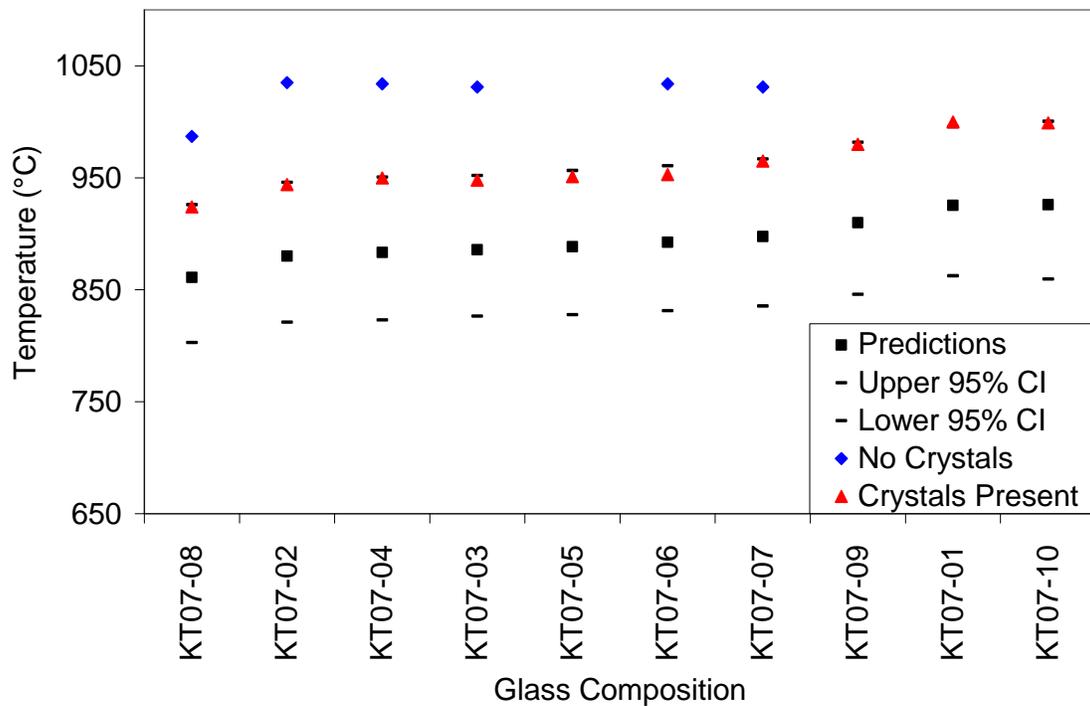


Figure 3-5. Liquidus Temperature Estimates for the KT07-Series Glasses.

The estimated T_L values for the KT10-series glasses are shown graphically in Figure 3-6. The predicted and estimated T_L values for each KT10-series glass are also included in Table A-2 in Appendix A. A review of Figure 3-6 shows that all of the glasses had crystals present at temperatures that were at or very close to the upper bound of the 95% confidence interval of the model predicted T_L value. The KT10-series glasses contained noble metals, and the results are very similar to those for the KT07-series glasses. Crystallization at higher temperatures was not determined since the data in Figure 3-6 were sufficient to show a continued trend of the current model predicting a T_L value below the actual value for high TiO_2 concentration glasses (6-7 wt % TiO_2 for the KT10-series).

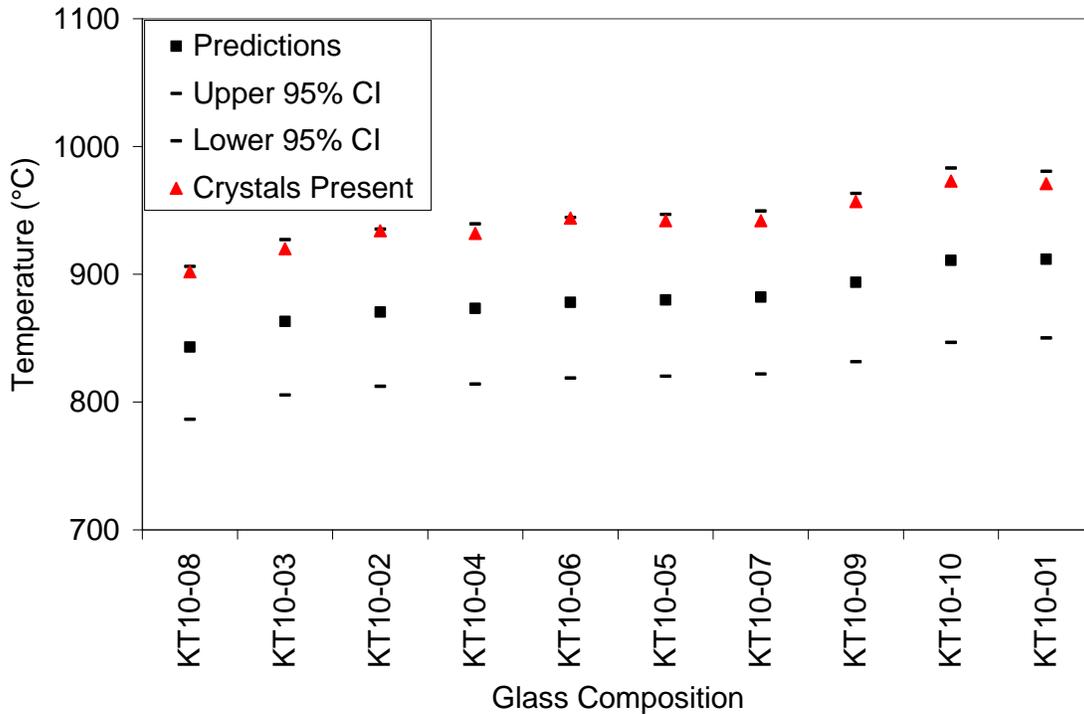


Figure 3-6. Liquidus Temperature Estimates for the KT10-Series Glasses.

In summary, the measured and estimated liquidus temperatures for the KT-series glasses demonstrate a prediction bias in the current T_L model for high TiO_2 concentration glasses. The current model predicted T_L values are lower than the measured or estimated values for almost all of the study glasses. The inclusion of noble metals indicates that the heat treatment times may need to be increased for future liquidus temperature measurements, although the time period used here did not impact the trend of the current model under predicting the measured T_L data. It is important to note that these TiO_2 concentrations are well above the region of applicability defined for the current T_L model of 0-1.8549 wt % TiO_2 ;⁸ therefore, the issues identified are not necessarily unexpected.

Observations of crystallization within all of the study glasses during the T_L evaluations via optical and scanning electron microscopy indicated that the primary crystalline phases forming were spinels, including $TiFe_2O_4$. The formation of spinels is consistent with the development of the current T_L model in that the model is designed to predict the spinel liquidus temperature from glass composition.³

As mentioned earlier, the measured T_L values for the KT01-series glasses (the only series where T_L values were measured rather than estimated) were under predicted by the current model, but the trend between the measured and the predicted values was consistent. In other words, there was a fairly consistent offset between the predicted and measured values, rather than random differences. This offset may indicate that the coefficients of the model can be refit in order to eliminate the prediction bias for glasses with high TiO_2 concentrations, while the mechanistic basis of the model remains valid. In fact, Brown et al. recommended that if compositions outside the composition space of the model development glasses become likely for DWPF processing then the model may have to be adjusted.⁸ Therefore, the path forward for the T_L model evaluation work will be to measure actual T_L values (rather than estimates) for the KT-series

glasses. These data will then allow for further evaluation to determine whether the coefficients of the current T_L model can be refit to better predict the T_L values of the high TiO_2 concentration glasses.

4.0 Summary of Studies of Potential Impacts of SCIX on DWPF Glass Formulation

4.1 Results of the Paper Study

Fox and Edwards performed a paper study evaluation using updated projections for sludge batch compositions and SCIX CST and MST addition rates.¹⁰ This paper study evaluated composition projections for Sludge Batches 8 through 17 with MST added during batch preparation and with CST added to either Tank 40 or Tank 42/51. Additions of CST to Tank 40 were made incrementally during processing, while additions of CST to Tank 42/51 were made in a single transfer. Two production rates were evaluated, along with the inclusion or exclusion of SWPF streams. The sludge compositions (a total of 120) were evaluated with an array of 1,144 candidate frit compositions using Nominal Stage Measurement Acceptability Region (MAR) assessments with the DWPF PCCS models.

This study found that, as a result of the updated composition projections,^a several viable options were predicted to be available for incorporation of the SCIX streams, with CST being sent to either Tank 40 or a sludge batch preparation tank. Transfer of the CST to a sludge batch preparation tank was the preferred option since it allowed more compositional flexibility for frit optimization while maintaining sufficient projected operating windows. The report identified several assumptions and limitations associated with the current PCCS models, and recommended that these be further evaluated. The experimental program was therefore developed to provide the data necessary to address many of these assumptions.

4.2 Results of the Experimental Studies

Ten series of glass compositions were selected and characterized in support of the SCIX program. Each series was labeled with the identifier KT. The results for each series of glasses have been documented in separate reports, and they will be reviewed and summarized here. Table 4-1 provides an overview of the objectives and outcomes for each series of glasses. These results will be reviewed in further detail in the following sections.

^a A similar study by Peeler and Edwards in 2007 determined that the periodic addition of CST to Tank 40 was not a viable option in terms of producing PCCS acceptable glass compositions.¹¹

Table 4-1. Summary of Studies for SCIX Impacts on DWPF Glass Formulation.

Study ID	Objectives	Outcomes	Reference
KT01	- Study impacts of individual oxides on incorporation of 8 wt % TiO ₂	- No crystallization of Ti-containing phases observed, regardless of whether they were quenched or subjected to the canister centerline cooled (CCC) heat treatment - No obvious effects of individual oxides - Durability was acceptable and generally predictable - Viscosity was acceptable and generally predictable - Liquidus temperatures higher than predicted	4
KT02	- Study impacts of individual oxides on incorporation of 12 wt % TiO ₂	- Ti-containing crystals formed in several compositions during the CCC heat treatment - Increased Na ₂ O and K ₂ O concentrations appeared to hinder the formation of these phases	4
KT03	- Study impacts of individual oxides on incorporation of 8 wt % TiO ₂ with 3 wt % Nb ₂ O ₅ and 2.5 wt % ZrO ₂	- No crystallization of Ti-containing phases observed, regardless of whether they were quenched or subjected to the CCC heat treatment - No obvious effects of individual oxides - Durability was acceptable and generally predictable - Viscosity was acceptable and generally predictable - Most estimated liquidus temperatures fell within the range of the current model predictions	4
KT04	- Study PCCS MAR acceptable glasses based on LWO projections of SB8 through SB17 with CST added to Tank 40, at the final SRAT batch (TiO ₂ 4.3-5.0 wt % in glass)	- All glasses remained amorphous regardless of whether they were quenched or subjected to the CCC heat treatment - Viscosity and durability were acceptable and predictable - Most estimated liquidus temperatures fell within the range of the current model predictions, although they were all greater than the predicted values	4
KT05	- Study the effect of Na ₂ O on glasses known to form crystals containing TiO ₂	- Ti-containing phases formed, although Na ₂ O had little, if any, impact - Recommended studying effects of Al ₂ O ₃ and K ₂ O	12
KT06	- Study PCCS MAR acceptable glasses with wide variation placed around the SB8 to SB17 composition region (TiO ₂ 6 wt % in glass)	- Ti-containing phases observed in some glasses after the CCC heat treatment - All durability values were acceptable, although some were not predictable (combination of high TiO ₂ , Fe ₂ O ₃ , and Al ₂ O ₃) - All viscosity values were acceptable, although some were not predictable (combination of high TiO ₂ and low Fe ₂ O ₃) - Most estimated liquidus temperatures fell within the range of the current model predictions	12

Table 4-1. Summary of Studies for SCIX Impacts on DWPF Glass Formulation. (continued)

Study ID	Objectives	Outcomes	Reference
KT07	- Similar to KT04, but with noble metals added	- All glasses remained amorphous regardless of whether they were quenched or subjected to the CCC heat treatment - Viscosity and durability were acceptable and predictable - Liquidus temperatures are not well predicted	9
KT08	- Similar to KT04, but with noble metals, thorium, and uranium added	- All but one of the glasses remained amorphous, regardless of whether they were quenched or subjected to the CCC heat treatment - Durability was acceptable and predictable - Viscosity was acceptable and generally predictable - No unexpected effects when uranium and thorium were included - Liquidus temperature not measured for radioactive glasses	13
KT09	- Study the effects of Al ₂ O ₃ and K ₂ O on glasses known to form crystals containing TiO ₂	- Increased Al ₂ O ₃ concentrations not successful in preventing crystallization of iron titanates - Increased K ₂ O concentrations successful in hindering crystallization of iron titanates in some of the glasses after the CCC heat treatment, although results were dependent upon composition	13
KT10	- Similar to KT04, but with noble metals added and with Nb ₂ O ₅ , TiO ₂ , and ZrO ₂ concentrations increased to 150% of projected maximums (TiO ₂ 6-7 wt % in glass)	- All glasses remained amorphous regardless of whether they were quenched or subjected to the CCC heat treatment - Durability was acceptable and generally predictable - Viscosity was acceptable and generally predictable - Liquidus temperatures are not well predicted	13

4.2.1 *KT01 through KT04-Series Glasses*

The KT01 and KT02-series of glasses were designed to allow for the identification of the influence of the concentrations of major components of the glass on the incorporation of TiO₂. The KT03-series of glasses was designed to allow for the identification of these influences when higher Nb₂O₅ and ZrO₂ concentrations are included along with TiO₂. The KT04-series of glasses was designed to investigate the properties and performance of glasses based on the best available projections of actual compositions to be processed at the DWPF (i.e., future sludge batches including the SCIX streams). The glasses were fabricated in the laboratory without the radioactive components. They were characterized using X-ray diffraction (XRD) to identify crystallization, inductively coupled plasma – atomic emission spectroscopy (ICP-AES) to verify chemical compositions, and the Product Consistency Test (PCT) to measure durability. The viscosity and liquidus temperature of several of the glasses were also measured.

The XRD results showed no titanium containing phases in the KT01-series glasses, regardless of whether they had been air quenched or slowly cooled using the CCC heat treatment. The targeted TiO₂ concentration had to be increased to 12 wt % in glass in the KT02-series before any compositional impacts on TiO₂ incorporation (e.g., the formation of titanium containing crystals) were apparent. Titanium containing crystalline phases formed in the CCC versions of all of the KT02 compositions except for the low Al₂O₃ concentration glass, the low Fe₂O₃ concentration glass, the high Na₂O concentration glass, and the high K₂O concentration glass. Note however that the 12 wt % TiO₂ concentrations in these glasses are unrealistic for DWPF processing with the SCIX streams and material from SWPF based on current projections. Spinel was identified in some of the KT03 glasses after the CCC heat treatment. The spinel did not adversely impact the durability of the glasses. The KT04-series glasses were amorphous regardless of whether they were quenched or subjected to the CCC heat treatment.

No issues were found upon review of the chemical composition measurements, nor were any issues found upon review of the PCT measurements. All of the glasses studied were considerably more durable than the benchmark Environmental Assessment (EA) glass. The measured PCT responses were compared with the predicted values from the current DWPF durability model. One of the KT01-series and two of the KT03-series glasses had measured PCT responses that were outside the lower bound of the durability model. All three of these glasses had intentionally high K₂O concentrations (to evaluate the impact of K₂O on TiO₂ incorporation), which may indicate a lack of applicability for the durability model in this composition region. However, the lack of applicability in this region is likely of little practical importance since K₂O concentrations of this magnitude are unrealistic for actual compositions to be processed at the DWPF. All of the KT04 glasses had durabilities that were predictable regardless of whether they were quenched or subjected to the CCC heat treatment.

All but two of the KT01, KT03, and KT04-series glasses had measured viscosities that were predictable using the current DWPF viscosity model. The viscosities of two of the high K₂O concentration glasses, KT01-HK and KT03-MK, fell above the upper confidence intervals for the model predictions. These glasses have K₂O concentrations that are above the DWPF viscosity model development range for K₂O.¹⁴ Another high K₂O concentration glass, KT03-HK, had a measured viscosity that was well predicted by the current DWPF model. While these results indicate a lack of applicability for the DWPF viscosity model for increased K₂O concentrations, it is again important to note that these K₂O concentrations are unrealistic for actual DWPF processing. Overall, the measured viscosity values of the KT01, KT03, and KT04-series glasses were well predicted by the current DWPF viscosity model. The results of the T_L measurements

for the KT01 glasses and the T_L estimates for the KT03 and KT04 glasses were discussed earlier in Section 3.0.

4.2.2 KT05 and KT06-Series Glasses

The KT05-series glasses were designed, fabricated, and characterized to further study HLW glass compositions where iron titanate crystals had been found to form. The intent was to better understand the mechanisms and compositions that favored the formation of crystals containing titanium. Formation of these crystalline phases was confirmed. Increased Na_2O concentrations had little, if any, impact on reducing the propensity for the formation of the iron titanate crystalline phases. Other physical properties of these glasses were not measured since the intent was to focus on crystallization. It was recommended that the baseline compositions in the KT05-series be further investigated to identify the potential influence of increased K_2O and Al_2O_3 concentrations on hindering the formation of titanium-containing crystalline phases. As will be shown below, these recommendations were addressed in the design of the KT09-series glasses.

The KT06-series glasses were designed, fabricated, and characterized to further study HLW glass compositions that, while broader than the current projections for DWPF feeds with SCIX material, are potential candidates for future processing (i.e., the compositions are acceptable for processing by PCCS with the exception of the current TiO_2 concentration constraint). The measured chemical compositions of these glasses were consistent with the targeted values. The PCT responses of all the glasses were acceptable relative to the EA benchmark. Minor spinel crystallization was identified in some of the CCC glasses, although this crystallization did not impact chemical durability. Estimates of the liquidus temperatures of the KT06-series glasses were discussed earlier in Section 3.0.

Several of the KT06-series compositions had durability values that were acceptable but were not well predicted by the current PCCS models. A similar lack of fit for model predicted durabilities for glasses with more positive ΔG_p values has been seen in previous studies of DWPF-type glasses. It was shown that for the high TiO_2 concentration glasses (6 wt % TiO_2) in the KT06 study, relatively high Fe_2O_3 concentrations combined with relatively high Al_2O_3 concentrations led to unpredictable durabilities. The current durability models will have to be further evaluated should compositions in this region become necessary for DWPF processing.

Several of the KT06-series glasses also had measured viscosity values that were not well predicted by the current model. A statistical partitioning routine showed that the measured viscosities became unpredictable by the current model when the Fe_2O_3 concentration in the glasses was less than about 8.2 wt % at the elevated TiO_2 concentrations. The current viscosity model will have to be further evaluated should compositions in this region become necessary for DWPF processing. Note however that the KT06-series glasses were intentionally designed to cover compositional regions that are outside those currently projected for DWPF processing.

4.2.3 KT07-Series Glasses

The KT07-series glasses were designed to evaluate any potential impacts of noble metals on the properties and performance of the glasses. The glasses characterized in the previous KT-series studies did not include noble metals since they are not typically tracked in sludge batch composition projections. However, noble metals can act as nucleation sites in glass melts, leading to enhanced crystallization. This crystallization can potentially influence the properties and performance of the glass, such as chemical durability, viscosity, and liquidus temperature. A set of glass compositions developed earlier in the SCIX study, the KT04-series, was used as the basis for the KT07-series glasses. The noble metals Ag, Pd, Rh, and Ru were added. The

concentrations of these metals were obtained from measurements of Sludge Batch 6, which was considered to contain a high concentration of noble metals.¹⁵

After fabrication, the glasses were characterized to determine their crystalline content, chemical composition, durability, and viscosity. Liquidus temperature estimates were also completed, as described in Section 3.0. All of the KT07-series glasses, both quenched and CCC, were found to be amorphous by XRD. Chemical composition measurements showed that all of the glasses met the targeted compositions. The PCT results showed that all of the glasses, both quenched and CCC, had chemical durabilities that were far better than that of the EA benchmark glass. The measured PCT responses were well predicted by the current DWPF PCCS durability models. The measured viscosity values for each KT07-series glass were acceptable for DWPF processing and were well predicted by the current PCCS model.

Overall, the results indicate that the inclusion of relatively high concentrations of noble metals (in terms of expected values for a DWPF sludge batch) had no significant impact on the properties and performance of these glass compositions other than the liquidus temperature estimates. The lack of crystallization in the KT07-series glasses after fabrication and after the CCC, their measured PCT responses, and their measured viscosity values are very consistent with the KT04-series glasses, which did not contain noble metals. As discussed in Section 3.0, the noble metals led to faster crystallization at a given temperature. The trend of the model predicted T_L values being lower than the measured ranges for high TiO_2 concentration glasses continued.

4.2.4 KT08 through KT10-Series Glasses:

The KT08-series of glasses was designed to evaluate any impacts of the inclusion of uranium and thorium in high TiO_2 concentration glasses. The KT09-series of glasses was designed to study the effect of increasing Al_2O_3 and K_2O concentrations on the propensity for crystallization of titanium containing phases, based on recommendations from the KT05 study. The KT10-series of compositions was designed to evaluate any impacts of the SCIX components at concentrations significantly higher than currently projected. The glasses were fabricated in the laboratory and characterized using XRD to identify crystallization, ICP-AES to verify chemical compositions, and the PCT to measure durability. The viscosity and liquidus temperature of several of the glasses were also measured.

All but one of the KT08-series glasses were found to be amorphous by XRD. One of the CCC glasses contained a small amount of trevorite, which had no practical impact on the durability of the glass. The measured PCT responses of the KT08-series glasses were well predicted by the DWPF models, and the viscosities of the KT08-series glasses were generally well predicted by the DWPF model.

The KT09-series glasses were fabricated, subjected to the CCC heat treatment, and characterized via XRD only, since the type of crystallization formed, if any, was the characteristic of interest for these compositions. Increased Al_2O_3 concentrations were not successful in preventing the formation of iron titanate crystals in the KT09-series glasses. Increased K_2O concentrations were successful in hindering the formation of iron titanates in some of the glasses after the CCC heat treatment. However, this result did not apply to all of the CCC versions of the glasses, indicating a compositional dependence of this effect. In addition, high concentrations of K_2O have been shown to be detrimental to some glass properties other than crystallization (see the results for the KT01 and KT03 series in Section 4.2.1). The usefulness of increased K_2O concentrations in preventing the formation of iron titanates may therefore be limited.

All of the KT10-series glasses were XRD amorphous, regardless of whether they were quenched or subjected to the CCC heat treatment. Chemical composition measurements showed that the glasses met the targeted concentrations for each oxide. In general, the measured PCT responses of the KT10-series glasses were well predicted by the DWPF models. The measured, normalized release values for silicon for some of the glasses fell above the 95% confidence interval for the predicted values; however, the PCT responses for these glasses remain considerably lower than that of the benchmark EA glass. The viscosities of the KT10-series glasses were generally well predicted by the DWPF model. Liquidus temperature estimates for the KT10-series glasses were discussed earlier in Section 3.0.

5.0 Recommendations and Path Forward

This report summarizes a large amount of experimental work completed to identify the potential impacts of material from SCIX on glass formulation at the DWPF. The results indicate no significant issues with the predicted values of chemical durability and viscosity using the current PCCS models when the SCIX components are added to projected DWPF glass compositions. No modifications to the viscosity and durability models appear to be necessary at this time in order to incorporate the SCIX streams at DWPF. It is recommended that SRNL continue to verify the durability and viscosity models as the projected compositions for DWPF processing evolve. It is also recommended that the data generated thus far be reviewed and a determination be made as to how best to extend the validation ranges of the durability and viscosity models.

The liquidus temperatures for the experimental glasses were also reported and discussed in this report. The results show that the measured or estimated (based on measured data) liquidus temperature values for the glasses with SCIX components added are consistently higher than those predicted by the current model. Therefore, the PCCS liquidus temperature model will need to be modified in order to incorporate the SCIX streams at DWPF. It is recommended that SRNL carry out full measurements of the liquidus temperatures for those KT-series glasses where estimates have been made. These data should then be used to support an evaluation of whether a refitting of the liquidus temperature model coefficients will be sufficient to correctly predict the liquidus temperature of glasses containing the SCIX components (particularly higher TiO_2 concentrations), or whether additional modifications to the model are required. All further liquidus temperature experiments should include noble metals in the glass, and longer heat treatment periods should be considered.

While there are prediction issues with the current liquidus temperature model, they are not at this time expected to hamper the incorporation of SCIX streams at DWPF. The estimated liquidus temperatures, while higher than the model predicted values, remain below the current DWPF limit of 1050 °C for most of the study glasses. Note that the properties and performance of the glasses in this study are highly dependent on glass composition. Therefore, should significant changes be made to the projected compositions or processing rates for SCIX or DWPF, many of the assessments and experiments may have to be revisited.

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Appendix A. Measured and Estimated T_L Data for the KT-Series Glasses.

Table A-1. Model Predicted and Measured Liquidus Temperatures for the KT01-Series Glasses.

Glass ID	Model Predicted T_L (°C)	Model Prediction Lower Limit (°C)	Model Prediction Upper Limit (°C)	Measured T_L (°C)	Predictable?
KT01-HB	881	820	948	923 +/- 5	Yes
KT01-HF	934	868	1008	1056 +/- 5	No
KT01-HL	854	797	918	942 +/- 10	No
KT01-HN	860	801	925	915 +/- 10	Yes
KT01-HS	877	817	945	923 +/- 5	Yes
KT01-LA	847	789	911	913 +/- 5	No
KT01-LB	878	818	945	933 +/- 5	Yes
KT01-LF	833	778	895	908 +/- 5	No
KT01-LL	882	822	949	943 +/- 5	Yes
KT01-LN	909	846	980	965 +/- 5	Yes
KT01-LS	877	817	944	937 +/- 5	Yes

Table A-2. Model Predicted and Estimated Liquidus Temperature Data for Several of the KT-Series Glasses.

Glass ID	Model Predicted T_L (°C)	Model Prediction Lower Limit (°C)	Model Prediction Upper Limit (°C)	Estimated T_L (°C)
KT03-HA	944	877	1020	947 - 1024
KT03-HB	903	840	973	916 - 965
KT03-HF	965	895	1043	968 - 1047
KT03-HL	865	807	930	920 - 939
KT03-HN	871	812	938	876 - 940
KT03-HS	893	831	962	897 - 963
KT03-LA	884	823	951	897 - 946
KT03-LB	904	842	974	916 - 962
KT03-LF	856	799	921	856 - 920
KT03-LL	901	839	971	914 - 966
KT03-LN	914	850	985	914 - 989
KT03-LS	901	839	971	916 - 965
KT04-01	912	851	981	929 - 976
KT04-02	873	814	938	899 - 930
KT04-03	859	802	923	874 - 934
KT04-04	870	811	936	881 - 930
KT04-05	886	825	954	901 - 946
KT04-06	861	803	926	900 - 921
KT04-07	870	811	936	900 - 966
KT04-08	841	784	904	856.5 - 901
KT04-09	886	824	955	914 - 975
KT04-10	913	848	986	929 - 985
KT06-01	888	828	955	913 - 945
KT06-02	921	856	993	943 - 991
KT06-03	877	818	943	914 - 930
KT06-04	927	862	999	> 998
KT06-05	955	887	1031	965 - 1026
KT06-06	953	885	1028	963 - 1026
KT06-07	947	883	1019	964 - 1017

Table A-2. Model Predicted and Estimated Liquidus Temperature Data for Several of the KT-Series Glasses. (continued)

Glass ID	Model Predicted T_L (°C)	Model Prediction Lower Limit (°C)	Model Prediction Upper Limit (°C)	Estimated T_L (°C)
KT06-08	935	870	1008	965 - 1006
KT06-09	916	853	987	942.5 - 976
KT06-10	918	857	987	944.5 - 976
KT06-11	981	910	1061	991 - 1050
KT06-12	975	905	1054	< 995
KT06-13	932	869	1002	> 996
KT06-14	934	866	1011	966 - 1005
KT06-15	946	880	1020	964 - 1016
KT06-16	903	843	970	> 965
KT06-17	927	861	1002	940 - 990
KT06-18	967	898	1044	992 - 1041
KT07-01	925	863	996	> 1000
KT07-02	880	821	946	944 - 1035
KT07-03	886	827	952	948 - 1031
KT07-04	883	823	951	950 - 1034
KT07-05	889	828	957	> 951
KT07-06	893	831	961	953 - 1034
KT07-07	898	836	967	965 - 1031
KT07-08	861	803	926	924 - 987
KT07-09	910	846	982	> 980
KT07-10	926	860	1001	> 999
KT10-01	912	850	981	> 971
KT10-02	870	812	935	> 934
KT10-03	863	806	927	> 920
KT10-04	873	814	939	> 932
KT10-05	880	820	947	> 942
KT10-06	878	819	944	> 944
KT10-07	882	822	950	> 942
KT10-08	843	786	906	> 902
KT10-09	894	831	963	> 957
KT10-10	911	847	983	> 973

Distribution:

J. W. Amoroso, 999-W
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A. L. Billings, 999-W
J. M. Bricker, 704-27S
M. A. Broome, 704-29S
C. L. Crawford, 773-42A
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T. B. Edwards, 999-W
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S. D. Fink, 773-A
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B. A. Hamm, 766-H
C. C. Herman, 999-W
D. T. Herman, 735-11A
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P. R. Jackson, 703-46A
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S. L. Marra, 773-A
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D. K. Peeler, 999-W
F. M. Pennebaker, 773-42A
J. W. Ray, 704-S
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H. B. Shah, 766-H
D. C. Sherburne, 704-S
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K. H. Subramanian, 766-H
J. P. Vaughan, 773-41A