RPP-RPT-42649, Rev. 0

High-Level Waste Glass Formulation Model Sensitivity Study 2009 Glass Formulation Model versus 1996 Glass Formulation Model

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Richland, WA 99352
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Abstract: This document presents the differences between two HLW glass formulation models (GFM): the 1996 GFM and the 2009 GFM. A glass formulation model is a collection of glass property correlations and associated limits, as well as model validity and solubility constraints; it uses the pretreated HLW feed composition to predict the amount and composition of glass forming additives necessary to produce acceptable HLW glass. The 2009 GFM presented in this report was constructed as a nonlinear optimization calculation based on updated glass property data and solubility limits described in PNNL-18501 (2009). Key mission drivers such as the total mass of HLW glass and waste oxide loading are compared between the two glass formulation models. In addition, a sensitivity study was performed within the 2009 GFM to determine the effect of relaxing various constraints on the predicted mass of the HLW glass.

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EXECUTIVE SUMMARY

INTRODUCTION

The Hanford Tank Waste Operations Simulator (HTWOS) is a dynamic flowsheet and mass balance model that is an essential component of the mission planning process. HTWOS models the retrieval, transfer and processing of Hanford's tank waste. A main component of HTWOS is the high-level waste (HLW) treatment plant model and the central component of the HLW treatment plant model is the HLW glass formulation model.

A glass formulation model (GFM) is a collection of empirical property correlations and their associated limits and a set of model validity and solubility limits. Given a pretreated HLW feed, the glass formulation model can predict the amount and the composition of the resulting HLW glass. This information assists in predicting mission duration and long term disposal requirements. HTWOS currently uses a glass formulation model based mostly on 1996-era glass data, herein called the 1996 GFM.

Since 1996, large amounts of glass performance and processing data have been collected. This provided the opportunity to expand the range of the validity of the glass formulation model. Also, a clearer understanding of the solubility of the HLW glass components left some of the older solubility constraints in need of updating. In late 2009, PNNL issued an updated glass formulation model (herein, called the 2009 GFM) that incorporated these improvements.

This report compares the composition and mass of the HLW glass predicted by the 2009 GFM with the predictions from the 1996 GFM. In addition, a sensitivity study was performed within the 2009 GFM to determine the effect of relaxing various constraints on the predicted mass of the HLW glass.

RESULTS AND CONCLUSIONS

The two HLW glass models predict waste glass masses that are very similar (0.52% difference). The 1996 GFM predicts a waste glass mass of 46,063 metric tons and a 30.9% waste oxide loading (WOL). The 2009 GFM predicts a slightly larger glass mass at 46,303 metric tons with a 30.5% WOL.

In order of decreasing importance, the top five glass drivers for each model are:

- 2009 GFM: SO_3, nepheline discriminator, $T_{1\%}$-sp, Bi_2O_3, Na_2O
- 1996 GFM: SO_3, Al_2O_3, T_L-sp, Na_2O, T_L-zircon

SO_3 is the primary glass driver in both models. In the 1996 GFM, the Al_2O_3 validity limit is the second largest glass driver. The 2009 model relaxes the Al_2O_3 constraint and, as a result, the nepheline discriminator replaces Al_2O_3 as the second major glass driver (note that the nepheline discriminator is a function of the Al_2O_3 concentration, so Al_2O_3 is still important). The other noticeable difference is the appearance of the Bi_2O_3 model validity constraint as one of the top five glass drivers in the 2009 GFM.

HTWOS currently shows only 1.7% of the total SO_4 waste ending up in HLW glass (in the form of SO_3), with the majority of the balance going to low-activity waste glass. Both the 1996 GFM and the 2009 GFM model predict that SO_3 solubility constraint is the primary glass driver. There is a significant amount of uncertainty surrounding the sulfate partitioning assumptions currently used for system planning and modeling purposes. Because of SO_3's role as the primary glass driver, it is worth reexamining sulfate partitioning. Small decreases or increases in the amount of SO_4 reporting to the HLW melters will have dramatic effects on waste oxide loading and the final HLW glass mass. For example, SO_3 no longer plays a role as a glass driver when the amount of sulfate reporting to HLW is cut in half. The waste oxide loading increases from 30.5% to 36% and the total mass of glass decreases by 13% in that case. Despite these improvements, other constraints become more prominent glass drivers as SO_3's role is diminished, particularly nepheline, Bi_2O_3, F- and P_2O_5.

The 2009 GFM reduces the amount of glass that is limited by model validity constraints. This improvement is offset by the addition of new constraints, F- mass fraction, $X_{CaO} \cdot X_{P2O5}$, Bi_2O_3 mass fraction, and UO_3 mass fraction, which did not appear in the 1996 GFM. The combined effect of these two trends is the nearly static predicted average waste oxide loading between the 1996 and the 2009 GFM.

In the 2009 GFM, Na_2O, P_2O_5, Bi_2O_3, SO_3 and the nepheline discriminator were identified as the constraints that were most likely to be relaxed, given additional glass formulation work, and to provide a significant decrease in predicted waste glass mass. Of these constraints, the effect of SO_3 on the predicted glass mass was most significant. Relaxing the SO_3 solubility constraint to 1.0% by mass from 0.5% led to a 14.4% decrease in predicted waste glass mass. Even more conservative changes in the SO_3 constraint resulted in a 5.7% - 11.9% reduction in predicted waste glass mass. However, this behavior and the observation that SO_3 is the primary glass driver might change if the sulfate partitioning assumptions change (i.e., this could be an artifact of the sulfate partitioning assumptions).

The effect of the nepheline discriminator on the waste oxide loading was significantly less than that of the SO_3 constraint. Lowering the nepheline constraint to 0.45 showed a 2.6% decrease in predicted glass mass. Lowering the nepheline constraint to a more moderate value of 0.57 showed a similar decrease of 2.3% in predicted waste glass mass.

The Bi_2O_3, Na_2O and P_2O_5 constraints have an even smaller effect on the predicted waste glass mass. Relaxing the Bi_2O_3 constraint can lead to a 1.5% decrease in predicted waste glass mass, while relaxing either the Na_2O or P_2O_5 constraints results in less than a 1% reduction in predicted waste glass mass.

Large improvements in predicted HLW glass mass will require relaxing multiple constraints or possibly a drastic change in glass formulation, with the possible exception of SO_3 which, as already stated, may be an artifact of partitioning assumptions. Relaxing multiple constraints together has a greater effect than the sum of relaxing each constraint individually. For this report, only a few runs were performed where multiple constraints were relaxed. Two runs were performed where all five constraints were relaxed, resulting in a 23.0% and 16.7% reduction in predicted glass mass; the first run used the most relaxed values for all five constraints, while the second run used the most relaxed values for four of the constraints and a more conservative value of 0.7% for SO_3.

The overall results suggest that it would be worthwhile to investigate relaxing the SO_3 and the nepheline discriminator constraints. Although the Bi_2O_3, Na_2O and P_2O_5 constraints have less effect on the predicted waste oxide loading, relaxing them in conjunction with the nepheline discriminator or the SO_3 constraint will provide an additional decrease in predicted glass mass that is large enough to warrant an attempt to relax them. If the $T_{1\%}$ - spinel constraint was altered, it is likely that the empirical property correlation itself, as opposed to the property limit, would be changed, or the $T_{1\%}$-spinel constraint would be outright replaced with a different property constraint. For this reason, the effect of varying the $T_{1\%}$ - spinel constraint was not examined in this study. The $T_{1\%}$ - spinel constraint does limit the waste oxide loading in 13.5% of the waste glass, so any change that makes it more permissive could yield noticeable improvements in waste oxide loading.

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ABBREVIATIONS AND ACRONYMS

GFM	Glass Formulation Model
HLW	High Level Waste
HTWOS	Hanford Tank Waste Operations Simulator
PCT	Product Consistency Test
PNNL	Pacific Northwest National Laboratory
WTP	Waste Treatment Plant
WOL	Waste Oxide Loading

1.0 OBJECTIVE

An essential tool in Hanford's system planning processes is the dynamic flowsheet and mass balance model, the Hanford Tank Waste Operations Simulator (HTWOS). HTWOS models the disposal, retrieval, staging and treatment of Hanford's tank waste. HTWOS is essential for predicting mission duration and for evaluating the effectiveness of proposed treatment strategies. The waste treatment mission can be no shorter than the time required for treating the HLW fraction of the tank waste. Since the treatment method is vitrification, it is important to be able to project the quantity of HLW glass as a function of pretreated waste composition. A core piece of the HTWOS model is the HLW treatment plant model and a central part of the HLW treatment model is the HLW glass formulation model.

A glass formulation model (GFM) is a collection of glass property correlations and associated limits, as well as model validity and solubility constraints. The model uses the composition of the pretreated waste feed to predict the mass of the resulting vitrified HLW glass and the required glass forming additives. HTWOS currently uses a glass formulation model that is based on WHC-SD-WM-TI-768 and PNNL-11790. Two variants of the HTWOS model exist: the "Default Glass Properties Model" and the "Relaxed Glass Properties Model." The latter is the current baseline model for system planning purposes; it resulted from additional glass formulation research which followed the 1996 PNNL report but preceded the more significant changes that produced the 2009 model (details of the three constraints that were relaxed are documented in ORP-11242 Rev.4). This report uses the "Relaxed Glass Properties Model" and refers to it as the "1996 GFM."

Since 1996, large amounts of glass property data have been collected, directly or indirectly in support of the Waste Treatment and Immobilization Plant and lifecycle mission planning. This provided the opportunity to expand the range of glass compositions for which the glass property models are valid and a clearer understanding of the solubility of the waste glass constituents allowed the solubility constraints from the 1996 GFM to be replaced with more accurate limits. Details of the updated glass property models, which incorporate both the increased range of glass property data and the more accurate solubility limits, are documented in PNNL-18501, *Glass Property Data and Models for Estimating High-Level Waste Glass Volume*, prepared by Vienna, et al. In this study, this new glass model is referred to as the "2009 GFM."

Formulation of the glass requires determining the proper amounts of glass forming additives to be added to the pretreated HLW waste so that the resulting glass satisfies the various constraints imposed by the glass formulation model. Both the HTWOS model and this paper approach this as a constrained, non-linear programming problem, with the goal being to minimize the mass of the glass forming additives.

The objective of this report is to perform a sensitivity study comparing the old HLW glass formulation model (described in WHC-SD-WM-TI-768 Rev 0 (1996) and PNNL-11790 (1999) applying the relaxed limits described in ORP-11242 Rev.4) against the new HLW glass formulation model (described in PNNL-18501 (2009)). This report will also look at the effects of relaxing various constraints within the 2009 HLW glass formulation model.

2.0 SUMMARY OF RESULTS AND CONCLUSION

The two HLW glass models predict waste glass masses that are very similar (0.52% difference). The 1996 GFM model predicts a waste glass mass of 46,063 metric tons and a 30.9% WOL. The 2009 GFM predicts a slightly larger glass mass at 46,303 metric tons with a 30.5% waste oxide loading.

SO_3 is the primary glass driver in both models. In the 1996 GFM the Al_2O_3 limit is the second largest glass driver. The 2009 model relaxes the Al_2O_3 constraint and, as a result, the nepheline discriminator replaces Al_2O_3 as the second major glass driver (note that the nepheline discriminator is a function of the Al_2O_3 concentration, so Al_2O_3 is still important). The other noticeable difference is the appearance of the Bi_2O_3 model validity constraint as one of the top five glass drivers in the 2009 GFM.

In order of decreasing importance, the top five glass drivers for each model are:

- 2009 GFM: SO_3, nepheline discriminator, $T_{1\%}$-sp, Bi_2O_3, Na_2O
- 1996 GFM: SO_3, Al_2O_3, T_L-sp, Na_2O, T_L-zircon

Although only 1.7% of the waste SO_4 ends up in the HLW glass, both the 1996 GFM and 2009 GFM model predict that SO_3 is the primary glass driver. However, due to the uncertainties surrounding the sulfate partitioning assumptions currently used for system planning and modeling purposes, it would be worthwhile to reexamine sulfate partitioning. Even small errors in these partitioning assumptions could result in significant errors in predicted HLW glass mass.

The 2009 GFM reduces the amount of glass that is limited by model validity constraints. This improvement is offset by the addition of new constraints, F^- mass fraction, $X_{CaO} \cdot X_{P2O5}$, Bi_2O_3 mass fraction and UO_3 mass fraction, which predict a decreased WOL on a batch-by-batch basis and did not appear in the 1996 GFM. The combined effect of these two trends is the nearly static predicted average waste oxide loading between the 1996 and the 2009 GFMs.

In the 2009 GFM, Na_2O, P_2O_5, Bi_2O_3, SO_3 and the nepheline discriminator were identified as the constraints that were most likely to be relaxed, given additional glass formulation work, and to provide a significant decrease in predicted waste glass mass. Of these constraints, the effect of SO_3 on the predicted glass mass was most significant. Relaxing the SO_3 solubility constraint to 1.0% by mass from 0.5% led to a 14.4% decrease in predicted waste glass mass. Even more conservative changes in the SO_3 constraint resulted in a 5.7% - 11.9% reduction in predicted waste glass mass.

The effect of the nepheline discriminator on the waste oxide loading was significantly less than that of the SO_3 constraint. Lowering the nepheline constraint to 0.45 showed a 2.6% decrease in predicted glass mass. Lowering the nepheline constraint to a more moderate value of 0.57 showed a similar decrease of 2.3% in predicted waste glass mass.

The Bi_2O_3, Na_2O and P_2O_5 constraints have an even smaller effect on the predicted waste glass mass. Relaxing the Bi_2O_3 constraint from 3.2% to 6.7% leads to a 1.5% decrease in predicted waste glass mass, while relaxing either the Na_2O or P_2O_5 constraints results in less than a 1% reduction in predicted waste glass mass.

Relaxing multiple constraints together has a greater effect than the sum of relaxing each constraint individually. For this report, only a few runs were performed where multiple constraints were relaxed. The study is far from exhaustive in this regard; however, the results are promising. Two runs were performed in which all five constraints were relaxed; this resulted in a 23.0% and 16.7% reduction in predicted glass mass.

The overall results suggest that it would be worthwhile to investigate relaxing the SO_3 and the nepheline discriminator constraints. Although the Bi_2O_3, Na_2O and P_2O_5 constraints have less effect on the predicted waste oxide loading, relaxing them in conjunction with the nepheline discriminator or the SO_3 constraint will provide an additional decrease in predicted glass mass that is large enough to warrant an attempt to relax them. The effect of varying the $T_{1\%}$ - spinel constraint was not examined in this study, but because it limits the waste oxide loading in 13.5% of the waste glass, any change that made the constraint more permissive could yield noticeable improvements in waste oxide loading.

3.0 INTRODUCTION/BACKGROUND

3.1 GENERAL OVERVIEW

The final waste glass produced by the HLW Vitrification Facility must meet certain criteria to be considered acceptable glass. For the purposes of this report, an acceptable glass is one that meets specific composition and property constraints. Additional criteria such as canister fill volume and heat generation are outlined in the WTP contract (DE-AC27-01RV14136) but are outside of the scope of this report. This study focuses on the subset of criteria that are directly related to the composition and properties of the glass. Those criteria are organized into three broad categories: solubility constraints, model validity constraints and property constraints.

If certain crystalline solids or insoluble compounds are present in the melt they can precipitate out and collect on the bottom of the melter. This can corrode electrodes, gradually reduce the volume of the melter, or make it difficult to remove the glass from the melter. In addition, some insoluble compounds can form a scum on the top of the melt. This scum can contain high levels of harmful radionuclides and can also hinder the melting process. Solubility limits are constraints that minimize or eliminate the dangers of melter damage due to different or immiscible phases. Solubility constraints are generally expressed as a limit on the mass fraction of a compound in the waste glass.

The glass itself must have certain properties to be processed in the melter. For example, if the glass has too high of a viscosity, it can be difficult to process; if it has too low of a viscosity, it can be corrosive to the melter. Glass waste must also be chemically durable. The planned long term disposal of the waste glass in a geological repository makes it possible that the waste glass will be exposed to water. The waste glass must be able resist the corrosive effects of extensive contact with water. To ensure proper chemical durability, the final glass waste must meet product consistency test (PCT) constraints. These processing and acceptability constraints are grouped as property constraints. The property constraints all rely on empirical data. When a component's mass fraction falls outside the range of data that was used to find the empirical components of the model, the answer that a model gives becomes suspect. For this reason, all of the property models have model validity constraints. The model is only known to be reliable when the composition of the glass is within certain limits. Components whose mass fraction is limited in this way are included under the category of model validity constraints.

WTP is currently using six different glass forming additives (Al_2O_3, B_2O_3, Fe_2O_3, Li_2O, Na_2O, and SiO_2) and has the ability to use up to 11 different glass formers. The glass formers are added to the feed stream so that the glass will meet all solubility, model validity, and property constraints. Due to the high cost of the vitrification process and disposal, there is a large incentive to reduce costs when possible. A simple method of taking economic factors into consideration is to reduce the mass of waste glass – the batch is optimized so that the mass of the added glass forming additives is minimized. Often these constraints do not uniquely determine the waste oxide composition. When this occurs, additional constraints could be added to the system.

HTWOS currently employs a relatively old glass property model from 1996 (WHC-SD-WM-TI-768 Rev 0) and 1999 (PNNL – 11790), along with certain relaxed limits described in ORP-11242 Rev.4. Since 1996, large amounts of glass property data have been collected and the range of the validity of the glass property models has expanded. Also, a better understanding of the solubility of the HLW glass constituents has led to new solubility constraints that were not used by the previous model. In light of this, a new glass property report (PNNL-18501) has been issued that will ultimately be incorporated into HTWOS.

3.2 COMPARISON OF 1996 GFM AND 2009 GFM

The 2009 GFM relaxes some of the model validity constraints that are used by the 1996 GFM and is consequently applicable for a larger composition range than the 1996 GFM. More information about the solubility of the feed constituents was also incorporated into the new model. A comparison of the 1996 and 2009 constraints is displayed in **Table 3-2**. The most notable changes are the relaxation of some of the composition limits. The upper limits for Al_2O_3, Fe_2O_3 and Na_2O have been increased while the lower limit for SiO_2 has been relaxed. A clearer understanding of WTP requirements has lead to the replacement of the spinel liquidus temperature constraint with an equilibrium volume of 1% percent of crystals at 950°C constraint. In addition, to prevent undesirable phase separation, new solubility constraints on the mass fraction of F^- and the mass fraction of CaO multiplied by the mass fraction of P_2O_5 ($X_{CaO} \cdot X_{P2O5}$) have been put into place. For this study, an expanded set of glass forming additives was available. HTWOS uses six glass forming additives: Al_2O_3, B_2O_3, Fe_2O_3, Li_2O, Na_2O and SiO_2. PNNL-18501 lists 12 glass forming additives that can be used by WTP; this study used 11 of these. K_2O, a possible glass former, was not used because the WTP is not currently setup to use it (K^+ from potential recycle of K_2O might poison the Cs ion exchange columns). In addition to the six oxides currently used by HTWOS, this study uses CaO, MgO, TiO_2, ZnO, and ZrO_2.

This change in glass forming additives has minimal impact on the final results. The longer list of glass formers gave the 2009 model more degrees of freedom when performing the optimization calculations. Running the 2009 GFM with the shorter list of oxides from the 1996 GFM resulted in a glass mass of 46,901 metric tons, which is 1.3% more glass than was predicted using all 11 glass forming additives. Overall, the 2009 model achieved a 0.7% decrease in WOL from the 1996 GFM when using six glass forming additives, but only a 0.4% decrease in WOL when using the full suite of 11 glass formers. The improved waste oxide loading with more additives was due to the additional degrees of freedom. In both cases, the differences between the 1996 and 2009 predicted glass masses were small, and the conclusions of this report were drawn from the runs using all 11 glass forming additives.

In addition to the change in the glass former oxides, PNNL-18501 revised the oxidation states of 7 of the waste oxides. See **Table 3-1** below for the changes.

Table 3-1. Revised Oxidation States

Old Oxide	New Oxide
CeO_2	Ce_2O_3
Co_2O_3	CoO
MnO_2	MnO
Re_2O_3	Re_2O_7
Ru_2O_3	RuO_2
Tl_2O_3	Tl_2O
U_3O_8	UO_3

The mass of the base elements in the pretreated HLW is constant, but the mass of the associated oxygen is variable. This change in oxidation states reduced the waste oxide mass from 14,220 metric tons in the 1996 GFM to 14,141 metric tons in the new model.

Table 3-2. Comparison of 1996 and 2009 GFM Constraints

Constraint		1996 GFM Lower Limit	1996 GFM Upper Limit	2009 GFM Lower Limit	2009 GFM Upper Limit	1996 GFM reference	2009 GFM reference
Solubility Constraints	Cr_2O_3	▨	1.00%[1]	▨	1.20%	WHC-SD-WM-TI-768 Rev 0	PNNL-18501
	SO_3	▨	0.50%	▨	0.50%	WHC-SD-WM-TI-768 Rev 0	PNNL-18501
	$Ru_2O_3 + Rh_2O_3$	▨	0.25%	▨	▨	WHC-SD-WM-TI-768 Rev 0	▨
	$PdO+Rh_2O_3+RuO_2$	▨	▨	▨	0.25%	▨	PNNL-18501
	F	▨	▨	▨	2.00%	▨	PNNL-18501
	$X_{CaO}{\cdot}X_{P2O5}$	▨	▨	▨	0.00065	▨	PNNL-18501
	Li_2O	1.00%	4.00%	▨	6.00%		PNNL-18501
	P_2O_5	▨	3.00%	▨	2.50%	WHC-SD-WM-TI-768 Rev 0	PNNL-18501
Model Validity Constraints	Al_2O_3	▨	17%	1.90%	20.00%		PNNL-18501
	B_2O_3	5%	20%	4.00%	20.00%		PNNL-18501
	BaO	▨	▨	▨	4.70%	▨	PNNL-18501
	Bi_2O_3	▨	▨	▨	3.20%	▨	PNNL-18501
	CaO	▨	10%	▨	7.00%		PNNL-18501
	CdO	▨	▨	▨	1.50%	▨	PNNL-18501
	Fe_2O_3	2%	15%	4.00%	17.40%		PNNL-18501
	K_2O	▨	▨	▨	6.00%		PNNL-18501
	MgO		8%	▨	6.00%		PNNL-18501
	MnO	▨	▨	▨	7.00%	▨	PNNL-18501
	Na_2O	5%	20%	4.10%	21.40%		PNNL-18501
	Nd_2O_3	▨	▨	▨	5.90%	▨	PNNL-18501
	NiO	▨	▨	▨	3.00%	▨	PNNL-18501
	SiO_2	38%	57%	30.30%	53.00%		PNNL-18501
	SrO	▨	▨	▨	10.10%	▨	PNNL-18501
	ThO_2	▨	▨	▨	6.00%	▨	PNNL-18501
	TiO_2	▨	▨	▨	3.10%	▨	PNNL-18501
	UO_3	▨	▨	▨	6.30%	▨	PNNL-18501
	ZnO	▨	▨	▨	4.00%	▨	PNNL-18501
	ZrO_2	▨	15%	▨	13.50%		PNNL-18501
Property Constraints	η1150 (Pa*s)	4.5	10[1]	4	6	WHC-SD-WM-TI-768 Rev 0	PNNL-18501
	TL-sp (°C)	None[2]	1100[1]	▨	▨	PNNL - 11790	▨
	$T_{1\%\text{-sp}}$ (°C)	▨	▨	▨	950	▨	PNNL-18501
	TL-zr (°C)	▨	1050	▨	1050*	WHC-SD-WM-TI-768 Rev 0	PNNL-18501
	Nepheline	▨	0.62	▨	0.62	WHC-SD-WM-TI-768 Rev 0	PNNL-18501

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[1] Cr_2O_3 solubility, glass viscosity, and spinel liquidus temperature constraints were relaxed from their more conservative "default" values to the values shown in this table for the "Relaxed 1996 GFM" (ORP-11242 Rev.4) The values shown are the current baseline values used for system planning and modeling purposes.

[2] HTWOS used a lower limit of 850°C

4.0 INPUT DATA

The input data for this study consists of a spreadsheet (SVF-1748) containing the composition of 1922 batches of pretreated HLW from the following HTWOS run:

SP4 Planning Case-3.0-8.4r0-2009-03-30-at-20-02-39

The HTWOS model run for this spreadsheet is based on the same starting tank inventory, blending and partitioning assumptions (water wash factors, caustic leach factors, oxidative leach endpoint, post-leach wash efficacy) as the Baseline Case in ORP-11242, Rev 4. Use of a fixed set of pretreated HLW batches ensures that changes in the degree-of-blending of the feed delivered to the WTP do not confound the interpretation of the results of this study.

The input spreadsheet also contains the predicted waste loading, formulated glass composition (prior to application of melter splits) and glass properties for each batch using the 1996 GFM.

5.0 ASSUMPTIONS

1. The “best” glass composition is assumed to be the one that satisfies all constraints and minimizes the amount of added glass forming compounds.

2. Volatility and entrainment can lead to the loss of compounds during the melting process. A basic method of modeling this elemental loss is to multiply the components of the HLW glass by the fraction of the component that is retained. For this calculation it was assumed that no elemental loss occurred during processing and these melter splits were ignored.

3. Where the oxides used by the 1996 GFM and the oxides used by the 2009 GFM differed, the 2009 GFM oxides where used. A conversion factor was included in the model to account for this.

6.0 METHOD OF ANALYSIS

A spreadsheet, *2009 High Level Waste GFM*, SVF-1748, was created that calculates the waste glass composition for each of the batches of pretreated HLW. The overall glass mass and waste oxide loading was compared with the results predicted by the 1996 GFM as documented in WTP_HLW_Glass_SP4 Planning Case-3.0-8.4r0-2009-03-30-at-20-02-39_M1.xls. The constraints that limit waste oxide loading in the 2009 GFM were compared with those from the 1996 GFM. Finally, potential areas of improvement were indentified in the 2009 GFM and sensitivity studies were performed to determine what the effects of these potential improvements would be.

This study compares the glass compositions predicted by the 2009 GFM and the 1996 GFM. Any weakness in the underlying assumptions will be reflected in the results of the models. This may be particularly relevant with regards to SO_4 partitioning. In both GFM models, the SO_3 constraint is the glass driver for the largest mass of waste glass. Current partitioning assumptions direct most of the SO_4 to the low-level waste glass. Even slight uncertainties in these SO_4 partitioning assumptions could result in the GFMs predicting HLW glass masses that are significantly larger or smaller than the actual mass of glass that is produced. If the amount of SO_4 remaining in the pretreated HLW increases, then the SO_3 limit becomes more important; if it significantly decreases, then the SO_3 limit becomes less important.

6.1 NON-LINEAR OPTIMIZATION

The solubility, model validity, and property constraints do not in-and-of-themselves uniquely determine the composition of the waste glass. The mass of the glass formers can be adjusted so as to minimize the final mass of the waste glass subject to all of the relevant constraints. This is a classic optimization problem.

The final mass of the glass is the sum of the added glass forming compounds and the mass of waste oxide feed. The mass of the waste oxide feed is fixed, so the final mass of the glass can be minimized by minimizing the mass of the added glass forming compounds. This means the objective function (the function to be minimized) is:

$$\sum_{i=1}^{11} m_i$$

Where m_i is the mass of the *i*-th glass forming additives. This is a linear function.

The property functions are polynomials with the components' mass fractions as the variables. For example, the equation for the viscosity at 1150 is

$$Ln(\eta_{1150}) = \sum_{i=1}^{19} b_i x_i + \sum_{i=1}^{2} b_{ii} x_i^2 + \sum_{i=1}^{1} \sum_{j=1}^{2} b_{ij} x_i x_j$$

Where

$$x_i = \frac{m_{ifeed} + m_{iadditive}}{m_{total}}$$

These constraint equations are non-linear, so even though the objective function is linear, minimizing the mass of the added glass forming compounds is a nonlinear optimization problem. There are innumerable methods of solving this type of problem numerically, but for this study the *Solver* add-in for Excel was used.

6.2 DETERMINING DRIVERS

When comparing the 1996 and 2009 GFM it is instructive to look at the constraints that limit the waste oxide loading. It is rare for a batch to run up against a single constraint. A batch will usually meet multiple constraints. In order to determine a unique limiting constraint for a batch, the constraints have to be ranked. The solubility constraints are given priority, followed by the model validity constraints. Any batch that is not limited by either of two types of constraints will be limited by the property constraints.

The solubility constraints are "hard" constraints. There is a fixed amount of the solubility-limiting components in the waste feed and these amounts will determine the minimum mass of glass forming additives that can be added if the waste glass is to meet all constraints. For instance, the waste feed for batch 356 has 76.97 Kg of SO_3. The 2009 GFM limits SO_3 to 0.5% of the final mass of the waste glass. This sets the lower limit of the waste glass mass at 76.97 kg/.005 = 15394 kg. This is a limit that cannot be circumvented by altering the ratios of the added glass forming additives.

The model validity limits are also hard limits, so if they are hit, they uniquely determine the minimum mass of the waste glass. Unlike the solubility constraints, the model validity constraints represent epistemic limitations and do not necessarily reflect underlying physical limitations on the glass formulation. For this reason, the exceedingly rare times when a batch is limited by both model validity constraints and solubility constraints, solubility constraints are reported as the primary constraint on the waste oxide loading.

Both the solubility and model validity constraints involve components that can be added as glass forming compounds. When one of these components hits a constraint and it has been added as a glass forming compound, it is not treated as a hard constraint. In cases where a batch hits a model validity or a solubility constraint and it has been added as a glass forming compound, one of two situations apply:

- The final mass of the waste glass has been determined by another hard solubility or model validity constraint and the remaining degrees of freedom are used to determine the non-unique composition of glass forming oxides. The constraint that is hit due the added glass forming additives is the result of the application of the remaining degrees of freedom and does not uniquely determine waste oxide loading.

- When the maximum waste oxide loading has not been limited by model or validity constraints, the glass forming additive is adjusted so that the glass batch does not violate a specific property constraint. Although the added glass forming compound hits a constraint, the property constraint is what is limiting the waste oxide loading and the property constraint is reported as the glass driver.

In short, model validity or solubility constraints are only reported as glass drivers if they have not been added as a glass forming compound.

The glass properties are the function of most, if not all, of the components that can be added as glass formers. This gives the model large amounts of flexibility in determining the most efficient way to meet property constraints. Because of this flexibility, the property constraints are limiting only if the batch is not limited by model validity or solubility constraints.

6.3 SENSITIVITY STUDY WITHIN NEW MODEL

Sensitivity studies were performed using the 2009 GFM to assess the potential impacts of relaxing certain constraints. This information might be useful in shaping future glass formulation efforts. When determining which constraints to relax, two factors were considered. First, the constraint had to play a fairly significant role in limiting waste oxide loading. It would be unproductive to improve a constraint that limited the waste oxide loading in only 0.1% of the total predicted glass mass. Second, the constraint had to have the potential to be improved in practice. There is no reason to see what the improvement in WOL would be if a constraint was relaxed if there was no possibility of that constraint being relaxed in reality.

The first consideration was achieved by calculating the glass resulting from the pretreated HLW batches with the spreadsheet. The glass drivers were determined and the constraints that had a significant impact on the final glass mass were identified. The second consideration was slightly more subjective. *Glass Property Data and Models for Estimating High-Level Waste Glass Volume* PNNL-18501 gave a sense of what constraints might be improved with additional glass formulation effort. After this, the primary author of the report, John Vienna, was consulted and suggested the potential areas of improvement as shown in **Table 6-1**.

Table 6-1. Relaxed Constraints

Constraint	Current Value	Potential Value	Percent of Glass Limited by constraint	Reference
Nepheline	.62	.45	22.5%	PNNL-18501 Appendix A
SO_3	.5%	1.0%	36.3%	Personal Communication
Bi_2O_3	3.2%	16.37%	7.5%	PNNL-10987
Na_2O	21.4%	23.0%	5.2%	VSL-06R6480-3
P_2O_5	2.5%	4.5%	3.7%	Personal Communication

A parametric study was performed on the nepheline discriminator and SO_3 solubility limits. The values were gradually changed from the current value to the potential value. The effects of this on the waste oxide loading and the glass drivers were examined. The goal with the Bi_2O_3 was to determine at what upper limit (up to 16.37%) Bi_2O_3 was no longer a glass driver. The constraint was relaxed until that point was identified rather than varied over the entire range of potential model validity values for Bi_2O_3. The Na_2O and P_2O_5 constraints were adjusted in a single step from their current value to their potential values. In addition to these variations, a few studies were performed in which several of these constraints were varied at the same time. This provided a sense of how large or small the benefits would be if improvements were made to the model.

The $T_{1\%}$-sp constraint limits 13.5% of the glass mass. It is the constraint that limits the third largest glass mass. It would be worthwhile to investigate the effect that altering the $T_{1\%}$-sp constraint has on the waste oxide loading. However, due to the nature of the constraint, simply altering the limit value is not a realistic reflection of how the limit would be altered if the model were to be revised. Changing the $T_{1\%}$-sp constraint would probably involving redoing the underlying empirical correlations or replacing it with another constraint, so it was not included in this study.

7.0 USE OF COMPUTER SOFTWARE

Excel was chosen due to its ability to perform repetitive calculations on large amounts of data and the presence of an easy-to-use Solver add-in for constrained non-linear optimization. The current site standard versions of Excel and the Microsoft® Windows operating system were used:

- Microsoft® Excel 2007 SP1 MSO
- Microsoft® Windows XP Professional SP3

In addition, the following verified spreadsheets and associated Visual Basic for Applications code were used:

- 2009_HLW_GFM (SVF-1748 Rev. 2)
- 2009_GFM_SS (SVF-1755 Rev. 0)

8.0 RESULTS

8.1 COMPARISON OF 2009 AND 1996 GFM RESULTS

The amount of glass predicted by the 1996 GFM and the 2009 GFM was very similar (within 0.52% difference). The 2009 GFM predicted 46,303 metric tons of waste glass and a waste oxide loading of 30.5%. The older model predicted a slightly smaller amount of glass waste, 46,063 metric tons, and a larger waste oxide loading at 30.9%. The waste oxide loading predicted by both models is compared on a batch-by-batch basis in **Figure 8-1.** The models predict very similar waste oxide loading in most cases. The waste oxide loading predicted by the 2009 GFM is plotted against the waste oxide loading predicted by the 1996 GFM in **Figure 8-2.** As is expected the points tend to cluster around the X = Y line.

8.1.1 Comparison of Drivers

Table 8-1 and Table 8-2show the glass drivers for the 1996 GFM and the 2009 GFM. The active constraints are shown on the left side of the table. The right portion of the table shows the number of batches, the average waste oxide loading of the batches, the total waste oxide mass and the total glass mass that are limited by that constraint. The latter two columns are also displayed as a percentage of the overall waste oxide mass and overall glass mass. The red shading indicates constraints for which more than 5% of the glass mass is limited by that constraint.

The new GFM shows a slightly larger diversity of glass drivers than the 1996 model does. The 1996 GFM glass driver is limited by 10 different constraints while the 2009 GFM has 13 active constraints. The top five drivers in the 1996 GFM limit 92.4% percent of the total waste glass mass, while the top five drivers for the new model limit 85% of the final waste glass mass.

Figure 8-1 Waste Oxide Loading

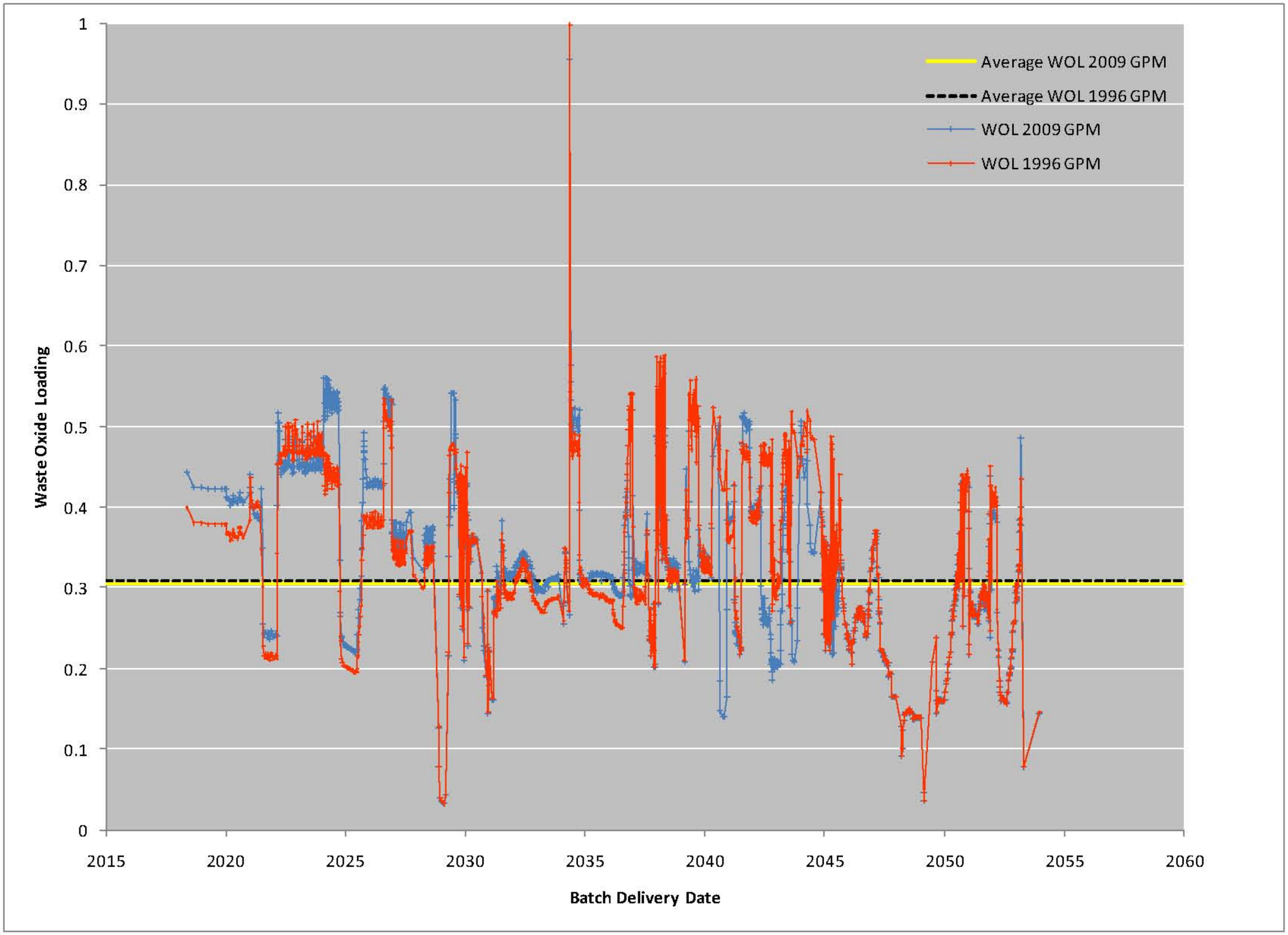

Figure 8-2 Comparison of Waste Oxide Loading

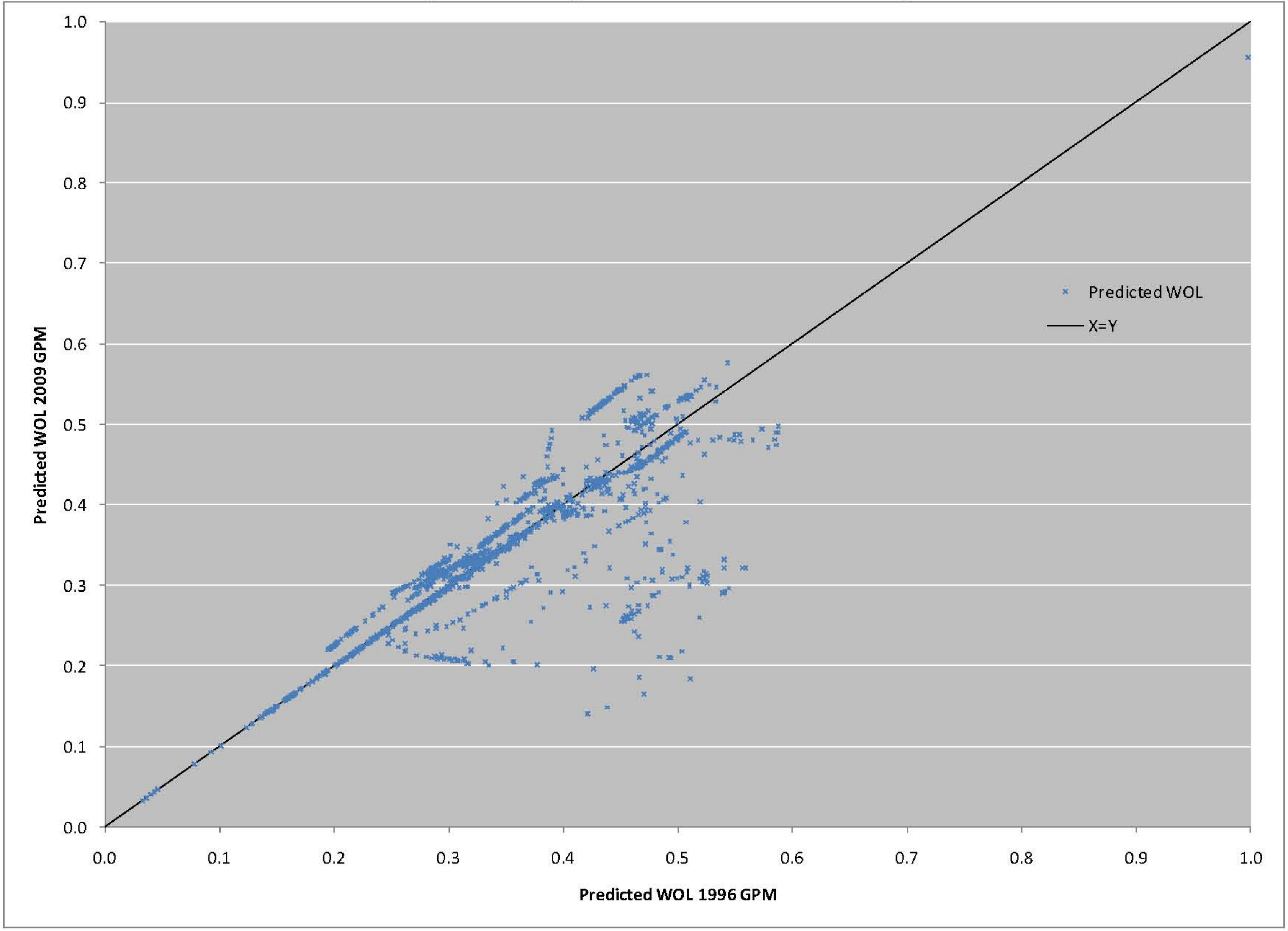

Table 8.1 2009 GFM Drivers

Constraints			Number of Batches	Waste Oxide Mass (MT)	Glass Mass (MT)	Average Waste Oxide Loading	Percent of Waste Oxide Mass	Percent of Glass Mass
Glass Composition Constraints	**Solubility Limited**	SO_3	560	3,898	16,793	23.2%	27.6%	36.3%
		F	43	337	1,240	27.1%	2.4%	2.7%
		$X_{CaO}\cdot X_{P2O5}$	27	223	471	47.4%	1.6%	1.0%
		Li_2O	0	0	0	n/a	0.0%	0.0%
		Cr_2O_3	0	0	0	n/a	0.0%	0.0%
		Subtotal	630	4,458	18,505	24.1%	31.5%	40.0%
	Model Validity Limited	Al_2O_3	0	0	0	n/a	0.0%	0.0%
		B_2O_3	0	0	0	n/a	0.0%	0.0%
		Bi_2O_3	124	926	3,464	26.7%	6.5%	7.5%
		CaO	0	0	0	n/a	0.0%	0.0%
		CdO	9	87	222	39.1%	0.6%	0.5%
		Fe_2O_3	0	0	0	n/a	0.0%	0.0%
		SiO_2	0	0	0	n/a	0.0%	0.0%
		MnO	18	104	267	39.0%	0.7%	0.6%
		Na_2O	127	881	2,391	36.9%	6.2%	5.2%
		P_2O_5	87	624	1,711	36.5%	4.4%	3.7%
		UO_3	28	210	633	33.2%	1.5%	1.4%
		ZrO_2	74	613	2,374	25.8%	4.3%	5.1%
		Subtotal	467	3,445	11,062	31.1%	24.4%	23.9%
Glass Property Constraints	Glass Composition Constraints Subtotal		1097	7,903	29,567	26.7%	55.9%	63.9%
	$T_{1\%\text{-sp}}$ involved		362	2,771	6,235	44.4%	19.6%	13.5%
	Only TL-zr involved		4	35	99	35.1%	0.2%	0.2%
	Only Nepheline		459	3,431	10,402	33.0%	24.3%	22.5%
	Glass Property Constraints Subtotal		825	6,237	16,736	37.3%	44.1%	36.1%
Total			1922	14,141	46,303	30.5%	100.0%	100.0%

Table 8-2 1996 GFM Drivers

Constraints			Number of waste feed batches	Waste oxide mass (MT)	Glass mass (MT)	Average waste loading in glass	Percent of waste oxide mass	Percent of glass mass
Glass composition constraints	**Solubility limited**	SO_3	629	4,442	18,104	0.245	31.2%	39.3%
		P_2O_5	91	648	1,815	0.357	4.6%	3.9%
		Cr_2O_3	15	91	222	0.410	0.6%	0.5%
		Subtotal	735	5,182	20,141	0.257	36.4%	43.7%
	Model validity limited	Al_2O_3	433	3,323	11,034	0.301	23.4%	24.0%
		Fe_2O_3	45	383	1,005	0.381	2.7%	2.2%
		Na_2O	211	1,515	4,055	0.374	10.7%	8.8%
		SiO_2	0	0	0	n/a	0.0%	0.0%
		Subtotal	689	5,221	16,095	0.324	36.7%	34.9%
	Glass composition constraints subtotal		1,424	10,402	36,236	0.287	73.2%	78.7%
Glass property constraints	Only Spinel T_L involved		399	3,002	6,606	0.454	21.1%	14.3%
	Zirc T_L involved		76	630	2,772	0.227	4.4%	6.0%
	Neither T_L involved		23	186	449	0.414	1.3%	1.0%
	Glass property constraints subtotal		498	3,818	9,827	0.388	26.8%	21.3%
Total			1,922	14,220	46,063	0.309	100.0%	100.0%

One of the goals of the new glass model was to reduce the number batches that were limited by model validity constraints. It met this goal. In the previous model, 34.9% (by final weight percent) of the glass was limited by model validity constraints. In the new model, this number was significantly reduced to 23.9%. Since the 2009 GFM predicted a smaller number of batches limited by model validity constraints, it would be expected to also predict a smaller final waste glass mass; instead, the two models predict very similar waste glass masses. The 2009 GFM predicted reduced waste mass in regards to model validity constraints, so in order to predict a similar final glass mass, it must predict a higher glass mass elsewhere. **Table 8-3** was developed to help explain the changes (or lack thereof) in glass mass.

Table 8-3 shows the glass drivers for batches where the 2009 GFM predicted more than a 5% larger glass mass than the 1996 GFM. A vast majority of cases are the result of the UO_3, F^-, $X_{CaO} \cdot X_{P2O5}$, P_2O_5 and Bi_2O_3 constraints. The F- and $X_{CaO} \cdot X_{P2O5}$ constraints are solubility constraints that were not used in the 1996 GFM. The UO_3 and Bi_2O_3 model validity constraints were not included in the previous model either. P_2O_5 was a constraint in the 1996 GFM, but the constraint was less restrictive at 3.0% than the 2.5% limit used by the 2009 GFM. The very similar predicted glass mass between the two models, despite a general decrease in the amount of glass limited by model validity constraints, is the result of these new constraints.

In both the 1996 and 2009 GFM, SO_3 is the largest glass driver on a batch number basis and as a percentage of the total glass mass. The older model predicted a larger total glass mass limited by SO_3 (39.3%) than the new model (36.3%). The SO_4 partitioning assumptions used to determine the composition of the pretreated HLW result in about 1.7% of the waste SO_4 reporting to the HLW glass with most of the remaining 98.3% reporting to the LAW glass. Small errors in these partitioning assumptions could result in significant errors in predicted HLW glass mass. For example, if the amount of residual SO_3 in the pretreated HLW were cut in half, the mass of the resulting HLW glass would decrease by 13%. Due to the uncertainties and limitations surrounding the sulfate partitioning assumptions currently used for system planning and modeling purposes, it would be worthwhile to reexamine both sulfate partitioning and possibly the starting SO_4 inventory.

The second most limiting constraint for the 1996 GFM was Al_2O_3 at 433 batches and 24.0% of the total glass mass. This constraint almost completely disappears in the 2009 GFM and is replaced with the nepheline discriminator which limits 459 batches and 22.5% of the total glass mass. The nepheline discriminator has the form:

$$\frac{X_{SiO2}}{X_{Al2O3} + X_{NaO2} + X_{SiO2}}$$

It is expected that the average nepheline value would decrease as the mass fraction of Al_2O_3 increases. The 2009 GFM relaxes the Al_2O_3 model validity constraint to 20% from the 17% used by the 1996 GFM so the batches that were previously limited by Al_2O_3 should be largely limited by nepheline in the new model. This is exactly what is happening in this instance.

Table 8-4 compares, on a batch-by-batch basis, the limiting constraints for the 1996 and 2009 GFM. The columns show the number of batches that are limited by the 1996 constraint shown at the top of the column. The rows show the number of batches that are limited by the 2009 constraint to the left of the row. The intersection of a column and a row shows the number of batches that were limited by the 1996 constraint that the column belongs to and by the 2009 constraint that the row belongs to. For example, if the arrow is followed from the top of Cr_2O_3 down to the 15 and over left to MnO, it shows that 15 batches that were limited by Cr_2O_3 in the 1996 GFM are now limited by the MnO constraint in the 2009 GFM. Similarly, the Al_2O_3 column shows that of the 433 batches that were Al_2O_3 limited, 380 are now limited by nepheline in the new model.

Table 8-3 2009 GFM Drivers that predict more than a 5% increase in HLW Mass

Constraints			Number of Batches
Glass Composition Constraints	**Solubility Limited**	SO_3	0
		F	38
		$X_{CaO} \cdot X_{P2O5}$	31
		Li_2O	0
		Cr_2O_3	0
		Subtotal	69
	Model Validity Limited	Al_2O_3	0
		B_2O_3	1
		Bi_2O_3	100
		CaO	1
		CdO	0
		Fe_2O_3	3
		SiO_2	1
		MnO	1
		Na_2O	0
		P_2O_5	59
		UO_3	27
		ZrO_2	0
		Subtotal	193
Glass Property Constraints	Glass Composition Constraints Subtotal		262
	$T_{1\%\text{-sp}}$ involved		2
	Only TL-zr involved		0
	Only Nepheline		1
	Glass Property Constraints Subtotal		3
Total			265

Table 8-4 Comparison of Drivers

Constraints		Old HLW Constraints (1996 GFM)										Total
		SO_3	P_2O_5	Cr_2O_3	Al_2O_3	Fe_2O_3	Na_2O	SiO_2	Only Spinel TL	Zirc TL	Neither TL involved	
New HLW Constraints (2009 GFM)	SO_3	549					6		5			560
	F	10					8		22	2	1	43
	$X_{CaO} \cdot X_{P2O5}$	16					7				4	27
	Li_2O											0
	Cr_2O_3											0
	Al_2O_3											0
	B_2O_3											0
	Bi_2O_3	25	50						49			124
	CaO											
	CdO					9						9
	Fe_2O_3											0
	SiO_2											0
	MnO			15			3					18
	Na_2O						126				1	127
	P_2O_5	21	41				25					87
	UO_3	3							25			28
	ZrO_2									74		74
	$T_{1\%-sp}$ involved	1			49	36	17		258		1	362
	Only TL-zr involved				4							4
	Nepheline	4			380		19		40		16	459
Total		629	91	15	433	45	211	0	399	76	23	1922

The switch between the Al_2O_3 driver and the nepheline driver is the major difference between the 1996 GFM and the 2009 GFM. A few other notable changes are shown by **Table 8-4**. The zircon liquidus temperature constraint in the 1996 model was almost completely replaced with a zircon model validity constraint in the 2009 model. This change in drivers had minimal effect on the predicted final glass mass. The second notable change is the effect of the Bi_2O_3 limit. Bi_2O_3 is the glass driver for 7.5% of the total glass mass in the 2009 GFM and is not present in the 1996 GFM. As was discussed above, **Table 8-3** shows that the Bi_2O_3 constraint generally predicts a lower waste oxide loading than the 1996 GFM does for the same batch. Out of the 124 batches that are limited by Bi_2O_3 in the 2009 GFM, 100 of them predicted a greater than 5% increase in glass mass than was predicted by older model. This has a small, but noticeable, effect on the predicted glass mass and is one of the primary reasons that, despite the relaxation of the model validity limits, the two models predict nearly identical glass masses.

8.2 SENSITIVITY STUDY FOR NEW MODEL

The constraints that were determined to be the most promising candidates for improvement were: SO_3, nepheline, Na_2O, P_2O_5, and Bi_2O_3. Of these SO_3, nepheline, and Bi_2O_3 were looked at in a parametric study. Na_2O and P_2O_5 were varied once to determine the effect on the mass of the predicted waste glass. In addition, several constraints were varied together to find their combined effect on the waste oxide loading. In every case, the predicted glass mass is reported as percentage of the reference case, where the reference case is the total waste glass mass when all batches are calculated using the 2009 GFM constraint values recommended in PNNL-18501 and reiterated in **Table 3-2**.

8.2.1 Nepheline Discriminator

The appendix to *Glass Property Data and Models for Estimating High-Level Waste Glass Volume* PNNL-18501 suggests that the lower limit for the nepheline discriminator could be as low as 0.45. The parametric study looked at the effects of varying nepheline constraint between 0.62 and 0.45. Optimization runs took place at constraint values of 0.62, 0.60, 0.57, 0.55, 0.53, 0.51 and 0.45.

Table 8-5 displays the results. The right side of the table shows the top five glass drivers along with constraints of interest (shown in bold). Nepheline is no longer a glass driver at a value of 0.45. At this point the predicted glass mass is 2.6% percent less than the reference case. While improvements in waste oxide loading are shown down to a nepheline discriminator value of 0.45, the returns sharply diminish after a value of 0.57. The total mass of the waste glass has a 1% decrease when the nepheline changes from 0.60 to 0.57, but only a 0.2% decrease when the nepheline constraint is dropped from 0.57 to 0.55. A similar 0.1% decrease is shown when the constraint is changed from 0.55 to 0.45.

The connection between Al_2O_3 and nepheline was discussed in section 8.1.1.The reverse phenomenon is seen here. As a reminder, the nepheline discriminator is:

$$\frac{X_{SiO2}}{X_{Al2O3} + X_{Na2O} + X_{SiO2}}$$

Table 8-5 Nepheline Sensitivity Study

				Top Five Drivers - by Final Glass Mass %					
Nepheline Discriminator	**Total Waste Glass Mass (MT)**	**Average WOL**	**Predicted Mass as percentage of reference case**	**SO_3**	**Nepheline**	**$T_{1\%\text{-sp}}$**	**ZrO_2**	**Bi_2O_3**	**Al_2O_3**
0.62	46,303	0.305	100.0%	36%	23%	14%	5%	8%	0%
0.60	45,686	0.310	98.7%	37%	18%	15%	5%	8%	2%
0.57	45,244	0.313	97.7%	38%	**4%**	13%	5%	8%	17%
0.55	45,151	0.313	97.5%	38%	**19 Batches**	12%	5%	8%	21%
0.53	45,107	0.313	97.4%	38%	**2 batches**	12%	5%	8%	22%
0.51	45,096	0.314	97.4%	38%	**1 batch**	12%	5%	8%	22%
0.45	45,079	0.314	97.4%	38%	**0%**	12%	5%	8%	22%

When the acceptable nepheline limit is lowered, the amount of sodium added to the glass can decrease. This causes the mass fraction of Al_2O_3 to increase. If the nepheline discriminator is lowered enough, X_{Al2O3} will increase and begin to hit its model validity limit.

8.2.2 Bi_2O_3

The goal of this portion of the study was to determine at what point the Bi_2O_3 constraint is no longer a glass driver. The model validity limit for Bi_2O_3 can be relaxed from 3.2% up to 16.37%. This value greatly exceeded the expected concentration of Bi_2O_3 in the glass, so a lower value was chosen for testing. The Bi_2O_3 constraint was raised to 10.0% and the glass resulting from all of the batches were calculated. For the calculated batches, the largest mass percent of Bi_2O_3 was 6.61%. Since the amount of Bi_2O_3 in the waste glass never exceeds 6.61%, 6.7% was identified as the value at which the Bi_2O_3 constraint would no longer limit WOL. Additional runs were performed at Bi_2O_3 upper limits of 6.6% and 6.7% to verify this result. At 6.6%, one batch was limited by the Bi_2O_3 constraint and at 6.7% no batches were limited by Bi_2O_3, thus confirming that 6.7% was the minimum value at which Bi_2O_3 was not an active constraint.

The impact of Bi_2O_3 on the predicted waste glass mass was not as great as that of the nepheline discriminator. Relaxing the constraint from 3.2% to 6.7% only led to a 1.5% improvement in waste glass mass. The right side of **Table 8-6** shows that the batches formerly limited by Bi_2O_3 were transferred fairly equally to the remaining constraints. As one constraint is relaxed, other constraints often become limiting with little improvement in waste loading.

8.2.3 SO_3

Of the constraints studied, SO_3 has, by far, the largest impact. The effect of varying the SO_3 constraint was tested at 0.5%, 0.6%, 0.7%, 0.8%, 0.9% and 1.0%. At the most relaxed value (1.0%) the predicted glass mass was reduced by 14.4%. The slightly relaxed value of 0.6% even shows a significant reduction in predicted glass mass, at 5.7%. Even at 1.0% solubility, SO_3 remained in the top five glass drivers, limiting the waste oxide loading for 7.9% of the glass. If the solubility limit could be increased past 1.0% it would continue to yield positive results.

Once again the top five glass drivers are shown on the right half of **Table 8-7.** As SO_3 drops from being the limiting constraint for over 1/3 of the waste glass to being the limiting constraint for 8% of the waste glass mass, the percent of the glass limited by both nepheline and Bi_2O3 increases. This strongly suggests that lowering the SO_3, nepheline, and Bi_2O_3 constraints at the same time would have an effect that is greater than the sum of relaxing each constraint individually.

8.2.4 Na_2O and P_2O_5

Unlike the previous three constraints, both Na_2O and P_2O_5 were only varied once. Na_2O was relaxed to 23.0% from 21.4% as suggested by VSL-06R6480-3. The P_2O_5 constraint was relaxed to the solubility limit of 4.5%. The results are shown in the first two lines of **Table 8-8**. The effects are minimal. Relaxing the Na_2O constraint resulted in a reduction of 0.5% of predicted waste glass mass. The relaxed P_2O_5 constraint reduced the glass mass by 0.4%. These are small improvements, but relaxing either of these constraints in conjunction with other constraints will show improvements that are greater than the sum of relaxing each individual constraint.

Table 8-6 Bi_2O_3 Sensitivity Study

				Top Five Drivers - by Final Glass Mass %					
Bi_2O_3 Model Validity Limit	**Total Waste Glass Mass (MT)**	**Average WOL**	**Predicted Mass as percentage of reference case**	**SO_3**	**Nepheline**	**$T_{1\%-sp}$**	**Na_2O**	**Bi_2O_3**	**P_2O_5**
3.2%	46,303	0.305	100.0%	36%	23%	14%	5%	8%	4%
4.2%	45,734	0.309	98.8%	38%	23%	14%	5%	**2%**	6%
6.6%	45,592	0.310	98.5%	38%	23%	14%	5%	**1 batch**	8%
6.7%	45,592	0.310	98.5%	38%	23%	14%	5%	**0%**	8%
10.0%	45,592	0.310	98.5%	38%	23%	14%	5%	**0%**	8%

Table 8-7 SO_3 Sensitivity Study

				Top Five Drivers - by Final Glass Mass %				
SO_3 Solubility Limit	**Total Waste Glass Mass (MT)**	**Average WOL**	**Predicted mass as percentage of reference case**	**SO_3**	**Nepheline**	**$T_{1\%\text{-sp}}$**	**NaO_2**	**Bi_2O_3**
0.5%	46,303	0.305	100.0%	36%	23%	14%	5%	8%
0.6%	43,641	0.324	94.3%	29%	25%	14%	6%	9%
0.7%	41,920	0.337	90.5%	23%	28%	15%	6%	10%
0.8%	40,788	0.347	88.1%	18%	31%	15%	6%	11%
0.9%	40,071	0.353	86.5%	12%	33%	17%	6%	13%
1.0%	39,652	0.357	85.6%	8%	34%	16%	7%	14%

Table 8-8 Relaxing Multiple Constraints

Constraint	Value	Relaxed Value	Predicted Glass Mass (MT)	%Mass of Reference Case	WOL
Na_2O	21.4%	23.0%	46,079	99.5%	0.307
P_2O_5	2.5%	4.5%	46,132	99.6%	0.307
P_2O_5	2.5%	4.5%	43,636	94.2%	0.324
Nepheline	0.62	0.57			
Bi_2O_3	3.2%	6.7%			
Nepheline	0.62	0.57	44,199	95.5%	0.320
Bi_2O_3	3.2%	6.7%			
P_2O_5	2.5%	4.5%	38,585	83.3%	0.366
Nepheline	0.62	0.57			
Bi_2O_3	3.2%	6.7%			
Na_2O	21.4%	23.0%			
SO_3	0.50%	0.70%			
P_2O_5	2.5%	4.5%	35,665	77.0%	0.396
Nepheline	0.62	0.57			
Bi_2O_3	3.2%	6.7%			
Na_2O	21.4%	23.0%			
SO_3	0.50%	1.00%			

8.2.5 Relaxing Multiple Constraints

In the previous sections, the change in glass drivers as a single constraint was lowered implied that lowering multiple constraints jointly would have a synergistic effect. That is what is displayed in runs 3 -6 on **Table 8-8**. Raising the P_2O_5 constraint to 4.5% only results in a 0.4% reduction in predicted waste glass mass. However, raising the P_2O_5 constraint to 4.5% in conjunction with relaxing the nepheline and Bi_2O_3 constraint has a larger impact on predicted glass mass. The predicted decrease in glass mass, if each constraint was relaxed separately is 4.5%. When all three constraints are relaxed simultaneously, the glass mass decreases by 5.8%. This is shown in runs 3 and 4 of **Table 8-8**.

Runs 5 and 6 give an idea of the benefit of relaxing all of the selected constraints jointly. Run 6 shows what occurs if nepheline is lowered to 0.57 and all the other constraints are relaxed to the maximum values used in this study. The predicted waste glass mass in this run was 23.0% lower than the reference case. Run 5 uses the same constraint values that run 6 does, but the SO_3 constraint is relaxed to 0.7% instead of 1.0%. In this case the predicted waste glass mass is 16.7% less than the reference case. Additional glass formulation work would be needed to support relaxing these constraints and it is likely that as multiple constraints are relaxed, other constraints will become more prominent drivers and the incremental improvements in waste oxide loading may diminish.

9.0 CONCLUSIONS

Despite relaxed model validity constraints, the 2009 GFM model predicts very similar waste oxide loading and HLW glass mass as the 1996 model does. This can be attributed to two solubility limits, F- and $X_{CaO} \cdot X_{P2O5}$, and two model validity limits, Bi_2O_3 and UO_3, that were not present in the older model.

In order of decreasing importance, the top five glass drivers for each model are:

- 2009 GFM: SO_3, nepheline discriminator, $T_{1\%}$-sp, Bi_2O_3, Na_2O
- 1996 GFM: SO_3, Al_2O_3, T_L-sp, Na_2O, T_L-zircon

SO_3 continued to be the primary glass driver. Al_2O_3 was second largest glass driver in the 1996 GFM with it limiting 24.0% of the total waste glass mass. The 2009 GFM relaxed the Al_2O_3 model validity constraint to 20% from 17%. As a result, the percentage of waste glass mass that was limited by Al_2O_3 plummeted to only 2 batches. Other less significant, but still noticeable, differences include an increased number of glass drivers in the 2009 GFM and the appearance of the Bi_2O_3 model validity constraint as a major driver.

Within the 2009 GFM the Na_2O, P_2O_5, Bi_2O_3, SO_3 and the nepheline discriminator were identified as the constraints that were most likely to be relaxed, assuming additional glass formulation work, and to have an effect on the predicted waste oxide loading. Of these constraints SO_3 had, by far, the largest impact on the predicted waste oxide loading. The most optimistic scenario relaxed the SO_3 constraint from 0.5% to 1.0%. This resulted in a 14.4% decrease in the predicted waste glass mass. Even a more conservative, and perhaps more realistic, relaxation of the SO_3 constraint to 0.7% showed a 9.5% decrease in predicted glass mass. It is important to note that SO_3's role as the primary glass driver is heavily dependent on the sulfate partitioning assumptions in HTWOS. Those assumptions have a significant amount of uncertainty associated with them, and any changes made to decrease or increase the amount of SO_3 that ends up in HLW glass may have dramatic effects on both waste oxide loading and the final mass of glass. For example, SO_3 no longer plays a role as a glass driver when the amount of sulfate reporting to HLW is cut in half. The waste oxide loading increases to 36% and the total mass of glass decreases by 13% in that case. Despite these improvements, other constraints become more prominent glass drivers as SO_3's role is diminished, particularly nepheline, Bi_2O_3, F- and P_2O_5.

The effect of relaxing the second most limiting constraint, the nepheline discriminator, is less impressive. Nepheline is no longer a glass driver at a value of 0.45. This results in a 2.6% improvement in predicted waste glass mass. The effect of reducing the nepheline discriminator lower limit begins to show significant diminishing returns after 0.57. At this point the predicted waste glass mass shows a 2.3% improvement from the reference case.

The other constraints show an even smaller effect when relaxed. Bi_2O_3 does not limit the waste oxide loading on any batches once the model validity limit is raised to 6.7%. The predicted waste glass mass is 1.5% less than the reference case when this occurs. When Na_2O and P_2O_5 are relaxed to 23.0% and 4.5%, respectively, both show less than a 1% decrease in predicted waste glass mass.

When multiple constraints are relaxed together, the effect is greater than the sum of relaxing each constraint individually. Relaxing nepheline to 0.57 and the rest of the constraints to their maximum values results in a 23.0% reduction in predicted waste glass mass. If the above scenario is repeated except with the SO_3 constraint relaxed to 0.7%, the predicted waste oxide mass is 16.7% less than the reference case.

10.0 RECOMMENDATIONS

PNNL-18501 shows that there is a relatively high level of uncertainty around the SO_3 constraint. Evidence suggests that this limit could go as high as 1.0%. Given the large impact that relaxing the SO_3 constraint has on the predicted waste oxide loading, it is recommended that more work be done to pinpoint the concentration of SO_3 that the melter can handle.

The mass balance for the SP4 initial planning case, SVF-1663, shows 1.7% of the SO_4 going to the HLW melters as part of the pretreated feed. As the *Review of Phosphate and Sulfate Wash and Leach Factors,* RPP-25903, suggests, there is a fairly high level of uncertainty surrounding the assumptions underlying the sulfate partitioning. Since SO_3 (which is the product of the sulfate decomposition reaction in the melter) has a large impact on the predicted waste oxide loading in both the 1996 and 2009 GFM, it may be prudent to revisit sulfate partitioning assumptions. HLW glass contains only 1.7% of the SO_4 and it becomes the limiting constraint for nearly 40% of the waste glass mass. Small inaccuracies in the partitioning assumptions could, therefore, led to predictions that widely over or under predict the amount of HLW glass produced.

The nepheline discriminator has a lesser impact on predicted waste glass mass, but lowering it to 0.45 does decrease the predicted waste glass mass by 2.6%. Reducing it to the more conservative value of 0.57 has a similar effect – a 2.3% reduction in predicted glass mass. There would be value in investigating whether the nepheline constraint can be lowered.

Bi_2O_3, Na_2O and P_2O_5 have even smaller effects on the predicted waste oxide loading. There probably is not a large incentive in lowering any of these constraints independently, but since lowering multiple constraints together has a greater impact than the sum of relaxing each constraint alone, it would be worth studying whether the Bi_2O_3, Na_2O, or P_2O_5 constraints could be relaxed.

The effect of varying the $T_{1\%}$ - Spinel constraint was not investigated in this study, but since it limits 13.5% of the total waste glass mass, any work done making the constraint less restrictive could yield beneficial improvements in predicted waste oxide loading.

11.0 REFERENCES

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