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IMPACT OF REDOX ON GLASS DURABILITY: THE GLASS SELECTION PROCESS

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Prepared for the U.S. Department of Energy Under Contract Number DEAC09-96SR18500

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EXECUTIVE SUMMARY

Recent glass formulation activities have focused on developing alternative frit compositions for use with specific sludge batches to maximize melt rate and/or waste throughput. The general trend has been to increase the total alkali content in the glass through the use of a high alkali based frit, a less washed sludge, or a combination of the two. As a result, predictions of durability have become a limiting factor in defining the projected operating windows for the Defense Waste Processing Facility (DWPF) for certain systems. An additional issue for these high alkali glasses has been the effect of REDuction/OXidation (REDOX) on the durability of the glass. Recent analyses have indicated that the application of the durability model's FeO ΔG_i value without consideration of the overall glass composition may lead to a more significant ΔG_P shift (larger magnitude) than needed. Therefore, activation of the REDOX term in the Product Composition Control System (PCCS) may have a significant impact on the predicted operational windows based on model predictions, but may not represent the realistic impact on the measured durability.

In this report, two specific issues are addressed. First, a review of the data used to develop PCCS (in particular the durability model) showed the potential for an Al_2O_3 – REDOX interaction that is not accounted for. More specifically, three terms (REDOX (as measured by Fe^{2+}/Fe_{total}), Al_2O_3, and a REDOX × Al_2O_3 interaction term) were added to the current model and were found to be statistically significant at a confidence level of 95%. These results suggest a possible interaction between REDOX and glass composition that is not accurately captured by the ΔG_P model leading to potentially conservative decisions regarding the durability of reduced glasses.

The second issue addressed in this report is the development of a 45 glass test matrix to assess the effect of REDOX on durability as well as to provide insight into specific interactive compositional effects on durability. The glasses were selected to support the assessment of the following specific objectives: (1) the impact of REDOX on glass durability (as measured by the Product Consistency Test (PCT)) and (2) the interactive effects that may mitigate the predicted negative impacts based on current free energy of hydration model theory (Jantzen et al. 1995). These glasses will be batched and melted under conditions that target both the projected compositions and intended REDOX states. Durability (as measured by the PCT) will be experimentally determined for each glass in triplicate using standard procedures (ASTM 2002). The measured response will then be compared to model based predictions to assess the applicability and/or potential conservatism of the model under REDOX activated conditions. The experimental results will be the focus of a subsequent report.

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DOE	Department of Energy
DWPF	Defense Waste Processing Facility
EA	Environmental Assessment
EV	extreme vertice
HLW	high level waste
IRD	Independent Research and Development
MAR	Measurement Acceptability Region
NL [B]	normalized boron release
PAR	Property Acceptability Region
PCCS	Product Composition Control System
PCT	Product Consistency Test
REDOX	REDuction/Oxidation
SB	sludge batch
SME	Slurry Mix Evaporator
SRS	Savannah River Site
SRTC	Savannah River Technology Center
THERMO^{TM}	Thermodynamic Hydration Energy Reaction Model
T_L	liquidus temperature
TTR	technical task request
WVDP	West Valley Demonstration Project
WL	waste loading

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1.0 INTRODUCTION

Approximately 130M L of sludge/supernate high-level radioactive waste (HLW) is currently stored in underground carbon steel tanks at the Savannah River Site (SRS) in Aiken, South Carolina. The Defense Waste Processing Facility (DWPF) began immobilizing these wastes in borosilicate glass in 1996. Currently, the radioactive glass is being produced as a "sludge-only" composition by combining high-level sludge with glass frit and melting. The molten glass is poured into stainless steel canisters that will eventually be stored in a permanent geological repository.

Prior to acceptance and processing of a sludge batch (SB) in the DWPF, completion of the waste qualification process is required. One phase of this process is a glass variability study as required by the DWPF Glass Product Control Program (Ray et al. 2003). In general, the objective of a variability study is to determine if the durability – ΔG_P (preliminary glass dissolution estimator based on free energy of hydration expressed in kcal/mol) correlation currently utilized by DWPF applies to the projected compositional region for the sludge batch to be processed.

Recent glass formulation activities have focused on developing alternative frit compositions for use with specific sludge batches (Peeler and Edwards (2002)) to maximize melt rate and/or waste throughput. The general trend has been to increase the total alkali content in the glass through the use of a high alkali based frit, a less washed sludge, or a combination of the two. As the alkali content of the glass continues to increase, predicted durability (as measured by the Product Consistency Test (PCT)) can become a limiting factor in defining the projected operating windows for the DWPF. Historically, predicted liquidus temperatures (T_L) have limited access to higher waste loadings (WLs) for SB1A, SB1B, and SB2. Recent frit development efforts for SB3 indicated that durability can become the limiting property if alkali contents are challenged and thus the objectives of the variability study become more interesting as durabilities are typically measured over a waste loading interval of interest.

One of the issues addressed in recent studies (Peeler and Edwards 2004a and 2004b) has been an assessment of the potential impact of REDuction/OXidation (REDOX) on the PCT response given the implementation of a revised PCCS algorithm (Brown, Postles, and Edwards (2002)), which has the capability to introduce a REDOX sensitive term (i.e., a ΔG_i term for FeO) into the durability evaluation. The results from those studies (primarily model-based predictions) indicated that the projected operational windows for various systems may be significantly altered given activation of the REDOX term in PCCS. This became a more significant issue during processing of SB1B, when SRTC recommended an acid addition strategy change whose intent was to improve melt rate or sludge processing based on a revised REDOX correlation (Lambert and Boley (1998)). The primary effect from the recommendation was to shift the REDOX of the system from a highly oxidizing feed toward a targeted $Fe^{2+}/\Sigma Fe$ of 0.2. Although the new acid addition strategy was implemented, the revised PCCS algorithm was not in place and therefore the SME acceptability decisions did not include or account for the potential impact of REDOX based on model predictions. However, with this system being T_L limited issues of REDOX on durability were of minimal concern.

With respect to durability, the theory supporting the model suggests that as the $Fe^{2+}/\Sigma Fe$ ratio shifts from a fully oxidized state toward the upper limit of 0.33, the durability of the glass should decrease given the presence of FeO in the glass (Jantzen et al. (1995)). Assuming a targeted REDOX > 0, the durability model partitions the REDOX of select species (e.g., Fe) based on assigned ΔG_i values (Jantzen et al. (1995)). The ΔG_i value for FeO is -21.33 kcal/mol compared to a +14.56 kcal/mol value for Fe_2O_3.[1]

[1] More positive ΔG_i values enhance the predicted durability. As a reference, the ΔG_i values for Al_2O_3 and Na_2O are 37.68 and -44.99 kcal/mole, respectively.

Thus, there is a negative impact on the predicted durability response (via the ΔG_p model) as REDOX shifts from fully oxidized to the REDOX upper limit (for the same targeted glass composition) – the glass is predicted to become less durable. For those systems in which the upper or lower waste loading limit is defined by the ΔG_p Slurry Mix Evaporator (SME) acceptability criterion, as REDOX transitions from fully oxidized toward the more reduced state, the result will be to reduce the waste loading range over which acceptability would be classified. The extent or magnitude of the ΔG_P shift (and ultimately the potential impact on the projected operation window) is highly influenced by the Fe concentration and the REDOX shift. Peeler and Edwards (2002) provided a matrix to indicate the difference in ΔG_i prediction as a function of Fe concentration and REDOX.[2]

Peeler and Edwards (2004a and 2004b) demonstrated that activation of the REDOX term in PCCS was not warranted for the Frit 200 / SB2 and Frit 320 / SB2 systems. This was accomplished by model-based predictions and experimental assessments over a range of REDOX values from 0.0 to 0.33 (Fe^{2+}/Fe_{total}). The experimental results indicated that measured PCT response for the same targeted glass composition that varied in REDOX showed no significant differences. More specifically, the effect of REDOX on that composition is within the random variation expected for the development of the model. These results support the hypothesis that an interaction between REDOX and the overall glass composition has not been accurately captured by the current ΔG_P model. These results provided further evidence that the application of the FeO ΔG_i value without consideration of the overall glass composition may lead to a more significant ΔG_P shift (larger magnitude) than needed. Use of this potentially conservative ΔG_i value was not only a concern for the Frit 320 / SB2 system, but also for future sludge batches in which PCT predictions bound the upper or lower waste loading. In fact, there is also a concern that systems limited by another property (such as T_L or viscosity) under fully oxidizing conditions may become durability limited under more reduced conditions.

In this report, a more detailed assessment of the potential compositional interactive effects on the measured durability response are examined. To provide a sound, technical basis, the theory supporting the current durability model is discussed with respect to REDOX. Assessments are then performed to gain insight into the potential compositional effects that are not accounted for in the current model. Finally, a test matrix is developed from which further insight into these compositional effects can be determined through an experimental assessment. It is noted that the information reported in this study is based solely on existing data with the results of the experimental portion to be documented elsewhere.

Objectives for this task are specified in Section 2.0. In Section 3.0, the impact of REDOX on durability is presented from both a theoretical and an experimental viewpoint. Section 4.0 summarizes an assessment of the data used to develop the current durability model with respect to potential interactive effects. In Section 5.0, the strategy of defining an experimental program to provide further insight into the effects of specific glass components on durability is discussed. The discussions lead into the development of a 45 glass test matrix which is also presented in Section 5.0. A summary is provided in Section 6.0.

[2] The matrix reported by Peeler and Edwards (2003) is provided in Appendix A of this report.

2.0 OBJECTIVES

The objectives of this task are to assess: (1) the impact of REDOX on glass durability (as measured by the Product Consistency Test (PCT)) and (2) the interactive effects that may mitigate the predicted negative impacts based on current model theory. These objectives will be addressed through a 2-phased approach. In Phase 1, data will be generated regarding the impact of REDOX on durability within a specific glass forming system (i.e., Frit 418 – SB2/3). The Phase 1 data will focus primarily on the impact of Al_2O_3 on the durability response over a range of REDOX values. The durability response will be measured and compared to model based predictions to assess the applicability and/or potential conservatism of the model under REDOX activated conditions. The Phase 1 data will also serve as a baseline for the Phase 2 glasses.

In Phase 2, the primary focus will be on the relationships among Al_2O_3, the sum of alkali, REDOX and durability. The Phase 2 results should provide guidance in terms of identifying a critical Al_2O_3 concentration in which the activation (or deactivation) of the REDOX term in PCCS would be dependent upon. It should be noted that this is a limited study and that although the results may show a significant compositional interaction, application of the findings may be restricted to the compositional region under consideration (i.e., may not be extrapolated).

This work was performed under the Savannah River Technology Center (SRTC) Independent Research and Development (IRD) Program, which was funded by the Department of Energy (DOE) Environmental Management Office of Science and Technology. Although this work was not performed in support of a specific Task Technical Request (TTR), it was performed according to the WSRC QA Program that is responsive to DOE Order 5700.6C, *Quality Assurance*, 10 CFR 830.120, "Quality Assurance", and other special quality program requirements, as defined in WSRC-RP-92-225, "WSRC Quality Assurance Management Plan", and as directed by the U.S. DOE. These programs are implemented through the use of the 1Q, WSRC QA Manual.

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3.0 THEORETICAL ASSESSMENT: REDOX VS. DURABILITY

The following discussion presents various scenarios of the theoretical impact of REDOX on PCT from both a predictability and an acceptability viewpoint. Predictability being based on the 95% two-sided confidence interval for an individual PCT response as generated by the ΔG_P model (Jantzen et al. 1995). Acceptability being defined based on the measured normalized release compared to log NL [B] = 1.0 g/L – a threshold established by Edwards and Brown (1998) in a review of data to identify alternative criteria for the homogeneity constraint. Use of the term "processable" is judged by the relationship of the measured SME products' predicted ΔG_P to the SME acceptability ΔG_P criterion of -12.7808 kcal/mol and ultimately the projected operating window.[3]

Hypothetically, consider a fully oxidized glass that is both predictable and processable. As the REDOX of this glass is shifted toward the more reduced state this glass could become unpredictable, unprocessable, and/or unacceptable. Figure 3-1 illustrates this concept. Point A is a glass that falls within the 95% confidence bands (i.e., the glass is predictable) and has a predicted ΔG_P more positive than the -12.7808 kcal/mol PAR SME acceptance criterion (i.e., the glass would be classified as processable from a durability perspective). Point B is the same targeted glass composition with the exception that REDOX has shifted to a more reduced state and it has been assumed that there was no practical impact of REDOX on the measured PCT response. Given the anticipated partitioning of both FeO and Fe_2O_3, this glass is now unpredictable (shifted outside the lower 95% confidence band) but would still be considered processable given its ΔG_P is more positive than the -12.7808 kcal/mol acceptance criterion. In the case of Point B, the model would be considered "conservative" given it over predicted the actual measured release.

The magnitude of the ΔG_P shift from Point A to Point B is solely dependent upon the application of the ΔG_i values for Fe_2O_3 and FeO, the concentration of Fe in the glass, and the shift in REDOX. Again, Points A and B are compositionally identical but differ in the targeted REDOX value. Appendix A provides a matrix of the ΔG_P impact as a function of Fe concentration in glass and REDOX. Referring to Table A.1 in Appendix A, assume Point A is an oxidized glass with a Fe concentration of 7 wt% and a predicted ΔG_P value of -10.0 kcal/mol. If the REDOX were shifted to 0.2 ($Fe^{2+}/\Sigma Fe$), the predicted impact or shift in terms of ΔG_P (strictly from partitioning and application of the ΔG_i values) would be -0.7172 kcal/mol – resulting in a predicted value for the more reduced version of that same glass (Point B) of -10.7172 kcal/mol which would still be acceptable from a SME acceptability standpoint. Based on the values shown in Appendix A, the higher the Fe concentration in glass and the larger the REDOX difference, the higher the magnitude of the shift. For those glass systems whose ΔG_P value already challenges the SME acceptability limit under oxidizing conditions, the probability of being classified as "unprocessable" from a prediction standpoint with a shift in REDOX is relatively high.

Referring back to Figure 3-1 and using Point B as a reference, as the $Fe^{2+}/\Sigma Fe$ ratio increases (i.e., the glass becomes more reduced), there is a possibility that the glass would become unpredictable and classified as unprocessable given the ΔG_P predicted value (again assuming no practical impact on the measured PCT – Point C). The fact that it is both unpredictable and unprocessable would be justified if the measured release challenged the Environmental Assessment (EA) (Jantzen et al. 1993) acceptance

[3] This value is the SME Acceptability value at the Property Acceptance Region (PAR) and will be used as a measure of acceptability in this section. The more restrictive Measurement Acceptance Region (MAR) value is not used given it is dependent upon the glass composition and thus the value changes with each glass. It should be noted that a glass deemed unacceptable at the PAR would be classified as unacceptable at the MAR given the restriction is ΔG_P based. Also note that the value of -12.7808 is the PAR limit for the pending version of PCCS. It is anticipated that this version of PCCS will be implemented in the near future.

criteria (Point D). If not, the conservatism in the model could limit access to both compositional and REDOX space that would produce an acceptable glass (Point C).

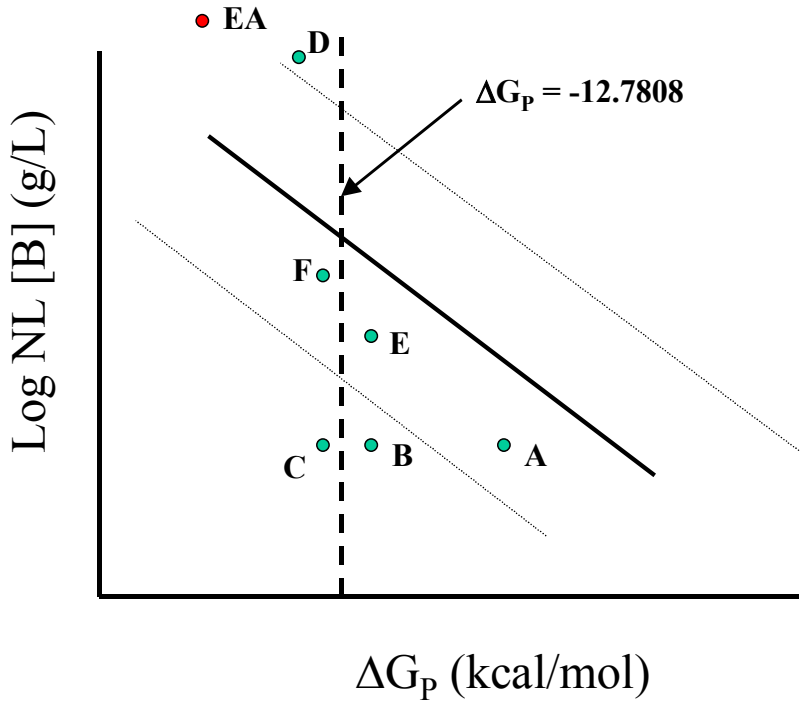

Figure 3-1. Schematic of ΔG_P vs. log NL [B] and Potential Prediction Scenarios.

Points E and F conceptualize the option in which an increase in the measured normalized boron release (NL [B]) occurs as REDOX transitions from the oxidized to the reduced state. Both points are predictable (lie within the 95% confidence bands) but Point E is processable from a PCCS perspective while Point F is not. In these cases, the impact of converting Fe_2O_3 to FeO as the glass becomes more reduced, does result in a higher NL [B] which falls within the 95% prediction bands of the model.

The concern for future sludge batches in which PCT predictions define the upper or lower waste loading, is the possibility that the conservatism in the model and/or the SME acceptability limit may restrict access to compositional regions of interest to DWPF. This is of particular interest to those systems which are PCT limited as a result of enhanced alkali concentration stemming from either the frit, less washed sludge, or both in an attempt to improve WL, melt rate, or waste throughput.

4.0 THE EFFECT OF GLASS COMPOSITION ON THE REDOX – DURABILITY INTERACTION: A LITERATURE REVIEW

The theory supporting the REDOX term in ΔG_P implies that the overall glass composition does not play a role in determining the magnitude of the shift in the ΔG_P value but that the shift is strictly a function of the Fe concentration and change in REDOX. Feng et al. (1990) studied the effect of REDOX on durability for West Valley Demonstration Project (WVDP) waste glasses. It was concluded that the REDOX effects on durability are strongly dependent on glass composition – not just on the Fe concentration. More specifically, the leach rate differed by a factor of 12 from the most oxidized to the most reduced glass at low Al_2O_3 concentrations (~3.3 wt%), while the factor fell to below 2 for glass compositions with higher Al_2O_3 concentrations (~5.7 wt% and ~9.9 wt%). Therefore, the application of the ΔG_i values without consideration of the overall glass composition may lead to a more significant ΔG_P shift (larger magnitude) than needed. The impact could be to restrict access to certain compositional regions of interest. This latter statement is based on the assumption that the potential effects of components such as Al_2O_3 have not been accounted for in the overall ΔG_P prediction with the REDOX term activated. This does not suggest that there is not an effect of REDOX on durability, but that the predicted effect via ΔG_P may be overly conservative without consideration of other possible compositional effects.

A review of the data used to develop PCCS (in particular the ΔG_P model) also shows the structure of a possible Al_2O_3 – REDOX interaction that is not accounted for. Figure 4-1 is a plot of the original THERMO^{TM} (ΔG_P) (Jantzen et al. 1995) fit with a 95% prediction interval for individual PCTs for glasses with reported REDOX values greater than or equal to 0.025 (not fully oxidized). The labels provided on select glasses correspond to the REDOX ($Fe^{2+}/\Sigma Fe$) and Al_2O_3 concentration (wt%) in glass, respectively. Although predictability or applicability of the ΔG_P model is typically of primary interest, the focus of this report is the impact of REDOX on the measured PCT response and an attempt to discern any first order compositional effects.

First, consider the "cluster" of labeled glasses that lie near the upper 95% confidence interval in Figure 4-1. The measured log NL [B] and ΔG_P values range from approximately 0.5 – 0.7 g/L and -11 to -13 kcal/mol, respectively. Compositionally, these glasses have relatively low Al_2O_3 concentrations ranging from approximately 1.4 – 3.0 wt% in glass. It is well known that Al_2O_3 suppresses the formation of amorphous phase separation in borosilicate glasses (Volf 1974; Jantzen et al. 1995; Jantzen and Brown 2000; Hrma et al. 1994) and that sufficient quantities of Al_2O_3 have a positive impact on durability (usually independent of any homogeneity classification). Thus the glasses in this cluster suggest a potential for REDOX to have a more significant impact on glass durability when coupled with lower Al_2O_3 concentrations. At the lower Al_2O_3 concentrations, there is an indication that the model actually under predicts the PCT response; this was one of the primary drivers for implementing a lower Al_2O_3 limit in PCCS (Brown, Postles, and Edwards 2002).

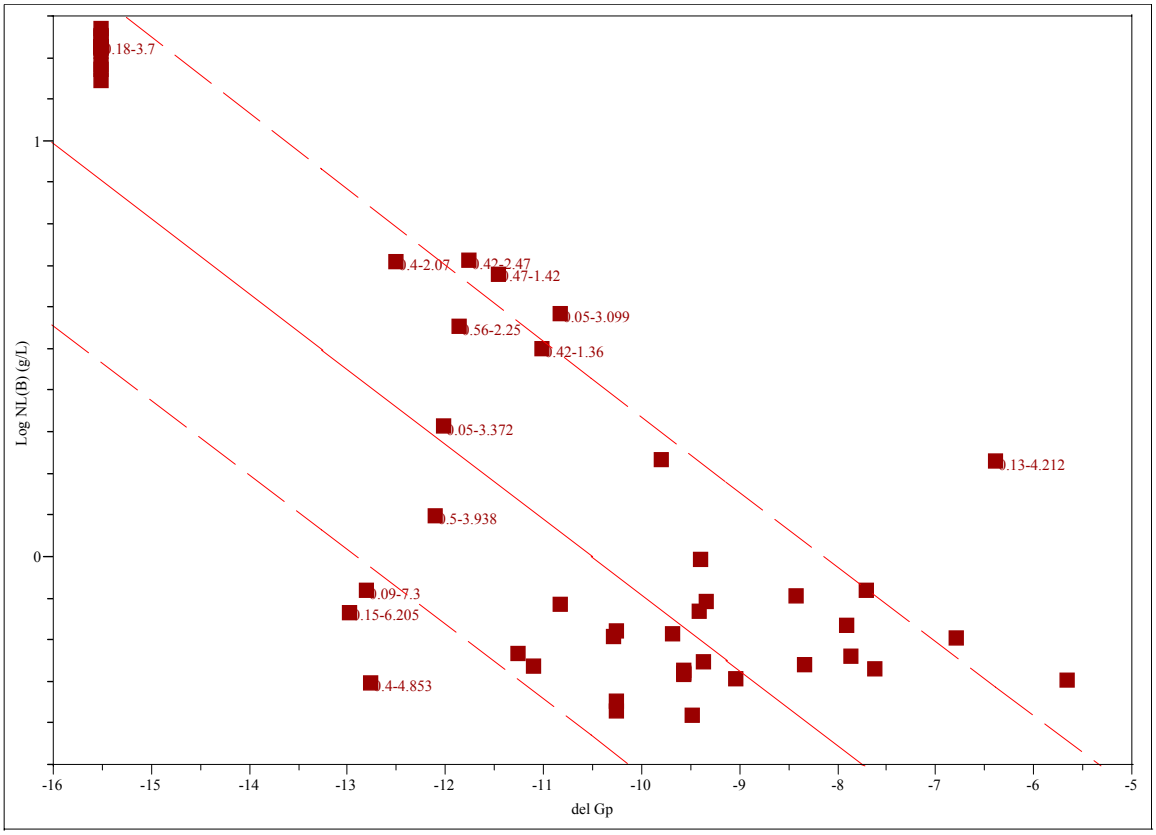

Figure 4-1. log NL [B] Versus for ΔG_P with a 95% prediction interval for the THERMO^{TM} glasses with reported REDOX values greater than 0.

As the concentration of Al_2O_3 increases (i.e., > 3.0 wt% for the THERMO^{TM} glasses shown in (Figure 4-1), the measured NL [B] release decreases (durability increases) even with an active REDOX term. In fact, for four of the labeled THERMO^{TM} glasses containing high Al_2O_3 concentrations (~ 4.0 wt% or greater), the model over-predicts the PCT response (i.e., the model is conservative). Three of the four glasses are not predictable by the model as they are located below the lower 95% confidence limit. Although these glasses are not predictable, they are acceptable with respect to their measured normalized release values as compared to the EA release values. These glasses may also be classified as unprocessable as their ΔG_P values lie close to (if not more negative than) the SME PAR acceptability limit (i.e., -12.7808 kcal/mol). The resulting impact is to unnecessarily restrict access to glass compositional regions that may be of interest to DWPF processing. As previously stated, the effects of overall glass composition, REDOX, and Al_2O_3 on durability are suggested by these data. The data indicate that a possible interaction between overall glass composition (in particular Al_2O_3 content) and REDOX has not been accounted for in the current ΔG_P prediction. In principle, these data agree with those reported by Feng et al. (1990).

To provide further insight into the possible interaction between REDOX and Al_2O_3, a modeling effort was performed as part of this study using the THERMO^{TM} database. The modeling effort added three terms to the current ΔG_P model for log NL [B (g/L)]: REDOX (as measured by Fe^{2+}/Fe^{3+}), Al_2O_3, and a REDOX × Al_2O_3 interaction term. Table 4-1 summarizes the results from the modeling effort, which indicate that all of the added terms are statistically significant at a confidence level of 95%. Moreover, the estimated effects for these data suggest that the normalized boron release increases with increasing REDOX,

increases slightly with increasing Al_2O_3 (wt%) content, but decreases dramatically as both REDOX and Al_2O_3 (wt%) content increase. These results suggest an interaction between REDOX and glass composition that is not fully captured by the ΔG_P model.

This analysis provides further evidence that the application of the FeO ΔG_i value without consideration of the overall glass composition may lead to a more significant ΔG_P shift (larger magnitude) than needed. Again, this does not suggest that there is not an effect of REDOX on durability, but that the predicted effect using the FeO ΔG_i term may be conservative without consideration of other possible compositional effects. Therefore, activation of the REDOX term in PCCS may have a significant impact on the predicted operational windows based on model predictions, but may not represent the realistic impact on the measured durability.

Table 4-1. Results of Modeling Effort with REDOX, Al_2O_3, and Interactive Terms Included.

Response Log NL(B) (g/L)
Summary of Fit

Rsquare	0.82287
RSquare Adj	0.817247
Root Mean Square Error	0.191188
Mean of Response	-0.02685
Observations (or Sum Wgts)	131

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	4	21.395784	5.34895	146.3353
Error	126	4.605635	0.03655	Prob > F
C. Total	130	26.001420		<.0001

Lack Of Fit

Source	DF	Sum of Squares	Mean Square	F Ratio
Lack Of Fit	83	4.5276155	0.054550	30.0645
Pure Error	43	0.0780199	0.001814	Prob > F
Total Error	126	4.6056354		<.0001
				Max RSq
				0.9970

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	-2.12974	0.14495	-14.69	<.0001
del Gp	-0.181955	0.009969	-18.25	<.0001
Al2O3(v)	0.0360392	0.011564	3.12	0.0023
REDOX	2.0824063	0.3728	5.59	<.0001
REDOX*Al2O3(v)	-0.415497	0.104149	-3.99	0.0001

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5.0 GLASS SELECTION PROCESS

Given the results of the THERMO^{TM} dataset for reduced glasses, the potential conservatism built into the current ΔG_P model (via application of the "constant" FeO ΔG_i value) may unnecessarily limit access to compositional regions of interest. To address this potential, a 2-phased program has been defined to experimentally assess the applicability/predictability of the ΔG_p model and the acceptability of the resulting glasses to a "local" and "global" compositional region of interest with REDOX activated.

Glasses are to be selected to provide ample opportunity for REDOX to have a significant impact on durability for glass compositions that challenge the SME acceptability envelope. With respect to providing ample opportunity for a REDOX effect to be observed, REDOX states ranging from fully oxidized to a targeted REDOX of 0.33 (the upper acceptance limit) are to be used. Targeting identical glass compositions while varying the REDOX state should provide an opportunity to assess the impact of REDOX on durability as defined by the PCT and predicted by the model.

5.1 The Glass Selection Process Strategy

In this section, the general strategy for selecting a test matrix is presented. The strategy spans both a "local" (Phase 1) and "global" (Phase 2) approach. The "local" approach is based on obtaining insight of the compositional effects (in particular Al_2O_3) on durability within a specific glass forming system. The Frit 418 – SB2/3 flowsheet was selected and will serve as a baseline from which further compositional interactions can be assessed (Phase 2). Lorier et al. (2003) demonstrated that model-based predictions of durability within this system were extremely conservative with the activation of the REDOX term in PCCS as compared to the measured durability response (i.e., glasses predicted to be non-durable by the model were acceptable based on the measured durability response). These conclusions were based on comparisons of model-based predictions with experimental assessments of durability for nominal sludge compositions – that is, they did not account for possible compositional variation in the sludge. The "local" strategy of this study will be based on a pool of extreme vertices (EVs) generated by Lorier et al. (2003) that introduce potential variation in sludge composition. This series of glasses will be referred to as Phase 1 and will provide a baseline from which compositional adjustments can be made to assess the potential Al_2O_3 concentration effects in Phase 2.

The "global" approach (or Phase 2) will focus on identifying a potential Al_2O_3 concentration that when exceeded the impact of REDOX on durability is mitigated. The Phase 2 glasses will attempt to define a lower Al_2O_3 limit which requires activation of the REDOX term in PCCS. It should be noted, that currently the lower Al_2O_3 limit is set a 3.0 wt% in PCCS (associated with the sum of alkali and Al_2O_3 constraints associated with durability as defined by Herman et al. (2002)). Application of the Measurement Acceptability Region (MAR) uncertainties increases this lower limit to ~ 3.1 wt% Al_2O_3. Thus there is no driver to assess lower Al_2O_3 concentrations as part of this study. In addition, given an Al_2O_3 concentration of at least 4 wt% in glass, Herman et al. (2002) did not impose a secondary criterion associated with the sum of alkali. That is, based on the data in hand, if the Al_2O_3 concentration in the glass was at least 4 wt%, there was no restriction on the sum of alkali with respect to ensuring a durable glass product. It is noted that that assessment was limited to glasses with relatively low sum of alkali and should not be used out of context. Thus the interval of Al_2O_3 concentrations of interest for the Phase 2 portion to this study will be 3 – 4 wt% Al_2O_3.

5.2 Phase 1

The glass selection strategy for Phase 1 was to identify a series of Frit 418 – SB2/3 EVs (from Lorier et al. 2003) which when assessed fully oxidized would be classified as "processable / acceptable" based on the PCCS MAR criteria. To met the programmatic objectives, a portion of this set of glasses should transition to an "unacceptable" classification (failing only durability) as REDOX shifts from fully oxidized to a target of 0.2. As REDOX continues to shift to the more reduced state (e.g., target of 0.33), all Phase 1 glasses should be classified as "unacceptable" with respect to durability. This selection strategy will allow for an assessment of the impact of REDOX on durability within this specific system as well as provide insight into the potential interactive compositional effects ignored by the current model. In addition, Phase 1 will serve as a baseline for Phase 2.

To provide guidance in the glass selection process for Phase 1, an assessment of the number of EVs that fail at various REDOX states was undertaken. Of the 1794 EVs identified by Lorier et al.(2003), 951 glasses were classified as acceptable at any targeted REDOX state ranging from 0.0 to 0.33. When a REDOX target of 0.33 was considered, 767 of the 1794 EV-based glasses were classified as "unacceptable". There were only 76 of the 1794 EV-based glasses that were classified as "unacceptable" at REDOX values of 0.2 and 0.33. Five specific EVs (#12, #44, #83, #548, and #1607 in Table 5-1) were selected to meet the Phase 1 objectives. More specifically, under fully oxidizing conditions, all five glasses are classified as "acceptable" based on model predictions. At a REDOX target of 0.2, three of the five glasses remain "acceptable" the other two (#44 and #83) are predicted to be unacceptable with respect to durability. Note the only difference is the partitioning between Fe^{3+} and Fe^{2+} and based on theory the result is a less durable product – even though the Al_2O_3 concentrations are 4.9 wt% or higher for all five glasses. At a target REDOX of 0.33, all five glasses are classified as "unacceptable" based on predictions of durability. Again, the ΔG_i value associated with FeO is driving the glasses toward a more negative ΔG_P past the point of "acceptability" (based on model predictions).

These five EV-based glasses will be produced targeting REDOX values of 0.0, 0.2, and 0.33. Therefore a total of 15 glasses will define the Phase 1 portion of the overall test matrix. Table 5-1 summarizes the target compositions of the 5 "baseline" Phase 1 glasses (assuming fully oxidizing conditions).
The targeted Al_2O_3 concentration in the Phase 1 glasses ranges from 4.9 to 5.7 wt% in glass. Previous results suggested that Al_2O_3 contents of ~4% or greater mitigated the predicted negative effects of REDOX on durability (see Section 4.0). The targeted sum of alkali content of the Phase 1 glasses range from 17.9 to 18.6 wt% in glass.

5.3 Phase 2

The primary objective of Phase 2 is to assess if there is a critical Al_2O_3 content which requires activation of the REDOX term in PCCS. Phase 2 will leverage the pending results of the Phase 1 matrix from the standpoint that the Al_2O_3 concentrations for the 5 baseline Phase 1 glasses will be adjusted to target 3.25 and 3.75 wt% (down from 4.9 or 5.7 wt%). The difference between the Al_2O_3 contents (original basis and the Phase 2 targets) for each glass will be consumed by Fe_2O_3. That is, the lower Al_2O_3 content required in the Phase 2 glasses will be balanced with an equal increase in the Fe_2O_3 concentration. Once REDOX is activated, this should exaggerate the predicted impact of REDOX on durability (lower Al_2O_3 concentrations will decrease durability (all other factors constant) and more Fe_2O_3 will partition into a higher concentration of FeO which should also decrease durability based on model predictions). As an example, consider EV #12 associated with the Phase 1 matrix (see Table 5-1). The target Al_2O_3 and Fe_2O_3 concentrations for this glass (assuming fully oxidized conditions) are 4.977 and 11.189 wt%, respectively. In Phase 2, when the Al_2O_3 content is targeted to be 3.75% (a 1.227 wt% difference) for EV #12, the Fe_2O_3 content is increased to 12.416 wt% (up from 11.189 wt% in the Phase 1 glass – a balance of 1.227 wt% Fe_2O_3). The counter-part Phase 2 glass that targets a 3.25 wt% Al_2O_3 content, increases its

Fe_2O_3 content by 1.727 wt% (from 11.189 wt% in Phase 1 to 12.916 wt% in Phase 2). All other components between the Phase 1 baseline glass and the two Phase 2 glasses remain the same.

Table 5-2 summarizes the ten "baseline" Phase 2 glasses assuming fully oxidized conditions. Given each glass will be fabricated targeting a REDOX state of 0.0, 0.2, and 0.33, thirty glasses will define the Phase 2 matrix.

Table 5-3 summarizes the target compositions of the 45 test matrix glasses (Phase 1 and Phase 2). The glasses have been grouped according to the targeted REDOX state (not as a function of Phase 1 or Phase 2). A unique "Glass ID" ("RX" followed by a number) is also shown in Table 5-3 for each glass which will be used in subsequent reports for identification purposes.

Table 5-4 summarizes the MAR-based assessments for each targeted glass composition. For those glasses in which REDOX is a non-zero value (i.e., those glasses targeting a 0.2 or 0.33 REDOX state), the assessments partitioned the appropriate quantity of Fe into the 3+ and 2+ states. More specifically, the REDOX term in PCCS was activated for the assessments. Given durability is the only model with a REDOX sensitive term, all other property predictions remain constant. A review of the MAR assessment indicates that the objectives of this task have been met (at least on paper). That is, all of the Phase 1 glasses when considered fully oxidized (RX-1 through RX-5) are classified as acceptable – no property is listed in the "Failed MAR" column. When REDOX is adjusted to target 0.2, three of the five glasses remain "acceptable" based on model predictions. RX-17 (EV #44) and RX-18 (EV #83) are classified as "unacceptable" based on ΔG_P predictions. When the REDOX target is 0.33, all five glasses are classified as "unacceptable" based on ΔG_P predictions. The transition of completely acceptable, to partially acceptable, to total unacceptable meets the intent of the Phase 1 objective.

With respect to the Phase 2 glasses, the strategy was to identify a potential Al_2O_3 concentration that when exceeded the impact of REDOX on durability is mitigated. There was no built-in strategy with respect to the number of glasses failing durability as a function of REDOX. The information presented in Table 4-5 indicates that all the fully oxidized glasses targeting both 3.25 and 3.75 wt% Al_2O_3 are classified as "acceptable" based on the MAR assessment. Transitioning to a target REDOX of 0.2, all of the "lower" Al_2O_3 glasses (targeting 3.25 wt%) are classified as "unacceptable" (failing the durability MAR criterion). Four of the five "higher" Al_2O_3 glasses (targeting 3.75 wt%) are also classified as "unacceptable". RX-25 being the only Phase 2 glass that remained "acceptable" once REDOX was increased to 0.2. At a target REDOX of 0.33, all of the Phase 2 glasses are classified as "unacceptable" regardless of Al_2O_3 content.

Table 5-1. Target Compositions of the Five "Baseline" Phase 1 Glasses (wt%, calcined oxide basis).

Phase	EV	Al_2O_3	B_2O_3	BaO	CaO	Ce_2O_3	Cr_2O_3	CuO	Fe_2O_3	K_2O	La_2O_3	Li_2O	MgO	MnO	Na_2O	NiO	PbO	SiO_2	TiO_2	U_3O_8	ZnO	ZrO_2
Phase 1	12	4.977	5.200	0.049	1.120	0.079	0.081	0.028	11.189	0.349	0.038	5.200	1.348	2.151	13.057	0.591	0.048	50.464	0.008	3.872	0.052	0.087
Phase 1	44	4.977	5.200	0.049	1.120	0.079	0.081	0.028	11.285	0.349	0.038	5.200	1.348	2.500	13.057	0.687	0.048	50.464	0.008	3.332	0.052	0.087
Phase 1	83	5.157	5.200	0.057	1.120	0.092	0.094	0.032	10.634	0.349	0.044	5.200	1.348	2.500	13.057	0.687	0.056	50.316	0.009	3.872	0.061	0.101
Phase 1	548	5.775	5.200	0.049	1.120	0.079	0.081	0.028	10.634	0.349	0.038	5.200	1.348	2.500	13.057	0.687	0.048	50.316	0.008	3.332	0.052	0.087
Phase 1	1607	4.977	5.200	0.049	0.964	0.079	0.081	0.028	12.359	0.349	0.038	5.200	1.348	2.500	12.384	0.591	0.048	50.316	0.008	3.332	0.052	0.087

Table 5-2. Target Compositions of the Ten "Baseline" Phase 2 Glasses (wt%, calcined oxide basis).

Phase	EV	Al_2O_3	B_2O_3	BaO	CaO	Ce_2O_3	Cr_2O_3	CuO	Fe_2O_3	K_2O	La_2O_3	Li_2O	MgO	MnO	Na_2O	NiO	PbO	SiO_2	TiO_2	U_3O_8	ZnO	ZrO_2
Phase 2	12	3.750	5.200	0.049	1.120	0.079	0.081	0.028	12.416	0.349	0.038	5.200	1.348	2.151	13.057	0.591	0.048	50.464	0.008	3.872	0.052	0.087
Phase 2	44	3.750	5.200	0.049	1.120	0.079	0.081	0.028	12.511	0.349	0.038	5.200	1.348	2.500	13.057	0.687	0.048	50.464	0.008	3.332	0.052	0.087
Phase 2	83	3.750	5.200	0.057	1.120	0.092	0.094	0.032	12.041	0.349	0.044	5.200	1.348	2.500	13.057	0.687	0.056	50.316	0.009	3.872	0.061	0.101
Phase 2	548	3.750	5.200	0.049	1.120	0.079	0.081	0.028	12.660	0.349	0.038	5.200	1.348	2.500	13.057	0.687	0.048	50.316	0.008	3.332	0.052	0.087
Phase 2	1607	3.750	5.200	0.049	0.964	0.079	0.081	0.028	13.585	0.349	0.038	5.200	1.348	2.500	12.384	0.591	0.048	50.316	0.008	3.332	0.052	0.087
Phase 2	12	3.250	5.200	0.049	1.120	0.079	0.081	0.028	12.916	0.349	0.038	5.200	1.348	2.151	13.057	0.591	0.048	50.464	0.008	3.872	0.052	0.087
Phase 2	44	3.250	5.200	0.049	1.120	0.079	0.081	0.028	13.011	0.349	0.038	5.200	1.348	2.500	13.057	0.687	0.048	50.464	0.008	3.332	0.052	0.087
Phase 2	83	3.250	5.200	0.057	1.120	0.092	0.094	0.032	12.541	0.349	0.044	5.200	1.348	2.500	13.057	0.687	0.056	50.316	0.009	3.872	0.061	0.101
Phase 2	548	3.250	5.200	0.049	1.120	0.079	0.081	0.028	13.160	0.349	0.038	5.200	1.348	2.500	13.057	0.687	0.048	50.316	0.008	3.332	0.052	0.087
Phase 2	1607	3.250	5.200	0.049	0.964	0.079	0.081	0.028	14.085	0.349	0.038	5.200	1.348	2.500	12.384	0.591	0.048	50.316	0.008	3.332	0.052	0.087

Table 5-3. Target Compositions of the Phase 1 and Phase 2 Glasses (wt%, oxide calcine basis).

Glass ID	Phase	Redox	EV	Al_2O_3	B_2O_3	BaO	CaO	Ce_2O_3	Cr_2O_3	CuO	Fe_2O_3	K_2O	La_2O_3	Li_2O	MgO	MnO	Na_2O	NiO	PbO	SiO_2	TiO_2	U_3O_8	ZnO	ZrO_2
RX-1	Phase 1	0	12	4.977	5.200	0.049	1.120	0.079	0.081	0.028	11.189	0.349	0.038	5.200	1.348	2.151	13.057	0.591	0.048	50.464	0.008	3.872	0.052	0.087
RX-2	Phase 1	0	44	4.977	5.200	0.049	1.120	0.079	0.081	0.028	11.285	0.349	0.038	5.200	1.348	2.500	13.057	0.687	0.048	50.464	0.008	3.332	0.052	0.087
RX-3	Phase 1	0	83	5.157	5.200	0.057	1.120	0.092	0.094	0.032	10.634	0.349	0.044	5.200	1.348	2.500	13.057	0.687	0.056	50.316	0.009	3.872	0.061	0.101
RX-4	Phase 1	0	548	5.775	5.200	0.049	1.120	0.079	0.081	0.028	10.634	0.349	0.038	5.200	1.348	2.500	13.057	0.687	0.048	50.316	0.008	3.332	0.052	0.087
RX-5	Phase 1	0	1607	4.977	5.200	0.049	0.964	0.079	0.081	0.028	12.359	0.349	0.038	5.200	1.348	2.500	12.384	0.591	0.048	50.316	0.008	3.332	0.052	0.087
RX-6	Phase 2	0	12	3.750	5.200	0.049	1.120	0.079	0.081	0.028	12.416	0.349	0.038	5.200	1.348	2.151	13.057	0.591	0.048	50.464	0.008	3.872	0.052	0.087
RX-7	Phase 2	0	44	3.750	5.200	0.049	1.120	0.079	0.081	0.028	12.511	0.349	0.038	5.200	1.348	2.500	13.057	0.687	0.048	50.464	0.008	3.332	0.052	0.087
RX-8	Phase 2	0	83	3.750	5.200	0.057	1.120	0.092	0.094	0.032	12.041	0.349	0.044	5.200	1.348	2.500	13.057	0.687	0.056	50.316	0.009	3.872	0.061	0.101
RX-9	Phase 2	0	548	3.750	5.200	0.049	1.120	0.079	0.081	0.028	12.660	0.349	0.038	5.200	1.348	2.500	13.057	0.687	0.048	50.316	0.008	3.332	0.052	0.087
RX-10	Phase 2	0	1607	3.750	5.200	0.049	0.964	0.079	0.081	0.028	13.585	0.349	0.038	5.200	1.348	2.500	12.384	0.591	0.048	50.316	0.008	3.332	0.052	0.087
RX-11	Phase 2	0	12	3.250	5.200	0.049	1.120	0.079	0.081	0.028	12.916	0.349	0.038	5.200	1.348	2.151	13.057	0.591	0.048	50.464	0.008	3.872	0.052	0.087
RX-12	Phase 2	0	44	3.250	5.200	0.049	1.120	0.079	0.081	0.028	13.011	0.349	0.038	5.200	1.348	2.500	13.057	0.687	0.048	50.464	0.008	3.332	0.052	0.087
RX-13	Phase 2	0	83	3.250	5.200	0.057	1.120	0.092	0.094	0.032	12.541	0.349	0.044	5.200	1.348	2.500	13.057	0.687	0.056	50.316	0.009	3.872	0.061	0.101
RX-14	Phase 2	0	548	3.250	5.200	0.049	1.120	0.079	0.081	0.028	13.160	0.349	0.038	5.200	1.348	2.500	13.057	0.687	0.048	50.316	0.008	3.332	0.052	0.087
RX-15	Phase 2	0	1607	3.250	5.200	0.049	0.964	0.079	0.081	0.028	14.085	0.349	0.038	5.200	1.348	2.500	12.384	0.591	0.048	50.316	0.008	3.332	0.052	0.087
RX-16	Phase 1	0.2	12	4.977	5.200	0.049	1.120	0.079	0.081	0.028	11.189	0.349	0.038	5.200	1.348	2.151	13.057	0.591	0.048	50.464	0.008	3.872	0.052	0.087
RX-17	Phase 1	0.2	44	4.977	5.200	0.049	1.120	0.079	0.081	0.028	11.285	0.349	0.038	5.200	1.348	2.500	13.057	0.687	0.048	50.464	0.008	3.332	0.052	0.087
RX-18	Phase 1	0.2	83	5.157	5.200	0.057	1.120	0.092	0.094	0.032	10.634	0.349	0.044	5.200	1.348	2.500	13.057	0.687	0.056	50.316	0.009	3.872	0.061	0.101
RX-19	Phase 1	0.2	548	5.775	5.200	0.049	1.120	0.079	0.081	0.028	10.634	0.349	0.038	5.200	1.348	2.500	13.057	0.687	0.048	50.316	0.008	3.332	0.052	0.087
RX-20	Phase 1	0.2	1607	4.977	5.200	0.049	0.964	0.079	0.081	0.028	12.359	0.349	0.038	5.200	1.348	2.500	12.384	0.591	0.048	50.316	0.008	3.332	0.052	0.087
RX-21	Phase 2	0.2	12	3.750	5.200	0.049	1.120	0.079	0.081	0.028	12.416	0.349	0.038	5.200	1.348	2.151	13.057	0.591	0.048	50.464	0.008	3.872	0.052	0.087
RX-22	Phase 2	0.2	44	3.750	5.200	0.049	1.120	0.079	0.081	0.028	12.511	0.349	0.038	5.200	1.348	2.500	13.057	0.687	0.048	50.464	0.008	3.332	0.052	0.087
RX-23	Phase 2	0.2	83	3.750	5.200	0.057	1.120	0.092	0.094	0.032	12.041	0.349	0.044	5.200	1.348	2.500	13.057	0.687	0.056	50.316	0.009	3.872	0.061	0.101
RX-24	Phase 2	0.2	548	3.750	5.200	0.049	1.120	0.079	0.081	0.028	12.660	0.349	0.038	5.200	1.348	2.500	13.057	0.687	0.048	50.316	0.008	3.332	0.052	0.087
RX-25	Phase 2	0.2	1607	3.750	5.200	0.049	0.964	0.079	0.081	0.028	13.585	0.349	0.038	5.200	1.348	2.500	12.384	0.591	0.048	50.316	0.008	3.332	0.052	0.087
RX-26	Phase 2	0.2	12	3.250	5.200	0.049	1.120	0.079	0.081	0.028	12.916	0.349	0.038	5.200	1.348	2.151	13.057	0.591	0.048	50.464	0.008	3.872	0.052	0.087
RX-27	Phase 2	0.2	44	3.250	5.200	0.049	1.120	0.079	0.081	0.028	13.011	0.349	0.038	5.200	1.348	2.500	13.057	0.687	0.048	50.464	0.008	3.332	0.052	0.087
RX-28	Phase 2	0.2	83	3.250	5.200	0.057	1.120	0.092	0.094	0.032	12.541	0.349	0.044	5.200	1.348	2.500	13.057	0.687	0.056	50.316	0.009	3.872	0.061	0.101
RX-29	Phase 2	0.2	548	3.250	5.200	0.049	1.120	0.079	0.081	0.028	13.160	0.349	0.038	5.200	1.348	2.500	13.057	0.687	0.048	50.316	0.008	3.332	0.052	0.087
RX-30	Phase 2	0.2	1607	3.250	5.200	0.049	0.964	0.079	0.081	0.028	14.085	0.349	0.038	5.200	1.348	2.500	12.384	0.591	0.048	50.316	0.008	3.332	0.052	0.087

Glass ID	Phase	Redox	EV	Al_2O_3	B_2O_3	BaO	CaO	Ce_2O_3	Cr_2O_3	CuO	Fe_2O_3	K_2O	La_2O_3	Li_2O	MgO	MnO	Na_2O	NiO	PbO	SiO_2	TiO_2	U_3O_8	ZnO	ZrO_2
RX-31	Phase 1	0.33	12	4.977	5.200	0.049	1.120	0.079	0.081	0.028	11.189	0.349	0.038	5.200	1.348	2.151	13.057	0.591	0.048	50.464	0.008	3.872	0.052	0.087
RX-32	Phase 1	0.33	44	4.977	5.200	0.049	1.120	0.079	0.081	0.028	11.285	0.349	0.038	5.200	1.348	2.500	13.057	0.687	0.048	50.464	0.008	3.332	0.052	0.087
RX-33	Phase 1	0.33	83	5.157	5.200	0.057	1.120	0.092	0.094	0.032	10.634	0.349	0.044	5.200	1.348	2.500	13.057	0.687	0.056	50.316	0.009	3.872	0.061	0.101
RX-34	Phase 1	0.33	548	5.775	5.200	0.049	1.120	0.079	0.081	0.028	10.634	0.349	0.038	5.200	1.348	2.500	13.057	0.687	0.048	50.316	0.008	3.332	0.052	0.087
RX-35	Phase 1	0.33	1607	4.977	5.200	0.049	0.964	0.079	0.081	0.028	12.359	0.349	0.038	5.200	1.348	2.500	12.384	0.591	0.048	50.316	0.008	3.332	0.052	0.087
RX-36	Phase 2	0.33	12	3.750	5.200	0.049	1.120	0.079	0.081	0.028	12.416	0.349	0.038	5.200	1.348	2.151	13.057	0.591	0.048	50.464	0.008	3.872	0.052	0.087
RX-37	Phase 2	0.33	44	3.750	5.200	0.049	1.120	0.079	0.081	0.028	12.511	0.349	0.038	5.200	1.348	2.500	13.057	0.687	0.048	50.464	0.008	3.332	0.052	0.087
RX-38	Phase 2	0.33	83	3.750	5.200	0.057	1.120	0.092	0.094	0.032	12.041	0.349	0.044	5.200	1.348	2.500	13.057	0.687	0.056	50.316	0.009	3.872	0.061	0.101
RX-39	Phase 2	0.33	548	3.750	5.200	0.049	1.120	0.079	0.081	0.028	12.660	0.349	0.038	5.200	1.348	2.500	13.057	0.687	0.048	50.316	0.008	3.332	0.052	0.087
RX-40	Phase 2	0.33	1607	3.750	5.200	0.049	0.964	0.079	0.081	0.028	13.585	0.349	0.038	5.200	1.348	2.500	12.384	0.591	0.048	50.316	0.008	3.332	0.052	0.087
RX-41	Phase 2	0.33	12	3.250	5.200	0.049	1.120	0.079	0.081	0.028	12.916	0.349	0.038	5.200	1.348	2.151	13.057	0.591	0.048	50.464	0.008	3.872	0.052	0.087
RX-42	Phase 2	0.33	44	3.250	5.200	0.049	1.120	0.079	0.081	0.028	13.011	0.349	0.038	5.200	1.348	2.500	13.057	0.687	0.048	50.464	0.008	3.332	0.052	0.087
RX-43	Phase 2	0.33	83	3.250	5.200	0.057	1.120	0.092	0.094	0.032	12.541	0.349	0.044	5.200	1.348	2.500	13.057	0.687	0.056	50.316	0.009	3.872	0.061	0.101
RX-44	Phase 2	0.33	548	3.250	5.200	0.049	1.120	0.079	0.081	0.028	13.160	0.349	0.038	5.200	1.348	2.500	13.057	0.687	0.048	50.316	0.008	3.332	0.052	0.087
RX-45	Phase 2	0.33	1607	3.250	5.200	0.049	0.964	0.079	0.081	0.028	14.085	0.349	0.038	5.200	1.348	2.500	12.384	0.591	0.048	50.316	0.008	3.332	0.052	0.087

Table 5-4. MAR Assessment for the Phase 1 and Phase 2 Glasses.

Glass ID	Phase	Redox	EV	MAR Constraint Failed
RX-1	Phase 1	0	12	-
RX-2	Phase 1	0	44	-
RX-3	Phase 1	0	83	-
RX-4	Phase 1	0	548	-
RX-5	Phase 1	0	1607	-
RX-6	Phase 2	0	12	-
RX-7	Phase 2	0	44	-
RX-8	Phase 2	0	83	-
RX-9	Phase 2	0	548	-
RX-10	Phase 2	0	1607	-
RX-11	Phase 2	0	12	-
RX-12	Phase 2	0	44	-
RX-13	Phase 2	0	83	-
RX-14	Phase 2	0	548	-
RX-15	Phase 2	0	1607	-
RX-16	Phase 1	0.2	12	-
RX-17	Phase 1	0.2	44	ΔG_p
RX-18	Phase 1	0.2	83	ΔG_p
RX-19	Phase 1	0.2	548	-
RX-20	Phase 1	0.2	1607	-
RX-21	Phase 2	0.2	12	ΔG_p
RX-22	Phase 2	0.2	44	ΔG_p
RX-23	Phase 2	0.2	83	ΔG_p
RX-24	Phase 2	0.2	548	ΔG_p
RX-25	Phase 2	0.2	1607	-
RX-26	Phase 2	0.2	12	ΔG_p
RX-27	Phase 2	0.2	44	ΔG_p
RX-28	Phase 2	0.2	83	ΔG_p
RX-29	Phase 2	0.2	548	ΔG_p
RX-30	Phase 2	0.2	1607	ΔG_p
RX-31	Phase 1	0.33	12	ΔG_p
RX-32	Phase 1	0.33	44	ΔG_p
RX-33	Phase 1	0.33	83	ΔG_p
RX-34	Phase 1	0.33	548	ΔG_p
RX-35	Phase 1	0.33	1607	ΔG_p
RX-36	Phase 2	0.33	12	ΔG_p
RX-37	Phase 2	0.33	44	ΔG_p
RX-38	Phase 2	0.33	83	ΔG_p
RX-39	Phase 2	0.33	548	ΔG_p
RX-40	Phase 2	0.33	1607	ΔG_p
RX-41	Phase 2	0.33	12	ΔG_p
RX-42	Phase 2	0.33	44	ΔG_p
RX-43	Phase 2	0.33	83	ΔG_p
RX-44	Phase 2	0.33	548	ΔG_p
RX-45	Phase 2	0.33	1607	ΔG_p

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6.0 SUMMARY

Recent glass formulation activities have focused on developing alternative frit compositions for use with specific sludge batches to maximize melt rate and/or waste throughput. The general trend has been to increase the total alkali content in the glass through the use of a high alkali based frit, a less washed sludge, or a combination of the two. As a result, predictions of durability have become a limiting factor in defining the projected operating windows for the DWPF for certain systems. An additional issue for these high alkali systems has been the effect of REDOX on the durability of the glass. Recent analyses have indicated that the application of the durability model's FeO ΔG_i value without consideration of the overall glass composition may lead to a more significant ΔG_P shift (larger magnitude) than needed. Therefore, activation of the REDOX term in PCCS may have a significant impact on the predicted operational windows based on model predictions, but may not represent the realistic impact of REDOX on the measured durability.

In this study, a modeling effort indicated that three terms (REDOX (as measured by Fe^{2+}/Fe^{3+}), Al_2O_3, and a REDOX × Al_2O_3 interaction term) were statistically significant at a confidence level of 95% for the data used to develop the current ΔG_P model. These results suggest a possible interaction between REDOX and glass composition that is not fully captured by the ΔG_P model.

A 45 glass test matrix has been developed to assess the effect of REDOX on durability as well as to provide insight into specific interactive compositional effects on durability. The glasses were selected to support the assessment of the following specific objectives: (1) the impact of REDOX on glass durability (as measured by the Product Consistency Test (PCT)) and (2) the interactive effects that may mitigate the predicted negative impacts based on current free energy of hydration model theory (Jantzen et al. 1995). These glasses will be batched and melted under conditions that target both the projected compositions and intended REDOX states. Durability (as measured by the PCT) will be formally measured on each glass in triplicate using standard procedures. The measured response will then be compared to model based predictions to assess the applicability and/or potential conservatism of the model under REDOX activated conditions. The experimental results will be the focus of a subsequent report.

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APPENDIX A

ΔG_P DELTA AS A FUNCTION FE CONCENTRATION AND REDOX

TABLE A.1. PREDICTED ΔG_P DELTA AS A FUNCTION OF FE CONCENTRATION IN GLASS AND REDOX.

	Fe Concentration (wt%) in Glass														
Redox (f)	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
0.00	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.01	-0.0051	-0.0102	-0.0154	-0.0205	-0.0256	-0.0307	-0.0359	-0.0410	-0.0461	-0.0512	-0.0564	-0.0615	-0.0666	-0.0717	-0.0768
0.02	-0.0102	-0.0205	-0.0307	-0.0410	-0.0512	-0.0615	-0.0717	-0.0820	-0.0922	-0.1025	-0.1127	-0.1230	-0.1332	-0.1434	-0.1537
0.03	-0.0154	-0.0307	-0.0461	-0.0615	-0.0768	-0.0922	-0.1076	-0.1230	-0.1383	-0.1537	-0.1691	-0.1844	-0.1998	-0.2152	-0.2305
0.04	-0.0205	-0.0410	-0.0615	-0.0820	-0.1025	-0.1230	-0.1434	-0.1639	-0.1844	-0.2049	-0.2254	-0.2459	-0.2664	-0.2869	-0.3074
0.05	-0.0256	-0.0512	-0.0768	-0.1025	-0.1281	-0.1537	-0.1793	-0.2049	-0.2305	-0.2561	-0.2818	-0.3074	-0.3330	-0.3586	-0.3842
0.06	-0.0307	-0.0615	-0.0922	-0.1230	-0.1537	-0.1844	-0.2152	-0.2459	-0.2766	-0.3074	-0.3381	-0.3689	-0.3996	-0.4303	-0.4611
0.07	-0.0359	-0.0717	-0.1076	-0.1434	-0.1793	-0.2152	-0.2510	-0.2869	-0.3227	-0.3586	-0.3945	-0.4303	-0.4662	-0.5020	-0.5379
0.08	-0.0410	-0.0820	-0.1230	-0.1639	-0.2049	-0.2459	-0.2869	-0.3279	-0.3689	-0.4098	-0.4508	-0.4918	-0.5328	-0.5738	-0.6148
0.09	-0.0461	-0.0922	-0.1383	-0.1844	-0.2305	-0.2766	-0.3227	-0.3689	-0.4150	-0.4611	-0.5072	-0.5533	-0.5994	-0.6455	-0.6916
0.10	-0.0512	-0.1025	-0.1537	-0.2049	-0.2561	-0.3074	-0.3586	-0.4098	-0.4611	-0.5123	-0.5635	-0.6148	-0.6660	-0.7172	-0.7684
0.11	-0.0564	-0.1127	-0.1691	-0.2254	-0.2818	-0.3381	-0.3945	-0.4508	-0.5072	-0.5635	-0.6199	-0.6762	-0.7326	-0.7889	-0.8453
0.12	-0.0615	-0.1230	-0.1844	-0.2459	-0.3074	-0.3689	-0.4303	-0.4918	-0.5533	-0.6148	-0.6762	-0.7377	-0.7992	-0.8607	-0.9221
0.13	-0.0666	-0.1332	-0.1998	-0.2664	-0.3330	-0.3996	-0.4662	-0.5328	-0.5994	-0.6660	-0.7326	-0.7992	-0.8658	-0.9324	-0.9990
0.14	-0.0717	-0.1434	-0.2152	-0.2869	-0.3586	-0.4303	-0.5020	-0.5738	-0.6455	-0.7172	-0.7889	-0.8607	-0.9324	-1.0041	-1.0758
0.15	-0.0768	-0.1537	-0.2305	-0.3074	-0.3842	-0.4611	-0.5379	-0.6148	-0.6916	-0.7684	-0.8453	-0.9221	-0.9990	-1.0758	-1.1527
0.16	-0.0820	-0.1639	-0.2459	-0.3279	-0.4098	-0.4918	-0.5738	-0.6557	-0.7377	-0.8197	-0.9016	-0.9836	-1.0656	-1.1475	-1.2295
0.17	-0.0871	-0.1742	-0.2613	-0.3484	-0.4354	-0.5225	-0.6096	-0.6967	-0.7838	-0.8709	-0.9580	-1.0451	-1.1322	-1.2193	-1.3063
0.18	-0.0922	-0.1844	-0.2766	-0.3689	-0.4611	-0.5533	-0.6455	-0.7377	-0.8299	-0.9221	-1.0143	-1.1066	-1.1988	-1.2910	-1.3832
0.19	-0.0973	-0.1947	-0.2920	-0.3893	-0.4867	-0.5840	-0.6814	-0.7787	-0.8760	-0.9734	-1.0707	-1.1680	-1.2654	-1.3627	-1.4600
0.20	-0.1025	-0.2049	-0.3074	-0.4098	-0.5123	-0.6148	-0.7172	-0.8197	-0.9221	-1.0246	-1.1270	-1.2295	-1.3320	-1.4344	-1.5369
0.21	-0.1076	-0.2152	-0.3227	-0.4303	-0.5379	-0.6455	-0.7531	-0.8607	-0.9682	-1.0758	-1.1834	-1.2910	-1.3986	-1.5061	-1.6137
0.22	-0.1127	-0.2254	-0.3381	-0.4508	-0.5635	-0.6762	-0.7889	-0.9016	-1.0143	-1.1270	-1.2398	-1.3525	-1.4652	-1.5779	-1.6906
0.23	-0.1178	-0.2357	-0.3535	-0.4713	-0.5891	-0.7070	-0.8248	-0.9426	-1.0604	-1.1783	-1.2961	-1.4139	-1.5318	-1.6496	-1.7674
0.24	-0.1230	-0.2459	-0.3689	-0.4918	-0.6148	-0.7377	-0.8607	-0.9836	-1.1066	-1.2295	-1.3525	-1.4754	-1.5984	-1.7213	-1.8443
0.25	-0.1281	-0.2561	-0.3842	-0.5123	-0.6404	-0.7684	-0.8965	-1.0246	-1.1527	-1.2807	-1.4088	-1.5369	-1.6650	-1.7930	-1.9211
0.26	-0.1332	-0.2664	-0.3996	-0.5328	-0.6660	-0.7992	-0.9324	-1.0656	-1.1988	-1.3320	-1.4652	-1.5984	-1.7316	-1.8647	-1.9979
0.27	-0.1383	-0.2766	-0.4150	-0.5533	-0.6916	-0.8299	-0.9682	-1.1066	-1.2449	-1.3832	-1.5215	-1.6598	-1.7982	-1.9365	-2.0748
0.28	-0.1434	-0.2869	-0.4303	-0.5738	-0.7172	-0.8607	-1.0041	-1.1475	-1.2910	-1.4344	-1.5779	-1.7213	-1.8647	-2.0082	-2.1516
0.29	-0.1486	-0.2971	-0.4457	-0.5943	-0.7428	-0.8914	-1.0400	-1.1885	-1.3371	-1.4857	-1.6342	-1.7828	-1.9313	-2.0799	-2.2285
0.30	-0.1537	-0.3074	-0.4611	-0.6148	-0.7684	-0.9221	-1.0758	-1.2295	-1.3832	-1.5369	-1.6906	-1.8443	-1.9979	-2.1516	-2.3053
0.31	-0.1588	-0.3176	-0.4764	-0.6352	-0.7941	-0.9529	-1.1117	-1.2705	-1.4293	-1.5881	-1.7469	-1.9057	-2.0645	-2.2234	-2.3822
0.32	-0.1639	-0.3279	-0.4918	-0.6557	-0.8197	-0.9836	-1.1475	-1.3115	-1.4754	-1.6393	-1.8033	-1.9672	-2.1311	-2.2951	-2.4590
0.33	-0.1691	-0.3381	-0.5072	-0.6762	-0.8453	-1.0143	-1.1834	-1.3525	-1.5215	-1.6906	-1.8596	-2.0287	-2.1977	-2.3668	-2.5359