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Integration of SWPF into the DWPF Flowsheet: Gap Analysis and Test Matrix Development

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EXECUTIVE SUMMARY

Based on Revision 19 of the High Level Waste (HLW) System Plan, it is anticipated that the Salt Waste Processing Facility (SWPF) will be integrated into the Defense Waste Processing Facility (DWPF) flowsheet in October 2018 (or with Sludge Batch 11 (SB11)). Given that, Savannah River Remediation (SRR) has requested a technical basis be developed that validates the current Product Composition Control System (PCCS) models for use during the processing of the SWPF-based coupled flowsheet or that leads to the refinements of or modifications to the models that are needed so that the models may be used during the processing of the SWPF-based coupled flowsheet.

To support this objective, Savannah River National Laboratory (SRNL) has completed three key interim activities prior to validation of the current or development of refined PCCS models over the anticipated glass composition region for SWPF processing. These three key activities include: (1) defining the glass compositional region over which SWPF is anticipated to be processed, (2) comparing the current PCCS model validation ranges to the SWPF glass compositional region from which compositional gaps can be identified, and (3) developing a test matrix to cover the compositional gaps.

To define the future SWPF-based glass compositional region, three critical inputs were required: (1) sludge compositions, (2) frit compositions, and (3) waste loading intervals. To support the development of the future glass compositional region of interest for SWPF processing, SRR issued an Engineering Position Paper that provided key input assumptions and information regarding material balances from SWPF, the Waste Acceptance Criteria (WAC) for transfers from SWPF to DWPF, and the nominal sludge-only projections from Revision 19 of the HLW System Plan. Based on this information and guidance, SRNL developed projected SWPF coupled operations compositions for each of the sludge batches listed in Revision 19.

SRNL used the SWPF-based coupled operations projections to perform Measurement Acceptability Region (MAR) assessments on each sludge batch to identify candidate frits that satisfied the waste loading acceptance criteria provided by SRR (i.e., a projected operating window of 36 – 44% Waste Loading (WL) while accounting for sludge variation at nominal SWPF volumes). The results of the Variation Stage MAR assessment suggested that frits were available that would allow DWPF to target 36%-44% WL for Sludge Batch 11 (SB11) – Sludge Batch 18 (SB18). For SB19 – SB23 (identified as the Tank Farm heels by SRR), the results suggested that WLs would have to be decreased to maintain processing at the volume of SWPF material expected to be incorporated. It is to be noted that the heel batch compositions make-up is not well-known when System Plan R-19 was developed. The targeted waste loadings for the heel sludge batches ranged from the low 30s to an upper limit of approximately 40%. One of the key assumptions used in the MAR assessment was that the current PCCS models are valid over the compositional regions being evaluated which include high TiO_2 concentration glass compositions (e.g., above the current 2 weight percent (wt%) upper limit for the Liquidus Temperature (T_L) model).

Although frits were identified for the SWPF-based projections, there were technical concerns flagged as part of this assessment. First, the high Na_2O content of the sludges forced frit development efforts to target relatively low total alkali contents which cause some concern over the formation of amorphous phase separation in the frit. Although this issue may be resolved either through the vendor's production process (e.g., water quenched rollers that kinetically limit the formation or scale of separation) or the addition of Al_2O_3 to the frit, the development of amorphous phase separation and the potential downstream impacts need to be monitored closely as the SWPF flowsheet matures.

The results of the MAR assessment provided two critical pieces of information that were needed to define the future SWPF-based glass processing region: (1) the WL intervals and (2) candidate frit compositions. Using this information along with the projected coupled operations compositions for the sludge batches, SRNL defined minimum and maximum values for those elements (or oxides) tracked in Revision 19 of the HLW System Plan in glass composition space. That is, using the frit and sludge compositions (including variation for the sludge batches) and knowing the WL intervals over which each sludge batch could be processed (based on predictions using the current PCCS models), the future SWPF glass compositional region could be identified through determinations of minimum and maximum values for oxides of interest.

With the definition of the SWPF glass processing region, SRNL developed a 50 glass test matrix which not only covers the future SWPF glass processing region but also provides a technical basis from which revisions or upgrades to current PCCS models can be made if warranted. The test matrix design was based on the integration of a layered approach with space filling points. All of the test matrix glasses were deemed MAR acceptable based on current PCCS models and their associated constraints – with the exceptions of the 2 wt% TiO_2 criterion and homogeneity and its associated constraints (i.e., low and high frit).

Based on the results of this study, the following recommendations are made:

(1) Physical (liquidus temperature, viscosity, and durability) properties and chemical compositions of the 50 test matrix glasses should be measured. Once complete, the data should be transmitted to SRNL where an assessment of the measured values versus the model predicted values will be made for the various key glass properties. Based on that assessment, SRNL will recommend to SRR a path forward on the need for refining or updating the associated PCCS models to support SWPF processing in DWPF.
(2) SRNL recommends that if low-alkali based frits are used to support SWPF processing through DWPF, assessments of potential downstream impacts due to potential phase separation must be performed. As noted in the report, the development of phase separation is likely in low-alkali borosilicate glasses which could be mitigated by the vendor's production process (i.e., use of water cooled rollers), addition of Al_2O_3 to the frit, or through the use of higher alkali frits if different sludge washings strategies were pursued. If phase separation cannot be mitigated through either of these strategies, the impact of their use in the DWPF process should be evaluated. The concern is the potential formation of a gel which could lead to transfer issues or practical impacts to rheology due to leaching of the frit during SME processing or in the frit decontamination system.
(3) SRNL recommends that SRR integrate the MAR assessment platform into the HLW System Planning process to assess the impacts of Tank Farm blending and washing strategies as well as pretreatment options that may be under consideration. Integration of MAR assessments into future planning will provide a more robust technical basis from which business decisions can be made as the entire flowsheet is evaluated.
(4) SRNL also recommends that SRR assess an appropriate measurement technique for Cs assuming it will be a reportable element for the SWPF-based flowsheet as the current projections suggest.

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LIST OF ABBREVIATIONS

ARP	Actinide Removal Process
CUA	Catholic University of America
DWPF	Defense Waste Processing Facility
ES	Energy*Solutions*
EV	Extreme Vertices
HLW	High Level Waste
IL	Inner Layer
LAW	Low Activity Waste
MAR	Measurement Acceptability Region
MCU	Modular Caustic Side Solvent Extraction Unit
MST	Mono-Sodium Titanate
OL	Outer Layer
PCCS	Product Composition Control System
SB	Sludge Batch
SE	Strip Effluent
SF	Space Filling
SME	Slurry Mix Evaporator
SRAT	Sludge Receipt and Adjustment Tank
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation
SWPF	Salt Waste Processing Facility
T_L	Liquidus Temperature
TTQAP	Task Technical and Quality Assurance Plan
η	Viscosity
VSL	Vitreous State Laboratory
WAC	Waste Acceptance Criteria
WL	Waste Loading

1.0 Introduction

The Salt Waste Processing Facility (SWPF) is being designed and constructed to remove cesium-137 (Cs-137), strontium-90 (Sr-90), and actinide radionuclides from salt solutions. The cesium is concentrated in a dilute nitric acid stream which is transferred to the Defense Waste Processing Facility (DWPF). The Sr-90 and actinide radionuclides are removed via adsorption onto mono-sodium titanate (MST). The loaded MST and entrained sludge solids are filtered using crossflow filtration and transferred to DWPF. Finally, DWPF mixes the retrieved sludge/MST slurry and the cesium stream and vitrifies into a borosilicate glass product that is intended for disposal at a federal repository. According to Revision 19 of the High Level Waste (HLW) System Plan (Chew and Hamm (2014)), SWPF is anticipated to be integrated into the DWPF flowsheet in October 2018 (or with Sludge Batch 11 (SB11)).

Savannah River Remediation (SRR) has issued scopes of work to the Savannah River National Laboratory (SRNL) and Energy*Solutions* (ES) and its partner the Vitreous State Laboratory (VSL) of The Catholic University of America (CUA) for glass formulation activities to support the integration of SWPF into the DWPF flowsheet. Specifically, SRR has requested that the glass formulation team of SRNL and ES-VSL develop a technical basis that validates the current Product Composition Control System (PCCS) models for use during the processing of the coupled flowsheet or that leads to the refinements of or modifications to the models that are needed so that the models may be used during the processing of the coupled flowsheet.

To support this objective, there are several key interim activities that must be completed prior to validation of the current or implementation of refined PCCS models over the anticipated glass composition region for SWPF processing. These key activities include: (1) defining the glass compositional region over which SWPF is anticipated to be processed, (2) comparing the current PCCS model validation ranges to the SWPF glass compositional region from which compositional gaps can be identified, (3) developing a test matrix to cover the compositional gaps, (4) fabricating and measuring key chemical and physical properties of the test matrix glasses, and (5) evaluating the applicability of the current models to predict the new data over the SWPF glass region of interest. The primary glass properties to be assessed are liquidus temperature (T_L), viscosity (according to American Society for Testing and Materials (ASTM) C965-Method A or B), and durability (as defined by ASTM C1285 – Product Consistency Test-Method A).

Peeler, Edwards, and Jantzen (2014a) issued a Task Technical and Quality Assurance Plan (TTQAP) that addressed SRNL's work scope to be performed in support of this task. The TTQAP was issued in response to the SRR Task Technical Request (Holtzscheiter (2014)). SRNL has completed the first three key activities on the pathway to supporting SWPF integration into the DWPF flowsheet. SRNL's initial focus was an investigation into the compositional region for the DWPF glass waste-form anticipated by the integration of SWPF into the DWPF flowsheet. Under guidance from SRR (Fellinger, Holtzscheiter, and Shah (2014)), SRNL modified the projections for future sludge-only batches from SRR's System Plan Revision 19 (Chew and Hamm (2014)) to reflect coupled operations at DWPF and developed candidate frit compositions that would support the processing of these coupled projections in a manner that would meet SRR's operational goals as described in the guidance document. The results from this investigation were summarized by Peeler, Edwards, and Jantzen (2014b) and used to develop the glass waste-form compositional region of interest for this study (Peeler and Edwards (2014a)). From these efforts, Peeler and Edwards (2014b) developed a test matrix of 50 glass compositions that is to serve as the basis for the completion of the activities associated with this task.

SRNL has issued memoranda documenting the high-level results of these efforts, but in some cases, specific details were not covered in an effort to expedite schedule. Therefore, this report will not only provide an overview of the three activities, but when necessary, add the details omitted from the previous related memoranda. This will provide a single detailed reference of the SRNL SWPF activities that led to and resulted in the development of the SWPF test matrix to fill compositional gaps.

2.0 Defining the Future SWPF Glass Compositional Region

As stated in the TTQAP, SRNL anticipates that there will be compositional gaps between the current DWPF model validity ranges and composition regions projected for future sludge batch processing. As an example, the volumes of salt to be processed through SWPF are expected to increase the TiO_2 concentration above the 2 weight percent (wt%) glass limit which currently defines the upper limit of the T_L model validation range and an individual solubility limit within PCCS (Brown et al. (2001); Brown et al. (2006)). Although TiO_2 is a key oxide that will be monitored, there are potentially other oxides that could challenge the current model validation ranges based on future blending or washing strategies (e.g., Na_2O will be another key factor). Other factors that may challenge the validation ranges include assumptions made about aluminum dissolution on specific sludge batches, the assumed volumes of SWPF salt to be processed, and the desire to target higher waste loadings (WLs) as defined by Revision 19 of the SRR HLW System Plan (Chew and Hamm (2014)). In addition to these factors, the compositions of candidate frits that could be used to process each sludge batch through DWPF while meeting process and product performance constraints will also play a role in defining the future glass processing region from which compositional gaps can be identified. More specifically, the integration of SWPF into DWPF is expected to challenge current model validity ranges for specific components and possibly introduce new components into the DWPF flowsheet, which could lead to the need to add new terms into the model or to modify coefficients for specific models to support future facility operations.

To support the development of the future glass compositional region of interest for SWPF processing, SRR issued an Engineering Position Paper (Fellinger, Holtzscheiter, and Shah (2014)) that provided key input assumptions and information regarding material balances from SWPF, the Waste Acceptance Criteria (WAC) for transfers from SWPF to DWPF, and the nominal sludge projections from Revision 19 of the HLW System Plan. Although details can be found in the Position Paper, several key assumptions of the guidance from SRR to SRNL are described here to provide a framework for the gap analysis: DWPF will only process in a coupled operations mode; the expected flow rates from SWPF were provided on a weekly basis; targeted nominal WL once SWPF comes on line will be 40%; frits identified for each sludge batch need to provide an operating window of 40% ± 4 WL points (or WLs of 36% - 44% have to be PCCS acceptable from a Slurry Mix Evaporator (SME) perspective as defined by Brown, Postles, and Edwards (2006)) while accounting for variation; and, if desired WLs cannot be achieved for a specific sludge batch, SRNL should prioritize integration of SWPF streams at the desired volume throughput over WL (i.e., reduce the WL interval over which a particular frit – sludge system is deemed viable while maintaining SWPF throughput volumes).

In determining the impact of coupled SWPF operations, several refinements to the assumptions in the Engineering Position Paper were required. The concentration of MST in the alpha removal stream to DWPF would be 3.73 wt% based on the 0.4 g/L MST double strike of Tank 39H feed as given in the Mass Balance Model output (P-ESR-J-00001 Rev. 2 (Parsons 2007) and M-CLC-J-00143 Rev. 0 (DesRocher 2011)). In order to be conservative with respect to titanium content, it was assumed that no sludge solids come forward with the stream sent to DWPF from alpha removal. Total sodium content in alpha removal stream (including the contribution from MST) was taken to be at the WAC limit value for sodium of 0.7M Na^+ (moles per liter slurry - includes sodium contribution from MST solids). The cesium from strip effluent (SE) was taken as the elemental concentration for the conservative case, the Tank 13H Material Balance Model output. The refinements were made based on discussions held with SRR.

In order to define the future compositional region for SWPF processing, three key parameters are needed: (1) the coupled operations sludge projections, (2) candidate frits for each sludge batch, and (3) the WL intervals desired for processing of each sludge batch. These inputs will be explored and discussed in the subsequent sections.

2.1 Coupled Operations Sludge Projections

Using the SRR inputs and assumptions document (specifically Table 1 from Fellinger, Holtzscheiter, and Shah (2014)), SRNL developed coupled operations sludge projections for SB11 through SB23, which are shown in Table 2-1. The projections shown in Table 2-1 are intended to reflect an average Sludge Receipt and Adjustment Tank (SRAT) composition during processing of that particular sludge batch. A review of the information presented in Table 2-1 provides some insight into the compositional trends (e.g., concentrations of Al_2O_3, Na_2O, and TiO_2). Note that the Al_2O_3 concentrations for SB11 through SB14 are on the low side given that there is a hard PCCS constraint on the minimum Al_2O_3 concentration as well as constraints related to the Al_2O_3 content and the alkali content in glass. Al_2O_3 contents as low as that seen in the projection for SB13 are expected to pose a challenge relative to these constraints.

The projected values for Na_2O concentration are of particular interest. A comparison of the sludge-only Na_2O values in Table 1 from Fellinger, Holtzscheiter, and Shah (2014) to the coupled operations Na_2O values of Table 2-1 indicates only increases of 1 to 3 wt% for SB11 through SB18 with the heel batches (SB19 through SB23) showing increases of 6 to 7 wt%. For SB11 through SB18, this is a relatively minor increase in Na_2O concentration, one that may not lead to difficulties in a single frit being able to successfully process the sludge-only as well as the coupled flowsheets for these batches. Thus, the nominal volumes of SWPF considered for SB11 through SB18 under the guidance of Fellinger, Holtzscheiter, and Shah (2014) make the transition from a sludge-only SRAT batch to a coupled SRAT batch (and vice versa) much less problematic. Although the majority of the assessments performed in support of this study are based strictly on a coupled operations flowsheet (per the SRR inputs and assumptions document), insight into the potential for DWPF to operate under both sludge-only and coupled operations with a single frit is also evaluated for one sludge batch (i.e., SB11).

The TiO_2 concentration for each sludge batch is approximately 12.5 wt% and is relatively consistent for each sludge batch. The “constant” TiO_2 concentration is not surprising given the assumptions made about how salt would be processed and integrated into the DWPF flowsheet per Fellinger, Holtzscheiter, and Shah (2014).

Finally, the projections for Cs_2O are of note. The projected values of Table 2-1 are all 1.82 wt% (in calcine sludge), which at 40% WL is approximately 0.73 wt% in glass, making cesium a reportable element for DWPF during the processing of these batches.[1] Another aspect of cesium in the DWPF flowsheet is that this element is an alkali, and, thus, becomes an additional contributor to the aluminum/alkali constraints in PCCS mentioned above.

[1] The criterion for reportable elements for DWPF is based on the elemental concentration being 0.5 wt% or greater in glass. The Cs_2O concentration evaluated in this report (based on the assumed WLs and SWPF/SE volumes and compositions) is approximately 0.73 wt% on an oxide basis which translates into a 0.69 wt% on an elemental basis; thus, making it a reportable element.

Table 2-1. SWPF Coupled Operations Sludge Projections.

	SB11	SB12	SB13	SB14	SB15	SB16	SB17	SB18	SB19	SB20	SB21	SB22	SB23
Oxide	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%
Al_2O_3	12.32	10.53	9.07	12.22	17.69	19.23	21.12	20.86	23.90	18.20	16.71	14.77	21.63
B_2O_3	0.04	0.02	0.01	0.00	0.00	0.00	0.00	0.02	0.03	0.02	0.01	0.01	0.00
BaO	0.14	0.16	0.19	0.18	0.13	0.12	0.11	0.10	0.13	0.31	0.35	0.45	0.29
CaO	1.88	1.87	1.82	1.46	1.22	1.59	1.50	1.38	1.72	2.93	3.20	3.87	3.03
Ce_2O_3	0.23	0.20	0.20	0.19	0.13	0.16	0.22	0.22	0.27	0.18	0.16	0.10	0.31
CoO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cr_2O_3	0.21	0.25	0.27	0.23	0.20	0.20	0.17	0.16	0.23	0.16	0.15	0.10	0.21
Cs_2O	1.82	1.82	1.82	1.82	1.82	1.82	1.82	1.82	1.82	1.82	1.82	1.82	1.82
CuO	0.08	0.08	0.08	0.07	0.05	0.07	0.06	0.05	0.06	0.04	0.04	0.03	0.07
Fe_2O_3	20.07	19.00	19.56	17.59	20.41	22.05	25.34	25.27	32.62	33.46	33.60	33.50	30.84
K_2O	0.25	0.28	0.25	0.21	0.20	0.25	0.20	0.20	0.13	0.08	0.08	0.05	0.15
La_2O_3	0.10	0.10	0.10	0.09	0.06	0.08	0.09	0.09	0.11	0.07	0.06	0.04	0.12
MgO	1.98	1.17	0.76	0.40	1.00	0.76	0.65	0.72	0.92	0.55	0.45	0.25	0.43
MnO	1.66	1.81	1.84	1.94	1.07	2.05	2.03	1.81	2.53	5.88	6.72	8.37	4.63
Na_2O	29.16	31.99	32.57	33.38	32.66	31.64	27.62	27.23	12.49	14.47	14.86	15.71	14.15
NiO	0.71	0.79	1.32	1.64	0.86	0.36	0.21	0.22	0.57	2.62	3.10	4.09	2.03
PbO	0.43	0.27	0.22	0.19	0.10	0.11	0.12	0.22	0.31	0.21	0.19	0.12	0.22
SO_4	0.46	0.46	0.46	0.46	0.46	0.46	0.46	0.46	0.46	0.46	0.46	0.46	0.46
SiO_2	5.15	5.46	5.01	3.21	3.86	3.48	3.33	4.13	5.75	3.84	3.30	1.87	3.11
ThO_2	1.57	0.86	0.48	0.17	0.07	0.02	0.01	0.03	0.06	0.05	0.06	0.04	0.64
TiO_2	12.47	12.47	12.47	12.47	12.47	12.47	12.47	12.47	12.49	12.49	12.49	12.48	12.48
U_3O_8	8.76	9.89	10.99	11.67	5.20	2.64	2.07	2.20	2.91	1.80	1.81	1.63	2.84
ZnO	0.12	0.11	0.11	0.09	0.06	0.11	0.08	0.05	0.14	0.15	0.15	0.10	0.16
ZrO_2	0.39	0.40	0.40	0.33	0.27	0.33	0.31	0.29	0.36	0.22	0.21	0.14	0.37

2.2 Candidate Frit Compositions for SB11 through SB18: MAR Assessments

SRNL used the coupled operations projections (Table 2-1) to perform Measurement Acceptability Region (MAR) assessments on each sludge batch to identify candidate frits that satisfy the WL criteria provided by SRR. The results of the MAR assessment were presented to SRR and are summarized in Peeler, Edwards, and Jantzen (2014b).

Prior to discussing the MAR results, one of the key assumptions used in the MAR assessment needs to be clearly identified and understood. Decisions as to whether a frit would provide an acceptable processing window (or WL interval of 36 – 44%) were made using the current PCCS models. Thus, it is assumed that the current PCCS models are valid over the compositional regions being evaluated which include high TiO_2 concentration glass compositions (e.g., above the current 2 wt% upper limit for the T_L model). It must be recognized that one of the primary objectives of the SWPF Integration Task is to experimentally assess whether the current models are applicable to the future processing region. Therefore, the use of the current models to make decisions regarding acceptability includes the risk that the extrapolation of the models covers compositional regions for which they may not be valid. However, in order to define the future glass region of interest, use of the current models is the best available strategy. In this section, the MAR results for SB11 through SB18 are discussed with the MAR results for the heel batches (i.e., SB19 through SB23) being addressed in the next section.

Table 2-2 provides a summary of the MAR results for these sludge batches. The table provides for each sludge batch the number of frits that met the criteria of an operating window from 36% WL to 44% WL with variation (as described above) accounted for, the range of alkali content for the candidate frits, and other notes from the MAR assessment. The total alkali content is provided given that sludge batches with high sodium content often require candidate frits to have low total alkali content, which may lead to the possibility of a phase separated frit. Implementation of a phase-separated frit into the DWPF process may be of concern during SME processing due to excessive boron, sodium, and/or lithium leaching leading to a potential negative impact on rheology. Also, the impact of the use of a phase separated frit during canister decontamination would need to be investigated as leaching in the frit decon hold tank may lead to gelation and issues with rheology or materials transport. Testing is recommended for low-alkali frits (generally less than 11 - 13 wt% total alkali) before they would be selected for use in DWPF. There are two potential options to suppress phase separation in low-alkali frits.

- If phase separation is observed in laboratory production of the frit where natural cooling is typically allowed (the molten glass product is poured onto a stainless steel plate and allowed to cool naturally – no forced cooling), any production technique that would rapidly cool the molten glass would kinetically limit the scale or formation of phase separation. If fact, the production process employed by both of DWPF's current frit vendors uses water-quenched rollers which may kinetically limit the development of phase separation, and
- It is well known that the addition of Al_2O_3 to a glass composition suppresses the formation of amorphous phase separation (Scholze 1991). Therefore, Al_2O_3 additions to candidate low-alkali frits could be a mitigation technique or strategy as long as there are no negative impacts on the projected operating windows.

Table 2-2. Summary of MAR Results for SB11 through SB18

Sludge Batch	Number of Frits	Total Alkali Content (wt%)	Na_2O Content of Frits (wt%)	Notes
SB11	3	9 – 10	1 – 2	Likely phase separated frits. Evaluated Al_2O_3 in frit: 1 to 2 wt% Al_2O_3 frits were able to maintain operating windows and slightly increase total alkali content.
SB12	5	8 – 10	1 – 6	Low Al_2O_3 content of sludge led to 1 – 2 wt% Al_2O_3 in frits. Al_2O_3 in frit may lessen the likelihood of phase separated frits due to low alkali content.
SB13	3	8 – 10	1 – 5	Low Al_2O_3 content of sludge led to 2 wt% Al_2O_3 in frits. Al_2O_3 in frit may lessen the likelihood of phase separated frits due to low alkali content.
SB14	4	8 – 10	1 – 4	Low Al_2O_3 content of sludge led to 1 – 2 wt% Al_2O_3 in frits. Al_2O_3 in frit may lessen the likelihood of phase separated frits due to low alkali content.
SB15	10	7 – 10	1 – 3	Likely phase separated frits.
SB16	8	8 – 10	1 – 2	Likely phase separated frits.
SB17	13	10 – 12	1 – 3	Possibly phase separated frits.
SB18	24	8 – 13	1 – 4	Possibly phase separated frits.

In general, candidate frits were identified for coupled operations flowsheets for SB11 through SB18 that met the SRR criteria as outlined in the inputs and assumptions document (more specifically operating windows of 36 – 44% WL were identified while accounting for variation). As previously mentioned, one of the major assumptions being made is that the current process control models are valid over the compositional region being assessed. A few specific comments are highlighted below for each sludge batch:

- SB11: Although three frits were identified meeting the SRR criteria, the primary concern for these compositions is the likelihood of amorphous phase separation due to the low-alkali content (9 – 10 wt%) in each of the candidate frits. As previously mentioned, the use of water-cooled rollers in the vendor's production process may minimize or eliminate its formation. If not, additions of Al_2O_3 to the frit may suppress its formation. This was demonstrated in the frit development efforts for SB8 where Frit 422 (8 wt% B_2O_3, 8 wt% Li_2O, 3 wt% Na_2O, and 81 wt% SiO_2) was produced in the laboratory (slowly or naturally cooled – not water quenched). Figure 2-1 (a) shows opalescent nature of Frit 422 indicative of amorphous phase separation. Figure 2-1 (b) and (c) show that through the addition of Al_2O_3 (1 and 2 wt% respectively, substituting for SiO_2) amorphous phase separation can be suppressed even though the resulting glass product is not rapidly cooled. With this knowledge in mind, Al_2O_3-containing frits (up to 2 wt%) were evaluated for SB11. The MAR results indicated that operating windows of 36 – 44% WL were still achievable and in some cases allowed higher total alkali contents in the frit which in addition to Al_2O_3 should reduce the potential for amorphous phase separation.

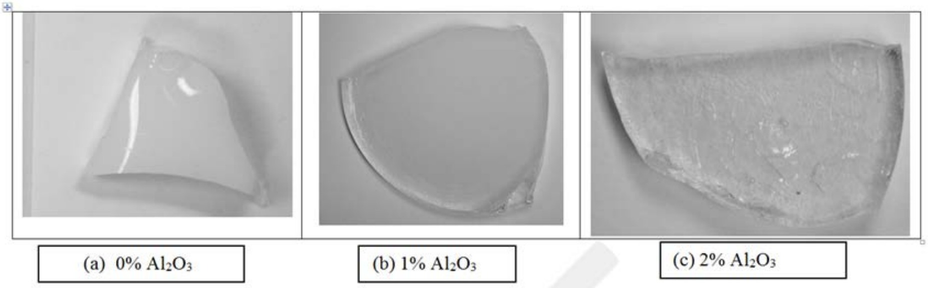

Figure 2-1. Laboratory Fabrications of Versions of Frit 422

- SB12: The low Al_2O_3 content of the SWPF-based sludge forced the addition of Al_2O_3 to the frit to primarily avoid failing the Al_2O_3 / sum of alkali constraints in PCCS at intermediate WLs. In fact, no frits were found based on the four primary oxides (B_2O_3, Li_2O, Na_2O, and SiO_2) that provided access to WLs of 36 – 44%. With the additions of 1 and 2 wt% Al_2O_3, candidate frits were identified that met the WL criteria but as with SB11, the low-alkali content of these frits raises issues with the potential for amorphous phase separation unless the Al_2O_3 content suppresses its formation.
- SB13: With approximately 9 wt% Al_2O_3 in the sludge, SB13 has the lowest Al_2O_3 content of all of the Revision 19 projections. At 36% WL, the Al_2O_3 content in glass would be approximately 3.3 wt% which would not pass the current PCCS lower Al_2O_3 constraint once uncertainties are applied. This forces the addition of Al_2O_3 to the frit or drives SRR to reconsider either blending or Al-dissolution strategies. Three candidate frits with 2 wt% Al_2O_3 were identified that provided access to the targeted 36 – 44% WL interval. However, as with previous sludge batches, the total alkali contents of these frits ranged from 8 – 10 wt% (1 – 5 wt% Na_2O, the balance Li_2O) which makes the frit susceptible to amorphous phase separation unless the 2 wt% Al_2O_3 or the vendor's production process can suppress its formation. It should be noted that for the 5 wt% Na_2O frits, the waste form affecting constraints of sum of alkali and durability are limiting at low and high WLs, respectively.
- SB14: The low Al_2O_3 content of the sludge requires the addition of Al_2O_3 to the frit in order to suppress sum of alkali issues at intermediate WLs. Similar to SB12 and SB13, Al_2O_3-containing candidate frits (1 and 2 wt% Al_2O_3) were found that provided projected operating windows of at least 36 – 44% WL with issues of phase separation still a concern due to the lower total alkali content in the frit.
- SB15 – SB18: The higher Al_2O_3 content in these sludges mitigates sum of alkali issues over the WL interval of interest which eliminates the need to add Al_2O_3 to the frit to meet related PCCS criteria of sum of alkali or minimum Al_2O_3 contents. However, additions of Al_2O_3 to the frit may be required to suppress phase separation as previously discussed. For SB15 through SB18, frits (without Al_2O_3) were identified that provide access to WLs of 36 – 44%. Although no formal MAR assessment was made, if phase separation in these candidate frits is an issue, addition of 1 – 2 wt% Al_2O_3 appears to be viable as previous assessments suggest that there is no impact on the operating windows while its addition should help to suppress phase separation.

2.3 Candidate Frit Compositions for SB19 through SB23: MAR Assessments

Perhaps the most significant difference between SB11-SB18 and the heel sludge batches (SB19 – SB23) is the Na_2O content. For SB11 – SB18, the sludge Na_2O concentration ranged from approximately 27 to 33 wt% for coupled operations. In contrast, sludge Na_2O concentrations of approximately 12 to 16 wt% are shown for the heel batches. The lower Na_2O content of the heel batches will provide frit development efforts the opportunity to add higher concentrations of alkali to the frit which should result in eliminating the development of amorphous phase separation from a compositional perspective. It is also noted that the Al_2O_3 contents for SB19 – SB23 are high enough that the lower Al_2O_3 constraint was not an issue with the MAR assessments.

For these sludge batches no frits were found that provided access to WLs of 36% to 44% with variation accounted for. Per the guidance from SRR, if desired WLs cannot be achieved for a specific sludge batch, SRNL was to prioritize integration of SWPF streams at the desired volume throughput over WL. Table 2-3 provides a summary of the MAR assessments.

Table 2-3. Summary of MAR Results for SB19 through SB23

Sludge Batch	Operating Window (% WL)	Number of Frits	Total Alkali Content in Frit (wt%)	Na_2O Content of Frits (wt%)	Notes
SB19	25 – 42	4	>20	12 – 17	There are additional frits with operating windows of 25% to 41% WL
SB20	25 – 40	6	>20	16 – 18	There are additional frits with operating windows of 25% to 39% WL
SB21	25 – 40	4	>20	17 – 19	There are additional frits with operating windows of 25% to 39% WL
SB22	31 – 40	1	>20	19	Relatively low Al_2O_3 content for this sludge. Sum of alkali issues at WLs from 28 – 30%
SB23	25 – 39	1	>20	16	There are additional frits with operating windows from 25% to 38% WL

A few high-level comments regarding the MAR results of SB19 through SB23 are highlighted below.

- Projected operating windows for the heel batches are approximately 25 – 40% WL with the exception of SB22.
- The total alkali content of all candidate frits was approximately 20 – 21 wt% so phase separation associated with frit production is not an issue. The lower Na_2O content of the heel batches provide frit development efforts the opportunity to target higher concentrations of alkali in the frit which should result in eliminating the development of amorphous phase separation from a compositional perspective.
- SB22 is perhaps the most interesting sludge batch from a Revision 19 MAR assessment perspective. The Al_2O_3 concentration is relatively low in this heel batch which could force the addition of Al_2O_3 to the frit if the sum of alkali constraint becomes an issue. While no frits were found that met the 36 – 44% WL criteria, only one frit was found that provided an operating window of 31 – 40% WL. Sum of alkali issues restrict access to lower WLs (< 31%) which would drive frit development efforts to add Al_2O_3 to the frit to mitigate this constraint. However, the addition of Al_2O_3 to the frit would likely result in predictions of nepheline becoming the limiting constraint at higher WLs – predictions of T_L limit access to upper WLs with the one candidate, non- Al_2O_3 frit. This suggests that for SB22 there is very little flexibility in frit development space to avoid negative impacts on the operating window even at lower WLs.

The results of the MAR assessments for the heel batches indicate that in order to maintain nominal SWPF volumes, the projected operating windows will need to be reduced.

2.4 Processing Sludge-Only versus Coupled Flowsheets

As noted above, the MAR assessments that were conducted as part of this SWPF gap analysis utilized only coupled flowsheet projections based upon information in the System Plan Revision 19. For recent sludge batches, the frit development process has faced a challenge when it comes to selecting a frit that can handle both a sludge-only and coupled flowsheet when the auxiliary stream comes from the Actinide Removal Process (ARP). The challenge stems from the increase in sodium concentration from the sludge without the ARP stream (sludge-only) to the concentration of sodium in the sludge with the ARP stream present (coupled operations): the larger the volume of the ARP stream, the greater the challenge (see, for example, Peeler and Edwards (2012)).

Consider the projected Na_2O concentrations for the sludge-only and coupled projections for batches SB11 through SB23 from the System Plan Revision 19 information presented in Table 2-4. For each batch from SB11 through SB18, there is just a 2 to 3 wt% difference between the two flowsheets, while for SB19 through SB23 the differences are on the order of 5 to 7 wt%. Thus, a single frit solution for the sludge-only and coupled flowsheets for this latter grouping of sludge batches is a much bigger challenge than for the former group of sludge batches.

Table 2-4. Na_2O Concentrations (wt%) in Sludge-Only and Coupled Projections

Sludge Batch	SB11	SB12	SB13	SB14	SB15	SB16	SB17	SB18	SB19	SB20	SB21	SB22	SB23
Sludge-Only	26.97	30.70	31.46	32.52	31.57	30.24	24.96	24.44	5.06	7.66	8.17	9.29	7.24
Coupled	29.16	31.99	32.57	33.38	32.66	31.64	27.62	27.23	12.49	14.47	14.86	15.71	14.15

To investigate this further, an additional MAR assessment of SB11 was conducted to evaluate whether the same frit can handle the variation between sludge-only and coupled operations for this sludge batch. Based on current process control models and their associated constraints, frits were identified that were robust enough to handle both sludge-only processing (no SWPF) and coupled operations (SWPF-based) for SB11 while meeting the targeted WLs (nominally 40%) and accounting for anticipated SRAT-to-SRAT sludge variation.

Thus, it appears that there is potential for finding a single frit to accommodate a sludge-only and coupled flowsheet (at the nominal SWPF volumes evaluated as part of this study) for some of the batches as projected by the HLW System Plan Revision 19. This flexibility is primarily driven by the DWPF WAC limit of 0.7 M Na^+ (moles per liter slurry - includes sodium contribution from MST solids) coming into the facility which minimizes the swing in Na_2O concentration from a SRAT perspective when comparing a sludge-only to a coupled operations flowsheet. This is in contrast to current ARP/ Modular Caustic Side Solvent Extraction Unit (MCU) operations which results in a significant shift in Na_2O content between sludge-only operations and coupled operations even with only 2000 gallons of ARP. Table 2-5 provides a compositional comparison of the nominal ARP (based on Martino 2014)) and SWPF streams.

Table 2-5. Contrasting Calcine Compositions of ARP and SWPF

Oxide	ARP (wt%)	SWPF (wt%)
Al_2O_3	-	2.43
Na_2O	80.3	39.08
SO_4^{2-}	2.3	2.08
TiO_2	17.4	56.41

2.5 Defining the SWPF Glass Compositional Region

The results of the Variation Stage MAR assessment suggested that frits were available that would allow DWPF to target 36%-44% WL for SB11 – SB18. For SB19 – SB23 (identified as the Tank Farm heels by SRR), the results suggested that WLs would have to be decreased to maintain processing at the volume of SWPF material expected to be incorporated. The targeted waste loadings for the heel sludge batches ranged from the low 30s to an upper limit of approximately 40%.

The results of the MAR assessment provided two critical pieces of information that were needed to define the future glass processing regions: (1) the WL intervals and (2) candidate frit compositions. Using this information along with the projected coupled operations compositions for the sludge batches (Table 2-1), SRNL could then define minimum and maximum values for those elements (or oxides) tracked in Revision 19 of the HLW System Plan in glass composition space. That is, using the frit and sludge compositions (including variation for the sludge batches) and knowing the WL intervals over which each sludge batch could be processed (based on predictions using the current PCCS models), the future SWPF glass compositional region could be identified through determinations of minimum and maximum values for oxides of interest.

Table 2-6 and Table 2-7 show the minimum and maximum values, respectively, for each sludge oxide coupled with SWPF based on the projected WL intervals of interest (36 – 44% WL). In addition to the WL interval, the 7.5% variation (-7.5% on the minimum values and +7.5% on the maximum values) around the major oxides has been included with a ±0.5 wt% variation being applied to minor oxides that were tracked individually. It should be noted that the application of the +7.5% or +0.5 wt% was based on the larger or maximum value. Also shown in Table 2-7 (see last column) are several oxides that will be tracked collectively as the test matrix is developed. Since each of these oxides has a very low maximum concentration, they will be tracked collectively in the test matrix in a group called “Others”.

Table 2-6. Minimum Oxides Values from Sludge Coupled with SWPF.

	SB11	SB12	SB13	SB14	SB15	SB16	SB17	SB18	SB19	SB20	SB21	SB22	SB23
Oxide	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%
Al_2O_3	3.65	3.12	2.68	3.62	5.24	5.69	6.25	6.18	7.08	5.39	4.95	4.37	6.40
B_2O_3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
BaO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CaO	0.44	0.44	0.42	0.31	0.23	0.35	0.32	0.28	0.39	0.78	0.86	1.08	0.81
Ce_2O_3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CoO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cr_2O_3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cs_2O	0.42	0.42	0.42	0.42	0.42	0.42	0.42	0.42	0.42	0.42	0.42	0.42	0.42
CuO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fe_2O_3	5.94	5.63	5.79	5.21	6.04	6.53	7.50	7.48	9.66	9.91	9.95	9.91	9.13
K_2O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
La_2O_3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
MgO	0.47	0.22	0.08	0.00	0.16	0.08	0.05	0.07	0.13	0.02	0.00	0.00	0.00
MnO	0.37	0.42	0.43	0.46	0.18	0.50	0.49	0.42	0.65	1.72	1.99	2.48	1.32
Na_2O	8.63	9.47	9.64	9.88	9.67	9.37	8.18	8.06	3.70	4.28	4.40	4.65	4.19
NiO	0.07	0.09	0.26	0.36	0.11	0.00	0.00	0.00	0.02	0.68	0.83	1.15	0.49
PbO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
SO_4	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
SiO_2	1.49	1.59	1.44	0.87	1.08	0.95	0.90	1.16	1.68	1.07	0.90	0.44	0.83
ThO_2	0.34	0.12	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.04
TiO_2	3.69	3.69	3.69	3.69	3.69	3.69	3.69	3.69	3.70	3.70	3.70	3.69	3.69
U_3O_8	2.59	2.93	3.25	3.45	1.50	0.68	0.50	0.54	0.77	0.41	0.42	0.36	0.75
ZnO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
ZrO_2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Table 2-7. Maximum Oxide Values from Sludge Coupled with SWPF.

	SB11	SB12	SB13	SB14	SB15	SB16	SB17	SB18	SB19	SB20	SB21	SB22	SB23	Others
Oxide	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	
Al_2O_3	5.83	4.98	4.29	5.78	8.37	9.09	9.99	9.87	11.31	8.61	7.90	6.99	10.23	
B_2O_3	0.24	0.23	0.22	0.22	0.22	0.22	0.22	0.23	0.23	0.23	0.23	0.22	0.22	
BaO	0.11	0.12	0.13	0.12	0.10	0.10	0.09	0.09	0.10	0.18	0.20	0.24	0.17	yes
CaO	1.05	1.04	1.02	0.86	0.76	0.92	0.88	0.83	0.98	1.51	1.63	1.92	1.55	
Ce_2O_3	0.14	0.13	0.13	0.13	0.10	0.11	0.14	0.14	0.16	0.12	0.11	0.09	0.18	yes
CoO	0.05	0.05	0.04	0.04	0.04	0.05	0.04	0.04	0.04	0.04	0.04	0.04	0.05	yes
Cr_2O_3	0.14	0.15	0.16	0.15	0.13	0.13	0.12	0.11	0.14	0.11	0.11	0.09	0.14	yes
Cs_2O	1.02	1.02	1.02	1.02	1.02	1.02	1.02	1.02	1.02	1.02	1.02	1.02	1.02	
CuO	0.08	0.08	0.08	0.07	0.07	0.08	0.07	0.06	0.07	0.06	0.06	0.06	0.08	yes
Fe_2O_3	9.49	8.99	9.25	8.32	9.66	10.43	11.99	11.95	15.43	15.83	15.89	15.84	14.59	
K_2O	0.15	0.17	0.15	0.13	0.13	0.16	0.13	0.13	0.10	0.08	0.08	0.07	0.11	yes
La_2O_3	0.09	0.09	0.09	0.08	0.07	0.08	0.08	0.08	0.09	0.07	0.07	0.06	0.10	yes
MgO	1.09	0.74	0.56	0.40	0.66	0.55	0.50	0.54	0.62	0.46	0.42	0.33	0.41	
MnO	0.95	1.01	1.03	1.07	0.69	1.12	1.11	1.02	1.33	2.81	3.18	3.96	2.26	
Na_2O	13.79	15.13	15.40	15.79	15.45	14.97	13.07	12.88	5.91	6.84	7.03	7.43	6.69	
NiO	0.53	0.57	0.80	0.94	0.60	0.38	0.31	0.32	0.47	1.37	1.59	2.02	1.11	
PbO	0.23	0.16	0.14	0.13	0.09	0.09	0.10	0.14	0.18	0.14	0.13	0.10	0.14	yes
SO_4	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	yes
SiO_2	2.49	2.62	2.43	1.63	1.92	1.75	1.68	2.04	2.75	1.91	1.67	1.04	1.59	
ThO_2	0.91	0.60	0.43	0.29	0.25	0.23	0.23	0.23	0.25	0.24	0.25	0.24	0.50	
TiO_2	5.90	5.90	5.90	5.90	5.90	5.90	5.90	5.90	5.91	5.91	5.91	5.90	5.90	
U_3O_8	4.15	4.68	5.20	5.52	2.51	1.38	1.13	1.19	1.50	1.01	1.01	0.94	1.47	
ZnO	0.10	0.09	0.09	0.08	0.07	0.09	0.08	0.07	0.11	0.11	0.11	0.09	0.11	yes
ZrO_2	0.21	0.22	0.22	0.19	0.16	0.19	0.18	0.17	0.20	0.14	0.14	0.11	0.21	yes

Table 2-8 summarizes the minimum and maximum values from sludge coupled with SWPF that would be expected to bound the future glass compositional region for SWPF processing based on the inputs and assumptions used.[2] To be clear, the values shown in Table 2-8 represent bounding values for those sludge components tracked by SRR's HLW System Plan expressed in glass composition space. For example, Fe_2O_3 concentrations in the SWPF glass composition space would be expected to range from 5.2 to 15.9 wt% in glass based on the added variation (in this case ±7.5 wt%) over WLs of 36 to 44% WL – assuming no contribution of Fe_2O_3 from frit. Consider SiO_2 as another example. Based on the sludge projections and the variation applied, SiO_2 values in glass composition space based on the contribution from sludge and SWPF are expected to be between 0.44 and 2.75 wt%. The primary contribution of SiO_2 will come from the frit, but the contribution from the sludge must be accounted for in defining the overall range of SiO_2 content in the SWPF compositional region of interest. Also, note that this table identifies (by means of the last column) those oxides that are to be handled collectively as an "Others" term in the development of the test matrix for this study.

Table 2-8. Minimum and Maximum Values Across All Projected Sludge Batches (Glass Composition, wt%).

Oxide	Minimum	Maximum	Others
Al_2O_3	2.68	11.31	
B_2O_3	0.00	0.24	
BaO	0.00	0.24	yes
CaO	0.23	1.92	
Ce_2O_3	0.00	0.18	yes
CoO	0.00	0.05	yes
Cr_2O_3	0.00	0.16	yes
Cs_2O	0.42	1.02	
CuO	0.00	0.08	yes
Fe_2O_3	5.21	15.89	
K_2O	0.00	0.17	yes
La_2O_3	0.00	0.10	yes
Li_2O	0.00	0.00	
MgO	0.00	1.09	
MnO	0.18	3.96	
Na_2O	3.70	15.79	
NiO	0.00	2.02	
PbO	0.00	0.23	yes
SO_4	0.00	0.25	yes
SiO_2	0.44	2.75	
ThO_2	0.00	0.91	
TiO_2	3.69	5.91	
U_3O_8	0.36	5.52	
ZnO	0.00	0.11	yes
ZrO_2	0.00	0.22	yes

[2] Note: ±7.5% on the major oxides and 0.5 wt% on the minor oxides have been added.

Coupling the information shown in Table 2-8 with the potential frit compositions identified in the MAR assessment, SRNL developed minimum and maximum values for the future SWPF-based processing region in terms of oxide concentrations in glass. These values are shown in Table 2-9 and are the proposed values for designing a test matrix to cover the SWPF glass composition region. It should be noted that the major frit oxides identified in the MAR assessment were B_2O_3, Li_2O, Na_2O, SiO_2, and Al_2O_3. Al_2O_3 was added to some of the candidate frits to address potential frit phase separation issues or to meet the lower Al_2O_3 glass limit currently implemented in PCCS (approximately 3.5 wt%).

The minimum and maximum values for most of the sludge oxides shown in Table 2-9 (glass composition space) could be taken directly from the values shown in Table 2-8 (since they were computed with WLs and the variation accounted for). For example, the computed values for BaO, CaO, Ce_2O_3, CoO, Cr_2O_3, Cs_2O, CuO, Fe_2O_3, K_2O, La_2O_3, MgO, MnO, NiO, PbO, SO_4, ThO_2, U_3O_8, ZnO, and ZrO_2 were taken from Table 2-8 and rounded upwards slightly. Consider the minor component BaO. Based strictly on the computations, the maximum concentration of BaO was reported as 0.24 wt% (see Table 2-8). The maximum limit proposed for the SWPF glass region is 0.25 wt%. Consider a couple of the major oxides as other examples – Fe_2O_3 and U_3O_8. Computationally, these two oxides had maximum concentrations (based on WLs and variation) of 15.89 and 5.52 wt%, respectively (refer to Table 2-8). Given these two components were not considered as frit additives, the proposed maximum values for the SWPF test matrix were rounded to 16 and 6 wt%, respectively. The minimum and maximum values for Al_2O_3, B_2O_3, Li_2O, Na_2O, SiO_2, and TiO_2 were established using a slightly different approach.

First, consider the Al_2O_3 values of 3.5 to 13 wt% (in glass) shown in Table 2-9. Based strictly on the sludge contributions in Table 2-8, a lower limit of approximately 2.7 wt% (in glass) could be defined. However, SME acceptability has a current lower limit of 3 wt% Al_2O_3 (without uncertainties accounted for and independent of the source of Al_2O_3 – frit or sludge). So, a lower limit of 3.5 wt% is proposed for the SWPF future composition regions. The basis for the upper limit of 13 wt% Al_2O_3 in glass (see Table 2-9) is as follows: The contribution from sludge alone is approximately 11.3 wt%. However, an upper Al_2O_3 limit of 13 wt% is proposed for the future SWPF glass compositional region to allow for the potential need to add Al_2O_3 to some frits to suppress amorphous phase separation.

The proposed minimum and maximum B_2O_3 values are 4.5 and 10 wt% (in glass), respectively. The lower glass limit (4.5 wt%) was established by the minimum B_2O_3 content in candidate frits (8 wt%) at the maximum WL of 44%. The upper limit was established based on the maximum content observed in potential frits (15 wt%) at the lower WL of 32%. It is noted that there is a small contribution of B_2O_3 from sludge (0.24 wt% - see Table 2-8) which was also considered.

The proposed minimum and maximum Li_2O concentrations were strictly based on the compositions of the potential frits and WL intervals over which each sludge batch could be processed. Based on those two factors, the proposed Li_2O range for the SWPF processing region is 1 to 7 wt% in glass.

SiO_2 concentrations for the SWPF future glass region were also driven primarily by the candidate frit compositions and WLs – recognizing that there was a small (but not insignificant) contribution from sludge of up to approximately 2.8 wt% (see Table 2-8). Based on this information, the proposed SiO_2 range for the SWPF processing region is 40 to 55 wt% in glass.

Table 2-9. Proposed Minimum and Maximum Oxides Values for the SWPF Future Glass Processing Region.

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

Perhaps of most interest was the basis to establish the TiO_2 and Na_2O limits for the future glass processing region. First consider the TiO_2. Given that TiO_2 is not a frit component, its contribution will be strictly based on the sludge concentration, the anticipated variation, and the WL interval of interest. This information was used to compute the minimum and maximum TiO_2 values of 3.7 and 5.9 wt% (in glass), respectively, as shown in Table 2-8. Obviously the projected 5.9 wt% TiO_2 in glass exceeds the upper limit over which the current T_L model is valid (i.e., 2 wt%) and this alone drives the need for an experimental program to fill in those gaps with additional data to evaluate model applicability for future operations. In addition, the lower projected TiO_2 limit of 3.9 wt% (in glass) represents a gap with the current 2 wt% limit. Therefore, to bridge the gap between 2 and 3.9 wt% TiO_2, the lower limit for the proposed glass processing region was set at 2 wt%. With a lower limit of 2 wt%

and an upper limit of 6 wt% (see Table 2-9), this will provide data to cover the span over which current data are limited up to the expected concentration in SWPF glasses.

Last, consider the strategy for establishing the minimum and maximum values for Na_2O. There are three primary sources of Na_2O in the DWPF flowsheet: Tank Farm washing strategies, Na_2O contribution in frit, and the Na_2O contribution from SWPF. The Revision 19 sludge-only projections provided by SRR assumed a single wash endpoint of 1.25M Na^+. In addition, the SWPF flowsheet assumptions were based on nominal operations (or a fixed set of conditions) that, if changed, could have a significant impact on the Na_2O content introduced into the SRAT by SWPF. Although these two factors were fixed based on the inputs and assumptions document, the other source of Na_2O is from the frit. The potential frits identified from the MAR assessments range from a low of 1 wt% up to a high of 18 wt% Na_2O.

The Na_2O contribution in glass from sludge alone has a range of approximately 3.7 to 15.8 wt% as shown in Table 2-8. The low Na_2O concentrations stem from SB19 – 23, which are considered heels; while the higher Na_2O concentrations are based on SB11 – SB18, which are defined by the projected Tank Farm wash endpoint and SWPF contributions to the SRAT. Two other factors were considered in establishing the proposed Na_2O limits: the PCCS constraint of Al_2O_3 concentration and sum of alkali, and the fact that other nuclear waste glasses (specifically low activity waste (LAW) glasses) have targeted up to 20 – 25 wt% Na_2O. It should be noted that for most LAW glasses, the high concentration of Na_2O in the low activity waste fraction or supernatant is the primary (if not the only) source of alkali in the overall glass composition. That is, very little, if any, alkali (Na_2O or Li_2O in particular) is added through glass forming chemicals (or frit) keeping the total alkali content in the lower-to-mid 20% range.

Having all of this information available, the ultimate decision to establish the upper bound at 18 wt% was based on the maximum allowable Na_2O concentration from the MAR assessments. That is, when glass compositions were evaluated as outputs of the sludge-frit mixtures over the WL interval of interest, the maximum concentration of Na_2O was approximately 18 wt%. So the question asked was: Is there really a need to go above 18 wt% for future operations? And the answer was “No” given the fact that the current models restricted higher Na_2O concentrations and that the total alkali content ($Na_2O + Li_2O + Cs_2O$) of this region could be up to 26 wt% based on the combined maximum values for these oxides. The upper limit of 18 wt% Na_2O is also consistent with previous DWPF studies associated with the Al_2O_3 and sum of alkali constraints in PCCS (Raszewski and Edwards (2009)). The lower limit of 8 wt% Na_2O is based on a similar review of the MAR results.

2.6 Selecting the Glass Compositions for the Test Matrix

The objective of this section is to identify glass compositions which not only cover the future SWPF glass processing region of Table 2-9 but also will provide a technical basis from which revisions or upgrades to current PCCS models can be made if warranted. The test matrix glasses were defined to cover the projected compositional region of interest to SWPF and are not based on specific frit – sludge combinations over a waste loading interval of interest. That is, although the test matrix glasses provide ample coverage, they are not intended to reflect direct feasibility of DWPF processing of specific sludge batches.

ES-VSL will fabricate these glasses and measure various properties (T_L, durability, and viscosity) to generate new data such that comparisons with current PCCS model predictions can be made. If differences of statistical or practical significance do exist for a property of interest, the data will be used by SRNL to refine or update the current DWPF process control model for that property to reflect more accurate predictions over the composition range of interest for future operations based on the SWPF flowsheet.

The compositional region for future SWPF processing is very similar to that used by Raszewski and Edwards (2009) to support DWPF’s implementation of an Al_2O_3 and sum of alkali constraint to support the ARP-based coupled operations flowsheet with one primary difference. In the 2009 study, the maximum TiO_2 concentration was 2 wt% in glass, while projections of future sludge batches based on anticipated SWPF volumes and the expected higher WLs have increased the expected TiO_2 concentration up to 6 wt% in glass. Those oxides indicated in Table 2-9 as part of the "Others" group will vary as the overall contribution of "Others" varies in the test matrix glasses while the relative ratios of the oxides within "Others" will be fixed.

2.6.1 Experimental Design

The test matrix design was based on the integration of an Extreme Vertices (EVs) approach combined with space filling points. A layered-EV approach has been the primary design basis for glass variability studies in support of DWPF operations (e.g., Peeler and Edwards (2011)). Table 2-10 provides the minimum and maximum values for a two-layer design: An outer-layer (OL) region derived directly from the values of Table 2-9 and an inner-layer region determined by adjusting the OL maximum and minimum values by 25%. Table 2-10 also summarizes the range of "Others" in both the outer (0 to 2.15 wt%) and inner (0.5375 to 1.6125 wt%) layers.

For the outer layer (OL), 36,989 EVs were developed using the Design of Experiments platform in JMP Version 11.1.1 (SAS Institute, Inc., 2014). Of the 36,989 outer layer EVs, only 3734 (or roughly 10%) were found to be MAR acceptable – without the 2 wt% TiO_2 in glass constraint and the homogeneity (or associated constraints) being imposed. In fact, of the EVs that were not MAR acceptable, 17,405 failed a process-related constraint such as viscosity or liquidus temperature while 15,850 failed a waste-form affecting constraint such as nepheline or durability. This identifies the potential risk of performing a broad glass compositional study based strictly on coverage – not feasibility (i.e., specific frit-sludge-WL combinations). All of the SWPF glasses will challenge the current 2 wt% TiO_2 constraint. In addition, some of the SWPF test matrix glasses will be selected to challenge the homogeneity and its associated constraints (i.e., low and high frit) for coupled operations with glasses having TiO_2 concentrations of > 2 wt%. This latter criterion is a recommendation from Raszewski and Edwards (2009).

Table 2-10. Minimum and Maximum Oxides Ranges for the Inner and Outer Layers

	Outer Layer		Inner Layer	
Oxide	Minimum	Maximum	Minimum	Maximum
Al_2O_3	3.5	13	5.875	10.625
B_2O_3	4.5	10	5.875	8.625
CaO	0.2	2	0.65	1.55
Cs_2O	0.3	1	0.475	0.825
Fe_2O_3	5	16	7.75	13.25
Li_2O	1	7	2.5	5.5
MgO	0	2	0.5	1.5
MnO	0.2	4	1.15	3.05
Na_2O	8	18	10.5	15.5
NiO	0	2	0.5	1.5
SiO_2	40	55	43.75	51.25
ThO_2	0	1	0.25	0.75
TiO_2	2	6	3.0	5.0
U_3O_8	0	6	1.5	4.5
Others	0	2.15	0.5375	1.6125

From the 3734 OL EVs that are considered MAR acceptable, the D-Optimality routine within SAS Version 8.2 (SAS Institute, Inc. (1999)) was then used to select 15 outer layer EVs that support the assessment of linearity with respect to compositional effects on various properties. These glasses provide coverage for the most extreme compositions in the projected SWPF glass region.

JMP was then used to determine the EVs for the inner layer (IL) region of Table 2-10. This yielded a set of 30,967 inner layer EVs. When screened with the current PCCS models and acceptance criteria, 10,365 were found to be acceptable (or roughly 33% of the inner layer EVs). In fact, of the EVs that were not MAR acceptable, 17,383 failed a process-related constraint such as viscosity or liquidus temperature while 3,219 failed a waste-form affecting constraint such as nepheline or durability. Again, this identifies the potential risk of performing a broad glass compositional study based strictly on coverage – not feasibility. The same SAS D-Optimality process then was used to select 15 EVs from the set of MAR acceptable, inner layer EVs. These inner layer design points were added to the OL design points yielding 30 glass compositions for the test matrix. In addition, the centroid (i.e., average) of the 15 outer layer EVs was determined and was included as a design point. The outer and inner layer design points and the centroid provided a test matrix of 31 glasses.

As a supplement to the 31 EV-based glasses, a set of space-filling design points for the OL region was generated using the Space Filling algorithm of JMP's Design of Experiments platform. A space-filling approach was utilized to provide a more uniform and thorough coverage of the interior of the compositional region of interest than the coverage afforded by the layered approach alone. An initial set of 50 space-filling points was generated, and 19 of these were found to be MAR acceptable (once again, the TiO_2 and the homogeneity constraints were not imposed during this assessment). In fact, of the space-filling points that were not MAR acceptable, 28 failed a process-related constraint such as viscosity or liquidus temperature while only 3 failed a waste-form affecting constraint such as nepheline or durability. The 19 space filling (SF) points that were MAR acceptable were added to the test matrix, which is provided in Table 2-11. The proposed SWPF test matrix includes 50 targeted glass compositions. It should be noted that the targeted compositions shown in Table 2-11 do not include RuO_2, which should be spiked in each test matrix glass at 0.1 wt%.

Table 2-11. Test Matrix for SWPF Gap Analysis Study (mass fraction)

(part 1 of 2) [3]

Glass ID	Type	Al_2O_3	B_2O_3	BaO	CaO	Ce_2O_3	CoO	Cr_2O_3	Cs_2O	CuO	Fe_2O_3	K_2O	La_2O_3	Li_2O
SWPF-01	D-Opt OL	0.03500	0.04500	0.00250	0.00200	0.00200	0.00100	0.00200	0.01000	0.00100	0.13450	0.00200	0.00100	0.07000
SWPF-02	D-Opt OL	0.03500	0.04500	0.00000	0.02000	0.00000	0.00000	0.00000	0.00300	0.00000	0.05000	0.00000	0.00000	0.07000
SWPF-03	D-Opt OL	0.03500	0.04500	0.00000	0.02000	0.00000	0.00000	0.00000	0.00300	0.00000	0.07700	0.00000	0.00000	0.07000
SWPF-04	D-Opt OL	0.03500	0.04500	0.00250	0.02000	0.00200	0.00100	0.00200	0.00650	0.00100	0.05000	0.00200	0.00100	0.07000
SWPF-05	D-Opt OL	0.03500	0.10000	0.00250	0.00200	0.00200	0.00100	0.00200	0.00300	0.00100	0.05000	0.00200	0.00100	0.01000
SWPF-06	D-Opt OL	0.03500	0.10000	0.00000	0.00200	0.00000	0.00000	0.00000	0.00300	0.00000	0.05000	0.00000	0.00000	0.07000
SWPF-07	D-Opt OL	0.03500	0.10000	0.00250	0.00200	0.00200	0.00100	0.00200	0.00300	0.00100	0.05000	0.00200	0.00100	0.07000
SWPF-08	D-Opt OL	0.03500	0.10000	0.00000	0.00200	0.00000	0.00000	0.00000	0.01000	0.00000	0.16000	0.00000	0.00000	0.01000
SWPF-09	D-Opt OL	0.03500	0.10000	0.00000	0.02000	0.00000	0.00000	0.00000	0.01000	0.00000	0.05000	0.00000	0.00000	0.07000
SWPF-10	D-Opt OL	0.03500	0.10000	0.00250	0.02000	0.00200	0.00100	0.00200	0.01000	0.00100	0.16000	0.00200	0.00100	0.01000
SWPF-11	D-Opt OL	0.05600	0.10000	0.00000	0.00200	0.00000	0.00000	0.00000	0.01000	0.00000	0.05000	0.00000	0.00000	0.01000
SWPF-12	D-Opt OL	0.13000	0.04500	0.00000	0.00200	0.00000	0.00000	0.00000	0.00300	0.00000	0.16000	0.00000	0.00000	0.07000
SWPF-13	D-Opt OL	0.13000	0.04500	0.00250	0.00200	0.00200	0.00100	0.00200	0.01000	0.00100	0.05000	0.00200	0.00100	0.07000
SWPF-14	D-Opt OL	0.13000	0.10000	0.00250	0.02000	0.00200	0.00100	0.00200	0.00300	0.00100	0.05000	0.00200	0.00100	0.07000
SWPF-15	D-Opt OL	0.13000	0.10000	0.00250	0.02000	0.00200	0.00100	0.00200	0.01000	0.00100	0.05000	0.00200	0.00100	0.07000
SWPF-16	centroid	0.06173	0.07800	0.00133	0.01040	0.00107	0.00053	0.00107	0.00650	0.00053	0.07943	0.00107	0.00053	0.05400
SWPF-17	D-Opt IL	0.05875	0.05875	0.00063	0.00650	0.00050	0.00025	0.00050	0.00825	0.00025	0.07750	0.00050	0.00025	0.02500
SWPF-18	D-Opt IL	0.05875	0.05875	0.00063	0.00650	0.00050	0.00025	0.00050	0.00825	0.00025	0.07750	0.00050	0.00025	0.05500
SWPF-19	D-Opt IL	0.05875	0.05875	0.00188	0.01550	0.00150	0.00075	0.00150	0.00475	0.00075	0.07750	0.00150	0.00075	0.02500
SWPF-20	D-Opt IL	0.05875	0.05875	0.00188	0.01550	0.00150	0.00075	0.00150	0.00475	0.00075	0.13250	0.00150	0.00075	0.05500
SWPF-21	D-Opt IL	0.05875	0.05875	0.00063	0.01550	0.00050	0.00025	0.00050	0.00825	0.00025	0.08288	0.00050	0.00025	0.02500
SWPF-22	D-Opt IL	0.05875	0.07413	0.00063	0.01550	0.00050	0.00025	0.00050	0.00825	0.00025	0.13250	0.00050	0.00025	0.02500
SWPF-23	D-Opt IL	0.05875	0.08625	0.00188	0.00650	0.00150	0.00075	0.00150	0.00475	0.00075	0.07750	0.00150	0.00075	0.02500
SWPF-24	D-Opt IL	0.05875	0.08625	0.00063	0.00650	0.00050	0.00025	0.00050	0.00825	0.00025	0.13250	0.00050	0.00025	0.02500
SWPF-25	D-Opt IL	0.05875	0.08625	0.00063	0.01550	0.00050	0.00025	0.00050	0.00475	0.00025	0.07750	0.00050	0.00025	0.05500
SWPF-26	D-Opt IL	0.05875	0.08625	0.00063	0.01550	0.00050	0.00025	0.00050	0.00825	0.00025	0.07750	0.00050	0.00025	0.05500
SWPF-27	D-Opt IL	0.10625	0.05875	0.00063	0.00650	0.00050	0.00025	0.00050	0.00475	0.00025	0.07750	0.00050	0.00025	0.05500
SWPF-28	D-Opt IL	0.10625	0.05875	0.00063	0.00650	0.00050	0.00025	0.00050	0.00825	0.00025	0.07750	0.00050	0.00025	0.05500
SWPF-29	D-Opt IL	0.10625	0.05875	0.00188	0.01550	0.00150	0.00075	0.00150	0.00825	0.00075	0.07863	0.00150	0.00075	0.05500
SWPF-30	D-Opt IL	0.10625	0.08625	0.00188	0.00650	0.00150	0.00075	0.00150	0.00825	0.00075	0.07750	0.00150	0.00075	0.02500
SWPF-31	D-Opt IL	0.10625	0.08625	0.00063	0.01550	0.00050	0.00025	0.00050	0.00475	0.00025	0.07750	0.00050	0.00025	0.02500
SWPF-32	SF	0.06527	0.05805	0.00114	0.01081	0.00091	0.00046	0.00091	0.00690	0.00046	0.07331	0.00091	0.00046	0.05253
SWPF-33	SF	0.07337	0.08295	0.00131	0.01047	0.00105	0.00052	0.00105	0.00642	0.00052	0.08927	0.00105	0.00052	0.04935
SWPF-34	SF	0.10013	0.06400	0.00114	0.00962	0.00091	0.00045	0.00091	0.00647	0.00045	0.06660	0.00091	0.00045	0.03074
SWPF-35	SF	0.07407	0.08758	0.00116	0.01029	0.00092	0.00046	0.00092	0.00653	0.00046	0.10966	0.00092	0.00046	0.05332
SWPF-36	SF	0.11004	0.06612	0.00123	0.01065	0.00099	0.00049	0.00099	0.00678	0.00049	0.07153	0.00099	0.00049	0.05594
SWPF-37	SF	0.04774	0.07683	0.00123	0.01061	0.00098	0.00049	0.00098	0.00653	0.00049	0.09952	0.00098	0.00049	0.04733
SWPF-38	SF	0.05165	0.07504	0.00113	0.01017	0.00090	0.00045	0.00090	0.00640	0.00045	0.11579	0.00090	0.00045	0.02280
SWPF-39	SF	0.05723	0.05847	0.00103	0.01053	0.00082	0.00041	0.00082	0.00635	0.00041	0.07138	0.00082	0.00041	0.04883
SWPF-40	SF	0.10475	0.07544	0.00135	0.01153	0.00108	0.00054	0.00108	0.00686	0.00054	0.09533	0.00108	0.00054	0.04441
SWPF-41	SF	0.05458	0.08139	0.00121	0.01069	0.00097	0.00048	0.00097	0.00650	0.00048	0.06590	0.00097	0.00048	0.05929
SWPF-42	SF	0.05575	0.06682	0.00110	0.00985	0.00088	0.00044	0.00088	0.00633	0.00044	0.06332	0.00088	0.00044	0.02275
SWPF-43	SF	0.06224	0.05829	0.00111	0.01103	0.00088	0.00044	0.00088	0.00650	0.00044	0.11316	0.00088	0.00044	0.05379
SWPF-44	SF	0.06402	0.07176	0.00122	0.01180	0.00098	0.00049	0.00098	0.00663	0.00049	0.07016	0.00098	0.00049	0.05088
SWPF-45	SF	0.06290	0.06496	0.00117	0.01069	0.00093	0.00047	0.00093	0.00638	0.00047	0.10685	0.00093	0.00047	0.02363
SWPF-46	SF	0.06012	0.05983	0.00126	0.01065	0.00100	0.00050	0.00100	0.00656	0.00050	0.07162	0.00100	0.00050	0.03441
SWPF-47	SF	0.07668	0.07765	0.00123	0.01105	0.00098	0.00049	0.00098	0.00650	0.00049	0.06779	0.00098	0.00049	0.04400
SWPF-48	SF	0.08923	0.08088	0.00113	0.01104	0.00090	0.00045	0.00090	0.00673	0.00045	0.07351	0.00090	0.00045	0.03785
SWPF-49	SF	0.05442	0.08183	0.00133	0.01041	0.00106	0.00053	0.00106	0.00662	0.00053	0.07403	0.00106	0.00053	0.03527
SWPF-50	SF	0.10685	0.06254	0.00129	0.01068	0.00103	0.00052	0.00103	0.00646	0.00052	0.07162	0.00103	0.00052	0.05776

[3] Note: RuO_2 is not shown in the targeted compositions. Each test matrix glass should be spiked such that the RuO_2 concentration in glass is 0.001 on a mass fraction basis. The RuO_2 addition is to support liquidus temperature measurements from a kinetics standpoint.

Table 2-11. Test Matrix for SWPF Gap Analysis Study (mass fraction)

(part 2 of 2).[4]

Glass ID	Type	MgO	MnO	Na_2O	NiO	PbO	SO_4	SiO_2	ThO_2	TiO_2	U_3O_8	ZnO	ZrO_2
SWPF-01	D-Opt OL	0.02000	0.00200	0.08000	0.00000	0.00250	0.00300	0.55000	0.01000	0.02000	0.00000	0.00200	0.00250
SWPF-02	D-Opt OL	0.00000	0.04000	0.08000	0.02000	0.00000	0.00000	0.55000	0.01000	0.02000	0.05700	0.00000	0.00000
SWPF-03	D-Opt OL	0.02000	0.04000	0.08000	0.00000	0.00000	0.00000	0.55000	0.00000	0.06000	0.00000	0.00000	0.00000
SWPF-04	D-Opt OL	0.00000	0.00200	0.08000	0.00000	0.00250	0.00300	0.55000	0.00000	0.06000	0.06000	0.00200	0.00250
SWPF-05	D-Opt OL	0.02000	0.04000	0.16850	0.02000	0.00250	0.00300	0.40000	0.01000	0.06000	0.06000	0.00200	0.00250
SWPF-06	D-Opt OL	0.00000	0.00200	0.09800	0.00000	0.00000	0.00000	0.55000	0.01000	0.02000	0.06000	0.00000	0.00000
SWPF-07	D-Opt OL	0.00000	0.04000	0.08000	0.02000	0.00250	0.00300	0.51850	0.00000	0.06000	0.00000	0.00200	0.00250
SWPF-08	D-Opt OL	0.02000	0.00200	0.08000	0.00000	0.00000	0.00000	0.45100	0.01000	0.06000	0.06000	0.00000	0.00000
SWPF-09	D-Opt OL	0.02000	0.00200	0.08000	0.02000	0.00000	0.00000	0.47300	0.00000	0.06000	0.06000	0.00000	0.00000
SWPF-10	D-Opt OL	0.00000	0.04000	0.12350	0.00000	0.00250	0.00300	0.40000	0.00000	0.02000	0.06000	0.00200	0.00250
SWPF-11	D-Opt OL	0.00000	0.00200	0.18000	0.02000	0.00000	0.00000	0.55000	0.00000	0.02000	0.00000	0.00000	0.00000
SWPF-12	D-Opt OL	0.00000	0.00200	0.08000	0.00000	0.00000	0.00000	0.40000	0.00000	0.04800	0.06000	0.00000	0.00000
SWPF-13	D-Opt OL	0.02000	0.04000	0.08000	0.00000	0.00250	0.00300	0.45150	0.00000	0.02000	0.06000	0.00200	0.00250
SWPF-14	D-Opt OL	0.02000	0.00200	0.08000	0.00000	0.00250	0.00300	0.48350	0.00000	0.02000	0.00000	0.00200	0.00250
SWPF-15	D-Opt OL	0.00000	0.04000	0.08000	0.00000	0.00250	0.00300	0.40000	0.01000	0.06000	0.00850	0.00200	0.00250
SWPF-16	centroid	0.00933	0.01973	0.09667	0.00667	0.00133	0.00160	0.48517	0.00400	0.04053	0.03637	0.00107	0.00133
SWPF-17	D-Opt IL	0.01500	0.01150	0.14838	0.00500	0.00063	0.00075	0.51250	0.00250	0.05000	0.01500	0.00050	0.00063
SWPF-18	D-Opt IL	0.00500	0.01150	0.15500	0.01500	0.00063	0.00075	0.49088	0.00750	0.03000	0.01500	0.00050	0.00063
SWPF-19	D-Opt IL	0.00500	0.03050	0.14313	0.00500	0.00188	0.00225	0.51250	0.00250	0.03000	0.01500	0.00150	0.00188
SWPF-20	D-Opt IL	0.01500	0.01150	0.10500	0.00500	0.00188	0.00225	0.44963	0.00750	0.05000	0.01500	0.00150	0.00188
SWPF-21	D-Opt IL	0.00500	0.03050	0.15500	0.01500	0.00063	0.00075	0.43750	0.00750	0.05000	0.04500	0.00050	0.00063
SWPF-22	D-Opt IL	0.00500	0.03050	0.15500	0.00500	0.00063	0.00075	0.43750	0.00250	0.03000	0.01500	0.00050	0.00063
SWPF-23	D-Opt IL	0.01363	0.01150	0.15500	0.00500	0.00188	0.00225	0.43750	0.00750	0.05000	0.04500	0.00150	0.00188
SWPF-24	D-Opt IL	0.00500	0.01150	0.10500	0.00500	0.00063	0.00075	0.46838	0.00750	0.03000	0.04500	0.00050	0.00063
SWPF-25	D-Opt IL	0.00500	0.03050	0.10500	0.00500	0.00063	0.00075	0.44888	0.00750	0.05000	0.04500	0.00050	0.00063
SWPF-26	D-Opt IL	0.01500	0.03050	0.10500	0.01500	0.00063	0.00075	0.45038	0.00250	0.03000	0.04500	0.00050	0.00063
SWPF-27	D-Opt IL	0.00500	0.03050	0.10500	0.01500	0.00063	0.00075	0.43750	0.00250	0.05000	0.04038	0.00050	0.00063
SWPF-28	D-Opt IL	0.01500	0.03050	0.11188	0.00500	0.00063	0.00075	0.43750	0.00750	0.03000	0.04500	0.00050	0.00063
SWPF-29	D-Opt IL	0.00500	0.01150	0.10500	0.00500	0.00188	0.00225	0.43750	0.00250	0.05000	0.04500	0.00150	0.00188
SWPF-30	D-Opt IL	0.00500	0.03050	0.12363	0.00500	0.00188	0.00225	0.43750	0.00750	0.05000	0.01500	0.00150	0.00188
SWPF-31	D-Opt IL	0.01500	0.01150	0.14788	0.01500	0.00063	0.00075	0.43750	0.00750	0.03000	0.01500	0.00050	0.00063
SWPF-32	SF	0.00864	0.01856	0.10105	0.00981	0.00114	0.00137	0.50958	0.00472	0.04479	0.02616	0.00091	0.00114
SWPF-33	SF	0.00926	0.01890	0.10292	0.00993	0.00131	0.00157	0.44558	0.00496	0.04002	0.04533	0.00105	0.00131
SWPF-34	SF	0.01052	0.01953	0.15740	0.00993	0.00114	0.00136	0.45882	0.00494	0.03605	0.01549	0.00091	0.00114
SWPF-35	SF	0.01083	0.02486	0.10191	0.00938	0.00116	0.00139	0.43421	0.00502	0.04331	0.01907	0.00092	0.00116
SWPF-36	SF	0.01038	0.02002	0.10482	0.01087	0.00123	0.00148	0.46367	0.00498	0.04109	0.01250	0.00099	0.00123
SWPF-37	SF	0.00917	0.01824	0.09543	0.01046	0.00123	0.00147	0.49638	0.00470	0.03901	0.02750	0.00098	0.00123
SWPF-38	SF	0.01020	0.02184	0.13472	0.00987	0.00113	0.00135	0.45009	0.00496	0.04107	0.03572	0.00090	0.00113
SWPF-39	SF	0.00930	0.01688	0.14337	0.00980	0.00103	0.00123	0.49714	0.00466	0.03974	0.01748	0.00082	0.00103
SWPF-40	SF	0.01024	0.02680	0.12857	0.00930	0.00135	0.00161	0.41671	0.00505	0.03943	0.01400	0.00108	0.00135
SWPF-41	SF	0.00963	0.02295	0.11660	0.00996	0.00121	0.00145	0.48684	0.00506	0.04192	0.01826	0.00097	0.00121
SWPF-42	SF	0.00985	0.01706	0.14609	0.00892	0.00110	0.00131	0.50834	0.00516	0.03845	0.03189	0.00088	0.00110
SWPF-43	SF	0.01001	0.01911	0.11701	0.00988	0.00111	0.00133	0.45826	0.00496	0.04048	0.02576	0.00088	0.00111
SWPF-44	SF	0.00949	0.02360	0.10643	0.00998	0.00122	0.00147	0.47154	0.00531	0.04199	0.04590	0.00098	0.00122
SWPF-45	SF	0.01022	0.01744	0.13699	0.00897	0.00117	0.00140	0.48370	0.00467	0.03827	0.01430	0.00093	0.00117
SWPF-46	SF	0.00932	0.01774	0.15761	0.01076	0.00126	0.00151	0.46280	0.00481	0.03837	0.04460	0.00100	0.00126
SWPF-47	SF	0.01150	0.02042	0.13490	0.01065	0.00123	0.00148	0.43344	0.00549	0.04905	0.04032	0.00098	0.00123
SWPF-48	SF	0.01059	0.02300	0.12419	0.01117	0.00113	0.00135	0.46261	0.00519	0.03972	0.01461	0.00090	0.00113
SWPF-49	SF	0.00870	0.01691	0.15607	0.00893	0.00133	0.00160	0.47522	0.00496	0.03443	0.02076	0.00106	0.00133
SWPF-50	SF	0.00950	0.02191	0.12153	0.00891	0.00129	0.00155	0.42360	0.00503	0.03865	0.04387	0.00103	0.00129

2.6.2 Glass Compositional Studies

While a layered-EV approach has been used in support of previous glass studies, the challenge in pursuing this approach is to balance coverage of the glass region of interest with the feasibility (specific frit-sludge-WL combinations that would directly support DWPF operations) of the selected glass compositions to be studied. Consider the OL and IL EVs, the SF points, and their respective MAR acceptability results as shown in Figure 2-2.

[4] Note: RuO_2 is not shown in the targeted compositions. Each test matrix glass should be spiked such that the RuO_2 concentration in glass is 0.001 on a mass fraction basis.

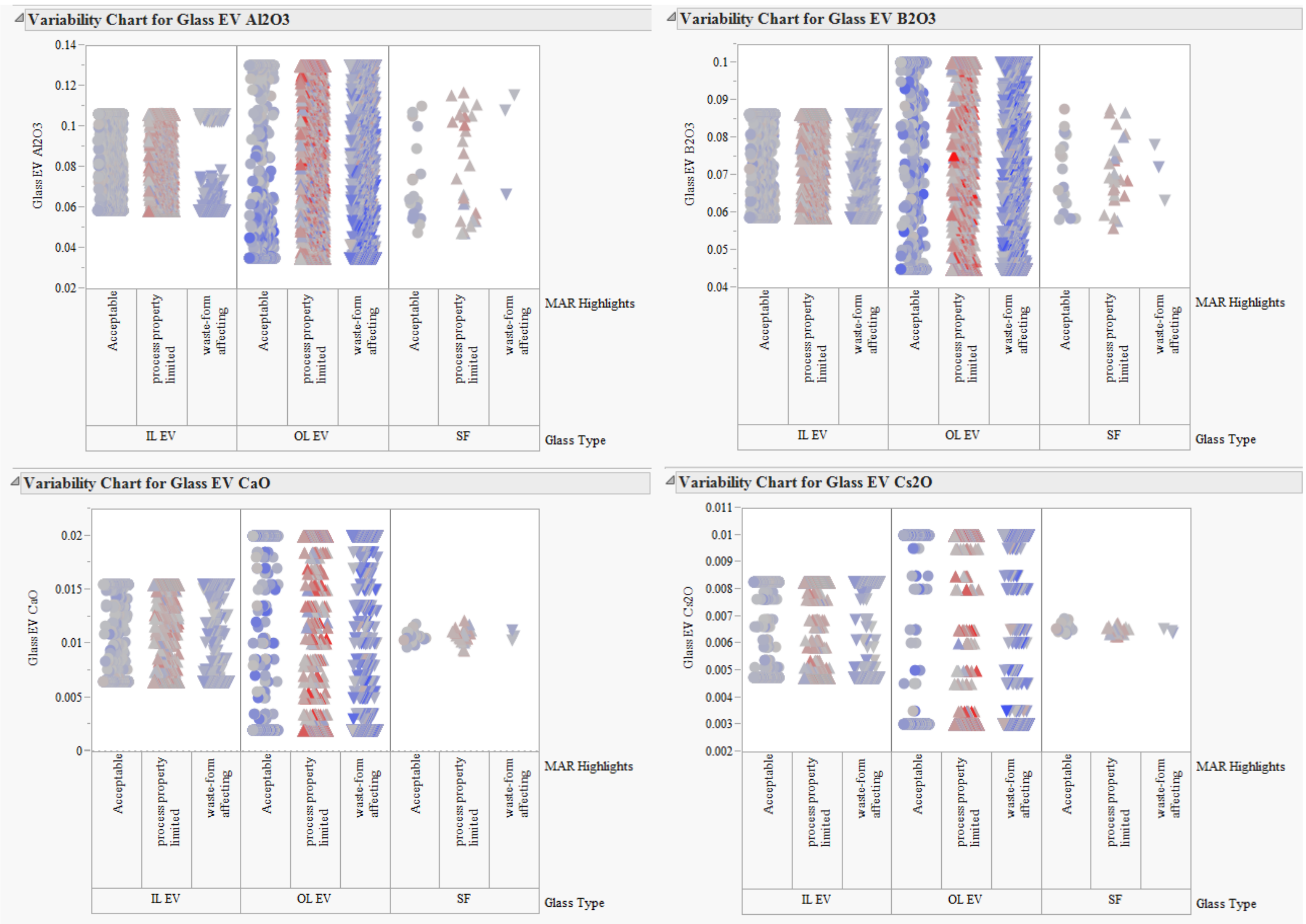

Figure 2-2. Oxide Concentrations for EV and SF Points

(Part 1 of 4; Note: y-axis reflects the mass fraction of the indicated oxide for x-axis categories)

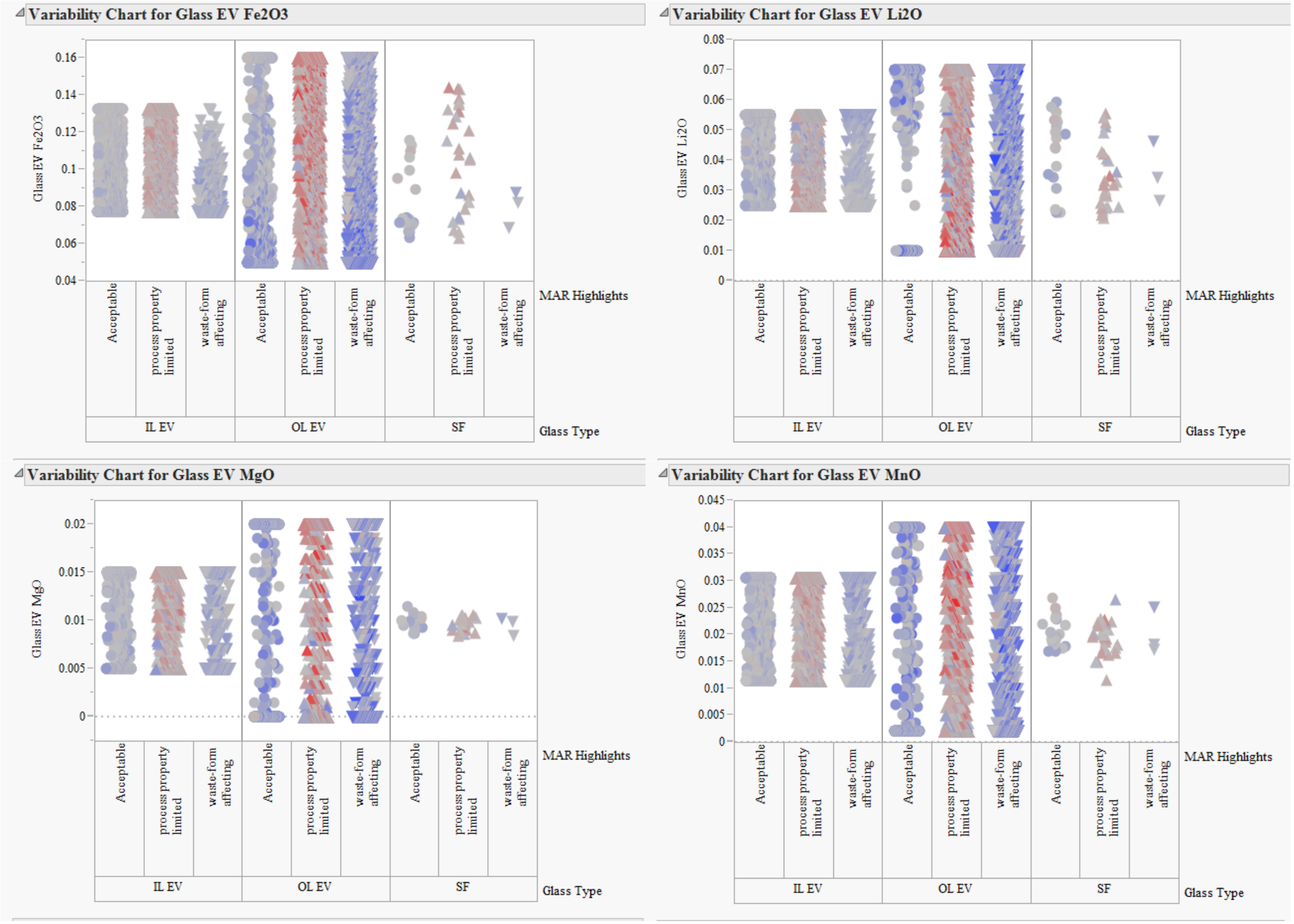

Figure 2-2. Oxide Concentrations for EV and SF Points
(Part 2 of 4; Note: y-axis reflects the mass fraction of the indicated oxide for x-axis categories)

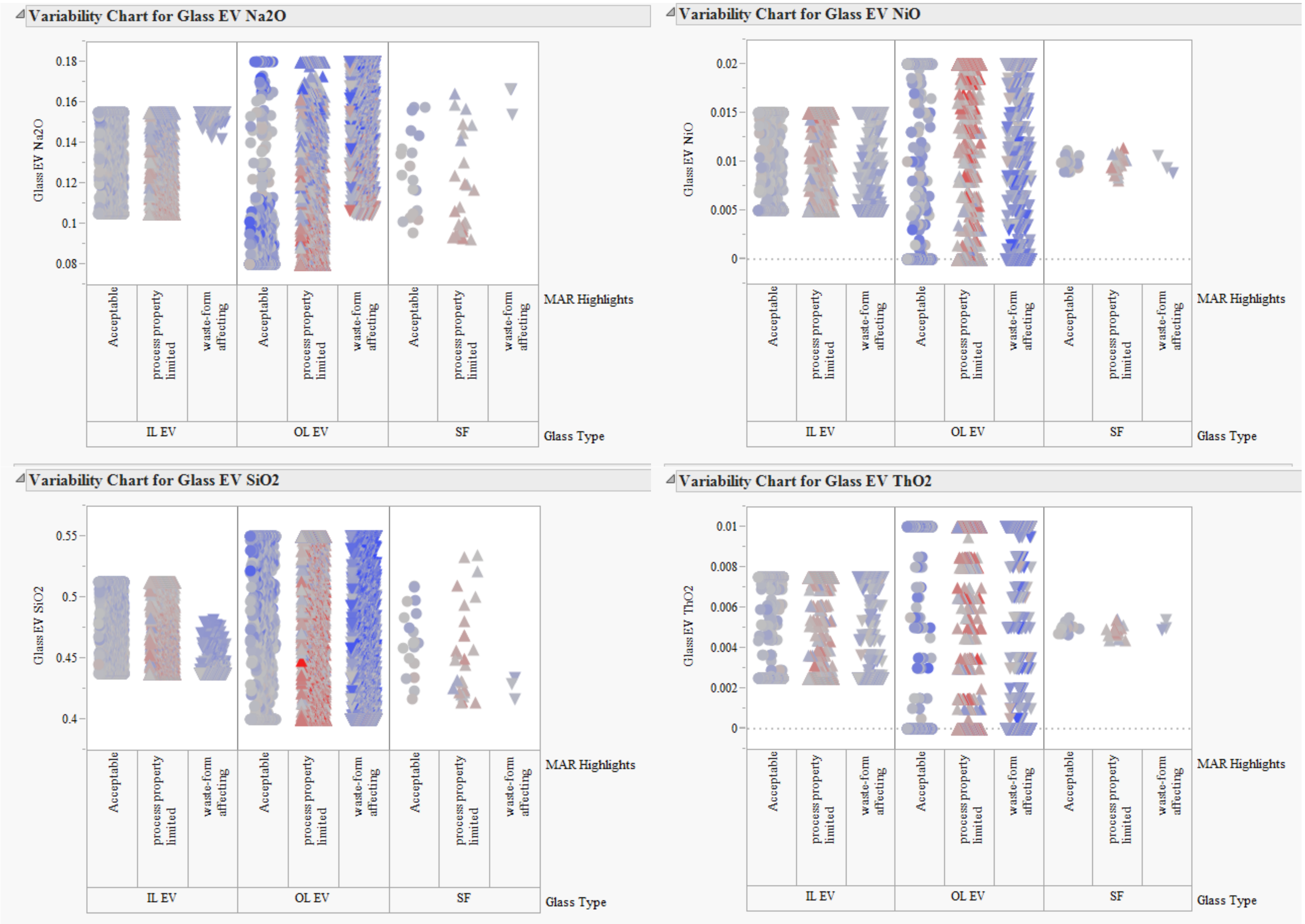

Figure 2-2. Oxide Concentrations for EV and SF Points
(Part 3 of 4; Note: y-axis reflects the mass fraction of the indicated oxide for x-axis categories)

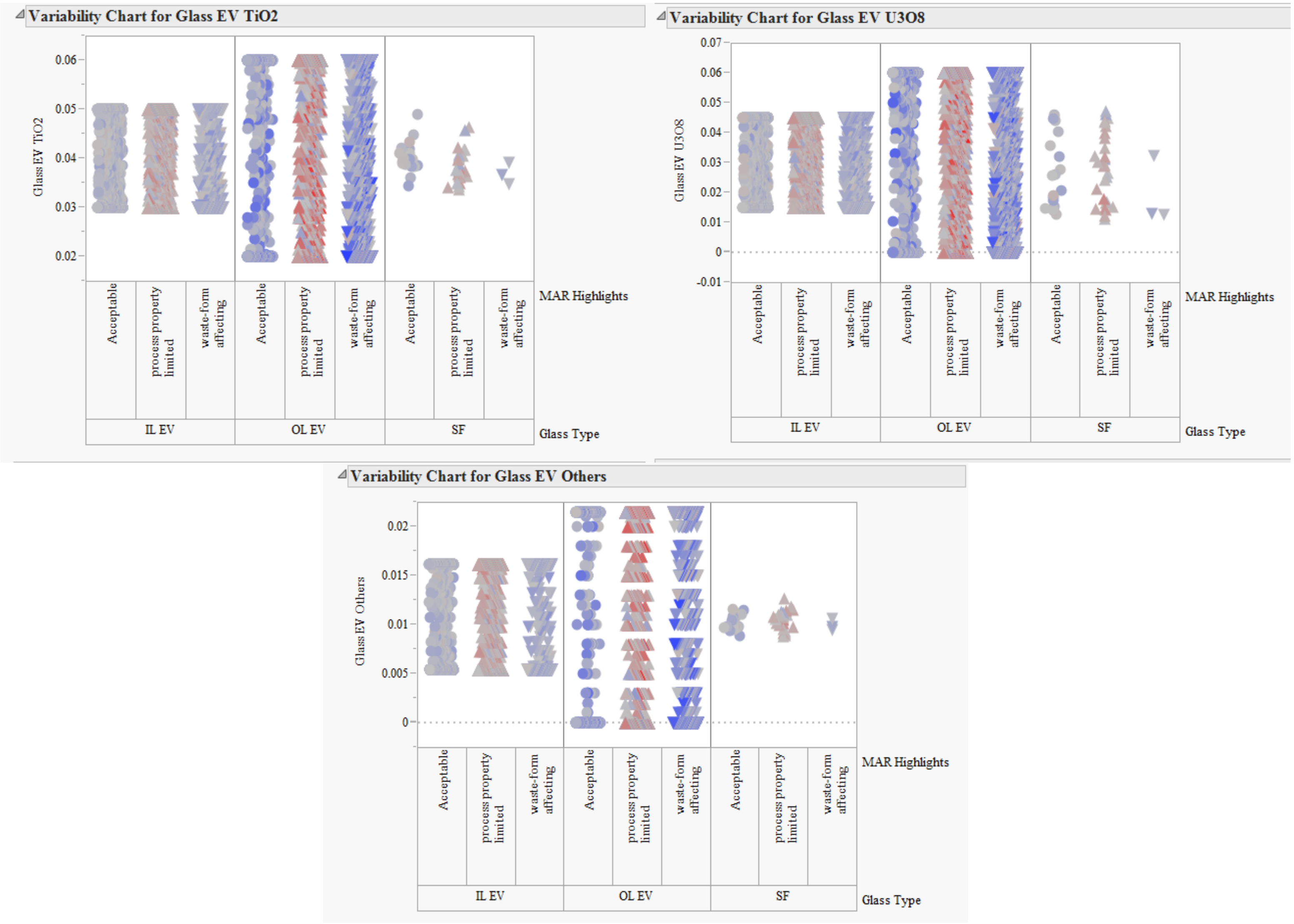

Figure 2-2. Oxide Concentrations for EV and SF Points
(Part 4 of 4; Note: y-axis reflects the mass fraction of the indicated oxide for x-axis categories)

The main insight provided by Figure 2-2 is that there is no immediate distinction between the concentrations for an oxide that lead to an acceptable MAR outcome and an unacceptable outcome (i.e., limited by process or waste form affecting constraints). Thus, whether a composition meets or fails the PCCS MAR acceptability criteria depends, in general, on more of the overall composition than a single oxide component.

The balance between developing a matrix to simply provide coverage of the glass region of interest versus selecting glasses based strictly on feasibility (e.g., specific frit-sludge-WL combinations) is complex with advantages and disadvantages. An obvious advantage of developing a matrix based strictly on feasibility is that the matrix represents or covers a specific, operationally relevant compositional region. This option is viable when the compositional region of interest is well known and relatively narrow as is the case when a variability study is performed for a specific sludge batch. In this case, a layered approach is typically used based on EVs of the specific sludge composition with a candidate frit to cover a range of WLs. This typically results in a 20 – 25 glass test matrix focused on a specific, well-defined composition region. However, the current assessment is evaluating over such a long time period (13 different sludge batches) performing a variability study on each sludge batch would drive the number of glasses to an unacceptable value and would be impractical given potential flowsheet changes.

A major disadvantage of designing a matrix based strictly on coverage is the increased risk of targeting compositions that would not possibly be processed through DWPF and the potential for a negative property response in a composition region over which it would be difficult to model. Consider the 36,989 OL EVs for the SWPF glass region. Of the 36,989 outer layer EV points, only 3734 (or roughly 10%) were found to be MAR acceptable – without the 2 wt % TiO_2 in glass constraint and the homogeneity (or associated constraints) being imposed. A similar result occurred when the IL EVs were selected and assessments regarding acceptability were made. These results indicate that the SWPF compositional region bounded by the minimum and maximum values in Table 2-9 form a non-continuous MAR acceptability region. One can think of this multi-dimensional space as being sponge-like, where the solid sponge material represents areas of glass space that are classified as acceptable by the current models while the air pockets are regions in glass space that would be classified as unacceptable. When performing a variability study, SRNL and SRR work together to define the sludge blending and washing strategies that, when coupled with the recommended frit over WLs of interest, ultimately land on a MAR acceptable region within this bounding space. Hence the importance of a variability study to demonstrate the applicability of the durability models over a well-defined and relatively narrow compositional region as compared to the projected SWPF region of interest. In fact, previous studies that have been based on coverage of broad regions have produced measured glass property values (e.g., durability responses) that challenge the predictability aspect of those models (e.g., Raszewski and Edwards 2009).

Figure 2-3 is an attempt at graphically representing (in only two dimensions, i.e., in the concentrations of two oxides represented on the x- and y-axes) the complexity of this relationship. If the light blue region of the left-hand graphic represents MAR acceptable compositions, then the approach taken in the development of the SWPF test matrix was to select compositions within this light blue region (indicated in the right-hand graphic by the small black dots). The black areas would represent compositional sub-regions within the bounded compositional space that are considered MAR unacceptable based on current models and their associated criterion. It should be reiterated that the current PCCS models are being used to make decisions regarding acceptability outside of their potential development or validation regions. Therefore, it would not be surprising if a subset of the 50 SWPF test matrix glasses ultimately presented challenges to the current models. Again, the value of the variability study is that it ultimately reduces the compositional region to a MAR acceptable specific frit-sludge system over a WL interval of interest.

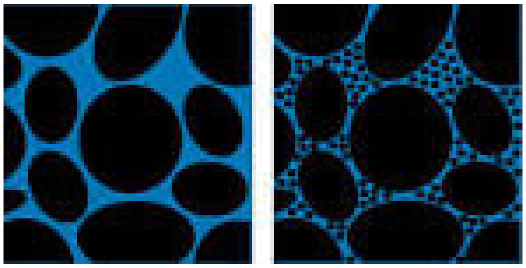

Figure 2-3. Graphical Representation of MAR Acceptable and Glass Compositional Region.

3.0 Conclusions

SRR has issued scopes of work to SRNL and ES-VSL for glass formulation activities to support the integration of SWPF into the DWPF flowsheet. Specifically, SRR has requested that the glass formulation team of SRNL and ES-VSL develop a technical basis that validates the current PCCS models for use during the processing of the coupled flowsheet or that leads to the refinements of or modifications to the models that are needed so that the models may be used during the processing of the coupled flowsheet.

To support this objective, there are several key interim activities that must be completed prior to validation of the current or implementation of refined PCCS models over the anticipated glass composition region for SWPF processing. These key activities include: (1) defining the glass compositional region over which SWPF is anticipated to be processed, (2) comparing the current PCCS model validation ranges to the SWPF glass compositional region from which compositional gaps can be identified, (3) developing a test matrix to cover the compositional gaps, (4) fabricating and measuring key chemical and physical properties of the test matrix glasses, and (5) evaluating the applicability of the current models to predict the new data over the SWPF glass region of interest. The primary glass properties to be assessed are T_L, viscosity (according to ASTM C965-Method A or B), and durability (as defined by ASTM C1285 – Product Consistency Test-Method A).

SRNL has issued memoranda documenting the high-level results of the first three key activities, but in some cases, specific details were not covered in an effort to expedite schedule. Therefore, this report not only provides an overview of these three activities, but when necessary, adds the details omitted from the previous related memoranda. This provides a single detailed reference of the SRNL SWPF activities that led to and resulted in the development of the SWPF test matrix to fill compositional gaps.

To define the future SWPF-based glass compositional region, three critical inputs were required: (1) sludge compositions, (2) frit compositions, and (3) waste loading intervals. To support the development of the future glass compositional region of interest for SWPF processing, SRR issued an Engineering Position Paper that provided key input assumptions and information regarding material balances from SWPF, the WAC for transfers from SWPF to DWPF, and the nominal sludge-only projections from Revision 19 of the HLW System Plan. Based on this information and guidance, SRNL developed projected SWPF coupled operations compositions for each of the sludge batches listed in Revision 19.

SRNL used the coupled operations projections to perform MAR assessments on each sludge batch to identify candidate frits that satisfy the WL criteria provided by SRR (i.e., a projected operating window of 36 – 44% WL while accounting for sludge variation at nominal SWPF volumes). One of the key assumptions used in the MAR assessment was that the current PCCS models are valid over the compositional regions being evaluated which include high TiO_2 concentration glass compositions (e.g., above the current 2 wt% upper limit for the T_L model). It must be recognized that one of the primary objectives of the SWPF Integration Task is to experimentally assess whether the current models are applicable to the future processing region. Therefore, the use of the current models to make decisions regarding acceptability includes the risk that the extrapolation of the models covers compositional regions for which the models may not be valid. However, in order to define the future glass region of interest, use of the current models is the best available strategy. The results of the MAR assessments indicated that candidate frits were identified for SWPF-based coupled operations flowsheets for SB11 through SB18 that met the SRR criteria as outlined in the inputs and assumptions document, although there were technical concerns flagged as part of the assessment. First, the high Na_2O content of the sludges forced frit development efforts to target frits with relatively low total alkali content which causes some concern over the formation of amorphous phase separation in the frit. Although this issue may be resolved either through the vendor's production process (i.e., water quenched rollers that kinetically limit the formation or scale of separation) or the addition of Al_2O_3 to the frit, the development of amorphous phase separation and the potential downstream impacts need to be monitored closely as the SWPF flowsheet matures.

The results of the Variation Stage MAR assessment suggested that frits were available that would allow DWPF to target 36%-44% WL for SB11 – SB18. For SB19 – SB23 (identified as the Tank Farm heels by SRR), the results suggested that WLs would have to be decreased to maintain processing at the volume of SWPF material expected to be incorporated. The targeted waste loadings for the heel sludge batches ranged from the low 30s to an upper limit of approximately 40%.

The results of the MAR assessment provided two critical pieces of information that were needed to define the future SWPF-based glass processing region: (1) the WL intervals and (2) candidate frit compositions. Using this information along with the projected coupled operations compositions for the sludge batches, SRNL defined minimum and maximum values for those elements (or oxides) tracked in Revision 19 of the HLW System Plan in glass composition space. That is, using the frit and sludge compositions (including variation for the sludge batches) and knowing the WL intervals over which each sludge batch could be processed (based on predictions using the current PCCS models), the future SWPF glass compositional region could be identified through determinations of minimum and maximum values for oxides of interest.

With the SWPF glass processing region defined, SRNL developed a 50 glass test matrix that not only covers the future SWPF glass processing region but also provides a technical basis from which revisions or upgrades to current PCCS models can be made if warranted. The test matrix design was based on the integration of a layered approach in combination with space filling points. Thirty-one (31) SWPF based glasses were identified based on the EV layered approach. In addition, 19 space-filling design points for the OL region were generated. All of the test matrix glasses were deemed MAR acceptable based on current PCCS models and their associated constraints – with the exceptions of the 2 wt% TiO_2 criterion and homogeneity and its associated constraints (i.e., low and high frit). It should be noted that the test matrix glasses were defined to cover the projected compositional region of interest to SWPF and are not based on specific frit – sludge combinations over a waste loading interval of interest. That is, although the test matrix glasses provide ample coverage, they are not intended to reflect direct feasibility of DWPF processing of specific sludge batches.

It is anticipated that ES-VSL will fabricate these glasses and measure various properties (T_L, durability, and viscosity) to generate new data such that SRNL can make comparisons with current PCCS model predictions. If differences of statistical or practical significance do exist for a property of interest, the data will be used by SRNL to refine or update the current DWPF process control model for that property to reflect more accurate predictions over the composition range of interest for future operations based on the SWPF flowsheet.

4.0 Recommendations

Based on the results of this study, the following recommendations are made:

(1) Physical (liquidus temperature, viscosity, and durability) properties and chemical compositions of the 50 test matrix glasses should be measured. Once complete, the data should be transmitted to SRNL where an assessment of the measured values versus the model predicted values will be made for the various key glass properties. Based on that assessment, SRNL will recommend to SRR a path forward on the need for refining or updating the associated PCCS models to support SWPF processing in DWPF.

(2) SRNL recommends that if low-alkali based frits are used to support SWPF processing through DWPF, assessments of potential downstream impacts due to potential phase separation must be performed. As noted in the report, the development of phase separation is likely in low-alkali borosilicate glasses which could be mitigated by the vendor's production process (i.e., use of water cooled rollers), addition of Al_2O_3 to the frit, or through the use of higher alkali frits if different sludge washings strategies were pursued. If phase separation cannot be mitigated through either of these strategies, the impact of their use in the DWPF process should be evaluated. The concern is the potential formation of a gel which could lead to transfer issues or practical impacts to rheology due to leaching of the frit during SME processing or in the frit decontamination system.

(3) SRNL recommends that SRR integrate the MAR assessment platform into the HLW System Planning process to assess the impacts of Tank Farm blending and washing strategies as well as pretreatment options that may be under consideration. Integration of MAR assessments into future planning will provide a more robust technical basis from which business decisions can be made as the entire flowsheet is evaluated.

(4) SRNL also recommends that SRR assess an appropriate measurement technique for Cs assuming it will be a reportable element for the SWPF-based flowsheet as the current projections suggest.

As directed by SRR, it is noted that while the System Plan is developed based on objectives and inputs set forth by its customer, the Department of Energy, integrating MAR assessments into the planning process could serve as an important tool in evaluating competing options for sludge batching. As an example, MAR assessments described in this report showed that Al_2O_3 would have to be added to frits for some sludge batches that had undergone Al-dissolution. This was necessary to meet current SME acceptability constraints associated with minimum Al_2O_3 contents in glass or the associated sum of alkali constraint. The MAR assessment platform could be used as a basis for SRNL to work with the SRR Planning group to evaluate the degree of Al-dissolution to be performed to reduce HLW sludge mass to be vitrified with the need to add Al_2O_3 back to the system through additions to the frit. It may well be the case that Al_2O_3 addition to the frit is the best approach to reduce overall mission life. Also, the washing strategy in the current System Plan coupled with additions of SWPF (i.e., a dilution effect on the major sludge oxides) drove the addition of Al_2O_3 to some frits to suppress phase separation in the frit (a potential processing issue at DWPF) due to the relatively low alkali frits that were identified as candidates. Assessments of different washing strategies and reducing the amount of aluminum removed through dissolution may provide options to SRR that would avoid the need for low-alkali frits while still meeting planned or contractual waste loading or canister production goals. In general, integration of the MAR assessment platform will allow for evaluations of the down-stream impacts of sludge blending strategies, Al-dissolution (for sludge mass reduction), and sludge washing strategies on the overall system. This will support well-informed planning of sludge retrieval and treatment along with meeting waste loading expectations and maximizing SWPF MST/Sludge Solids stream volumes.

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C.C. Herman, 773-A
E.N. Hoffman, 999-W
F.M. Pennebaker, 773-42A
W.R. Wilmarth, 773-A
J.W. Amoroso, 999-W
C.L. Crawford, 773-42A
T.B. Edwards, 999-W
K.M. Fox, 999-W
C.M. Jantzen, 773-A
F.C. Johnson, 999-W
C.J. Martino, 773-42A
D.K. Peeler, 999-W
M.E. Stone, 999-W

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J.M. Bricker, 704-S
J.S. Contardi, 704-56H
H.H. Elder, 704-27S
T.L. Fellinger, 766-H
E.J. Freed, 704-S
J.M. Gillam, 766-H
B.T. Geyer, 704-72S
B.A. Hamm, 766-H
E.W. Holtzscheiter, 766-H
J.F. Iaukea, 704-27S
J.W. Ray, 704-27S
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H.B. Shah, 766-H
E.A. Brass, 241-121H
A.G. Garrison, 241-121H
B.A. Gifford, 704-56H
D.J. Martin, 766-H
A.R. Shafer, 766-H
P.C. Suggs, 704-S
W.B. Van-Pelt, 766-H
J.R. Vitali, 704-30S
J.A. Crenshaw, 703-46A
A.W. Wiggins, 241-168H