

Contract No:

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

Disclaimer:

This work was prepared under an agreement with and funded by the U.S. Government. Neither the U. S. Government or its employees, nor any of its contractors, subcontractors or their employees, makes any express or implied:

- 1) warranty or assumes any legal liability for the accuracy, completeness, or for the use or results of such use of any information, product, or process disclosed; or
- 2) representation that such use or results of such use would not infringe privately owned rights; or
- 3) endorsement or recommendation of any specifically identified commercial product, process, or service.

Any views and opinions of authors expressed in this work do not necessarily state or reflect those of the United States Government, or its contractors, or subcontractors.



Selection of Glasses in Support of the Sludge Batch 9 Variability Study for Coupled Operation with the Salt Waste Processing Facility

F.C. Johnson

T.B. Edwards

March 2019

SRNL-STI-2019-00067, Revision 0



DISCLAIMER

This work was prepared under an agreement with and funded by the U.S. Government. Neither the U.S. Government or its employees, nor any of its contractors, subcontractors or their employees, makes any express or implied:

1. warranty or assumes any legal liability for the accuracy, completeness, or for the use or results of such use of any information, product, or process disclosed; or
2. representation that such use or results of such use would not infringe privately owned rights; or
3. endorsement or recommendation of any specifically identified commercial product, process, or service.

Any views and opinions of authors expressed in this work do not necessarily state or reflect those of the United States Government, or its contractors, or subcontractors.

Printed in the United States of America

**Prepared for
U.S. Department of Energy**

Keywords: *DWPF, variability study, PCCS, durability, Frit 803, Frit 625*

Retention: *Permanent*

Selection of Glasses in Support of the Sludge Batch 9 Variability Study for Coupled Operation with the Salt Waste Processing Facility

F.C. Johnson
T.B. Edwards

March 2019

Prepared for the U.S. Department of Energy under
contract number DE-AC09-08SR22470.



EXECUTIVE SUMMARY

Prior to the processing of Sludge Batch 9 (SB9) with Frit 803 at the Defense Waste Processing Facility (DWPF), assessments and experimental glass work were completed to support the qualification of SB9 coupled processing with streams from the Actinide Removal Process (ARP) and Modular Caustic Side Solvent Extraction Unit (MCU). This previous work did not address coupled processing with streams from the Salt Waste Processing Facility (SWPF) because the Product Composition Control System (PCCS) models limited the TiO_2 concentration in glass to 2 weight percent (wt.%). These high activity streams from SWPF include monosodium titanate (MST) and sludge solids from the Sludge Solids Receipt Tank as well as Cs-containing strip effluent. The incorporation of these SWPF streams is expected to reach TiO_2 concentrations in glass greater than 2 wt.% based on an MST addition of 0.4 g MST/L of salt solution. If double strike operation is required, then the MST addition is increased to 0.8 g MST/L of salt solution. Therefore, revisions to the models contained in PCCS were completed to allow the evaluation of glasses containing greater than 2 wt.% TiO_2 , but less than 6 wt.%. To support the implementation of the revised PCCS for SB9 – Frit 803 processing at DWPF prior to SWPF startup, the applicability of the new durability models for the SB9 variability study glasses was verified.

Since the initial SB9 qualification for ARP-MCU coupled operation, additional Tank 40 analyses have been completed, which served as the basis for an updated projection of the SB9 blend composition in Tank 40. To identify a frit optimized for SB9 coupled operation with SWPF, the Savannah River National Laboratory (SRNL) performed a paper-study by utilizing Measurement Acceptance Region (MAR) assessments with DWPF PCCS. Based on these MAR assessment results, Frit 625 was recommended for processing both single and double MST strike scenarios.

Savannah River Remediation (SRR) requested that SRNL perform a variability study with both Frit 803 and Frit 625 for SB9 coupled operation with SWPF. The objective of the variability study is to demonstrate that the Product Consistency Test (PCT) responses of the glasses are acceptable relative to the chemical durability of the Environmental Assessment (EA) reference glass and predictable by the current DWPF PCCS models for durability. This report documents the development of a test matrix that will support the variability study. To provide operational flexibility prior to SWPF startup, the predictability of glasses within the glass region for Frit 625-SB9 coupled operation with ARP-MCU was also confirmed.

Except for TiO_2 concentrations, the glass regions for coupled operation with ARP-MCU and coupled operation with SWPF overlap for both Frit 803 and Frit 625. Thus, SRNL recommends that eight glasses be fabricated, tested, and analyzed to confirm that the glasses are acceptable relative to the chemical durability of the EA reference glass and predictable by the current PCCS models for durability. These eight glasses will have TiO_2 concentrations greater than 2 wt.% to represent single and double MST strike operation and will supplement the previous Sludge Batch 8 (SB8) and SB9 variability study data.

For SB9 coupled operation with ARP-MCU and either Frit 803 or Frit 625, no additional experiments are required since 40 glasses from previous variability studies exist within the compositional region. Almost all the PCT results are well predicted by the durability models (i.e., the values fall within the 95% confidence band). Six of these variability study glasses exhibit some normalized concentrations that fall slightly outside of the lower 95% confidence band, which indicates that the models conservatively predicted the durability results. Thus, this document serves as the completion of the variability study for coupled operation with ARP-MCU and either Frit 803 or Frit 625.

TABLE OF CONTENTS

LIST OF TABLES	vii
LIST OF FIGURES	vii
LIST OF ABBREVIATIONS	viii
1.0 Introduction	1
2.0 Quality Assurance	1
3.0 Development of the SB9 Glass Composition Region	1
4.0 Review of the ComPro TM Database	3
4.1 Coupled Operation with ARP-MCU	3
4.2 Coupled Operation with SWPF	5
5.0 Glass Selection	6
6.0 Recommendation	8
7.0 References	8

LIST OF TABLES

Table 3-1. SB9 SRAT Intervals for Major Oxides (wt.%)	2
Table 3-2. Major Oxide Intervals for the Overall SB9 Glass Composition Region (wt.%)	3
Table 4-1. Previous Glasses Identified in the Anticipated Compositional Region for Coupled Operation with ARP-MCU	4
Table 4-2. Previous Glasses Identified in the Anticipated Compositional Region for Coupled Operation with SWPF (Ignoring TiO ₂ Criterion from Table 3-2)	6
Table 5-1. Recommended Glass Compositions (wt.%) for the Variability Study	7

LIST OF FIGURES

Figure 4-1. ΔG_p predictions (kcal/100 g of glass) versus the log of the normalized concentrations (g/L) of B, Li, Na, and Si.	5
---	---

LIST OF ABBREVIATIONS

ARP	Actinide Removal Process
DWPF	Defense Waste Processing Facility
EA	Environmental Assessment
EVs	extreme vertices
g	gram
kcal	kilocalorie
L	liter
MAR	Measurement Acceptance Region
MCU	Modular Caustic Side Solvent Extraction Unit
MST	monosodium titanate
NC_i	normalized concentration of element i
NGS	Next Generation Solvent
PCCS	Product Composition Control System
PCT	Product Consistency Test
PS	Production Support
SB7a	Sludge Batch 7a
SB8	Sludge Batch 8
SB9	Sludge Batch 9
SE	strip effluent
SME	Slurry Mix Evaporator
SRAT	Sludge Receipt and Adjustment Tank
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation
SSRT	Sludge Solids Receipt Tank
SWPF	Salt Waste Processing Facility
TTQAP	Task Technical and Quality Assurance Plan
TTR	Technical Task Request
WL	waste loading
wt. %	weight percent
ΔG_p	free energy of hydration

1.0 Introduction

Prior to the processing of Sludge Batch 9 (SB9) with Frit 803 at the Defense Waste Processing Facility (DWPF), assessments and experimental glass work were completed to support the qualification of SB9 coupled processing with streams from the Actinide Removal Process (ARP) and Modular Caustic Side Solvent Extraction Unit (MCU).¹⁻⁵ This previous work did not address coupled processing with streams from the Salt Waste Processing Facility (SWPF) because the Product Composition Control System (PCCS) models limited the TiO₂ concentration in glass to 2 weight percent (wt.%).⁶ These high activity streams from SWPF include monosodium titanate (MST) and sludge solids from the Sludge Solids Receipt Tank (SSRT) as well as Cs-containing strip effluent (SE). The incorporation of these SWPF streams is expected to reach TiO₂ concentrations in glass greater than 2 wt.% based on an MST addition of 0.4 g MST/L of salt solution.⁷ If double strike operation is required, then the MST addition is increased to 0.8 g MST/L of salt solution. Therefore, revisions to the models contained in PCCS were completed to allow the evaluation of glasses containing greater than 2 wt.% TiO₂, but less than 6 wt.%.⁸ To support the implementation of the revised PCCS for SB9 – Frit 803 processing at DWPF prior to SWPF startup, the applicability of the new durability models for the SB9 variability study glasses was verified.⁹

Since the initial SB9 qualification for ARP-MCU coupled operation, additional Tank 40 analyses have been completed, which served as the basis for an updated projection⁷ of the SB9 blend composition in Tank 40. To identify a frit optimized for SB9 coupled operation with SWPF, the Savannah River National Laboratory (SRNL) performed a paper-study by utilizing Measurement Acceptance Region (MAR) assessments with the revised DWPF PCCS.⁸ Based on these MAR assessment results, Frit 625 was recommended for processing both single and double MST strike scenarios.¹⁰

Savannah River Remediation (SRR) requested that SRNL perform a variability study with both Frit 803 and Frit 625 for SB9 coupled operation with SWPF.¹¹ The objective of the variability study is to demonstrate that the Product Consistency Test (PCT)¹² responses of the glasses are acceptable relative to the chemical durability of the Environmental Assessment (EA) reference glass and predictable by the current DWPF PCCS models for durability.^{8,13,14} This report documents the development of a test matrix that will support the variability study. To provide operational flexibility prior to SWPF startup, the predictability of glasses within the glass region for Frit 625-SB9 coupled operation with ARP-MCU was also confirmed.

2.0 Quality Assurance

This work was requested via a Technical Task Request (TTR)¹¹ and directed by a Task Technical and Quality Assurance Plan.¹⁵ The TTR indicates the portion of work scope covered by this report is classified as Production Support (PS) and not subject to RW-0333P requirements. Microsoft Excel, JMP[®] Pro Version 11.2.1,¹⁶ and SAS[®] Version 8.2¹⁷ were used to support this work.¹⁸ Given the PS designation, the use of the Level D software packages (i.e., JMP[®] Pro Version 11.2.1 and SAS[®] Version 8.2) is compliant. Requirements for performing reviews of technical reports and the extent of review are established in manual E7 2.60.¹⁹ This document, including all calculations, was reviewed by a Design Check. SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2.²⁰

3.0 Development of the SB9 Glass Composition Region

Using the Sludge Receipt and Adjustment Tank (SRAT) oxide intervals developed for the MAR assessments that resulted in the recommendation of Frit 625,¹⁰ the minimum and maximum concentrations of the major sludge components were determined for SB9 coupled operation with the ARP and SWPF flowsheets (Table 3-1). Compositional variation of $\pm 7.5\%$ is included in these concentrations (as used for the MAR assessments).

Table 3-1. SB9 SRAT Intervals for Major Oxides (wt.%)

Oxide	Coupled Operation with ARP-MCU			Coupled Operation with SWPF		
Al₂O₃	14.57	-	18.82	12.59	-	16.59
B₂O₃	0.06	-	0.83	0.12	-	1.26
CaO	1.17	-	2.36	0.84	-	2.08
Cs₂O	----			0.90	-	2.24
Fe₂O₃	26.73	-	34.52	21.50	-	29.40
MnO	7.84	-	10.13	6.31	-	8.63
Na₂O	22.57	-	34.06	25.05	-	31.19
NiO	1.32	-	2.52	0.96	-	2.22
SiO₂	2.92	-	4.30	2.25	-	3.74
ThO₂	0.62	-	1.75	0.40	-	1.56
TiO₂	----			5.83	-	15.01
U₃O₈	3.99	-	5.49	3.11	-	4.75

The values provided for coupled operation with ARP-MCU are based on ARP product additions (without MST)²¹ per SRAT batch in increments of ~0.8 wt.% Na₂O up to ~7 wt.% above the nominal sludge-only projection value of 24.4 wt.%.¹⁰ The values provided for SB9 coupled operation with SWPF are based on the following cases for nominal single and double MST strike operation:^{10,22}

- Case 1: Single MST strike operation, with aluminum in the SSRT stream, and no entrained insoluble sludge solids. This case represents the baseline.
- Case 2: Single MST strike operation, no aluminum in the SSRT stream,^{a,7} and no entrained insoluble sludge solids. This case was included as it has the highest maximum Na₂O concentration of the original five cases that were evaluated.
- Case 4: Double MST strike operation, with aluminum in the SSRT stream, and no entrained insoluble sludge solids.

These SWPF cases also consider two transfer volumes of sludge slurry from Tank 40 per SRAT batch (5200 and 5700 gallons), as well as SE containing either the baseline BOBCalixC6 solvent^b or the Next Generation Solvent (NGS).^{c,10} Case #3 was omitted since it included entrained insoluble sludge solids and the composition of any entrained solids is unknown. Case #5 (double MST strike operation with no aluminum) was omitted because the effect of the aluminum removal on the MAR assessment results was minimal.

For each flowsheet, Frit 803 and Frit 625 were combined with each component at 32% and 40% waste loading (WL) and the minimum and maximum concentrations of each component were selected to create one glass region. The bounds of each component for this glass region are shown in Table 3-2.

^a Per SRR-WSR-2018-00025, more conservative cases were developed where the aluminum in the SSRT effluent stream was set to 0 mg/L.

^b BOBCalixC6 is calix[4]arene-bis(tert-octylbenzo-crown-6), which uses a nitric acid strip solution.

^c NGS contains the extractant MaxCalix (1,3-alt-25,27-bis(3,7- dimethyloctyl-1-oxy)calix[4]arene-benzocrown-6), which uses a boric acid strip solution.

Table 3-2. Major Oxide Intervals for the Overall SB9 Glass Composition Region (wt.%)

Oxide	Coupled Operation with ARP-MCU			Coupled Operation with SWPF		
Al₂O₃	4.66	-	8.13	4.03	-	7.24
B₂O₃	4.82	-	5.70	4.85	-	5.84
CaO	0.37	-	0.94	0.27	-	0.83
Cs₂O ^{d,7,23}	----			0.29	-	0.90
Fe₂O₃	8.55	-	13.81	6.88	-	11.76
Li₂O	3.60		4.76	3.60		4.76
MnO	2.51	-	4.05	2.02	-	3.45
Na₂O	11.30	-	18.42	12.10	-	17.27
NiO	0.42	-	1.01	0.31	-	0.89
SiO₂	47.97	-	54.42	47.70	-	54.24
ThO₂	0.20	-	0.70	0.13	-	0.63
TiO₂	----			1.86	-	6.00
U₃O₈	1.28	-	2.20	1.00	-	1.90

4.0 Review of the ComPro™ Database

Prior to developing variability study glasses, the ComPro™ database²⁴⁻²⁶ was used to determine whether glasses from previous studies were already within the glass regions of interest. The ComPro™ database contains chemical composition and PCT data compiled from previous glass studies at SRNL and across the Department of Energy (DOE) complex. It is used as a tool during glass matrix development since identifying glasses in the frit-sludge batch region of interest could reduce the number of glasses required for the variability study. Compositions from studies that were performed after the last revision to the ComPro™ database were also reviewed, including:

- Sludge Batch 8 (SB8) variability study,²⁷
- Initial SB9 variability study,¹ and
- SWPF gap analysis study.^{28,29}

To enhance the potential for identifying glasses, the intervals for the oxides shown in Table 3-2 were expanded by ± 0.5 wt.%, except for SiO₂, which was expanded by ± 1 wt.% since it has the highest concentration in glass. Any of the minor oxides not included in Table 3-2 were limited to less than 0.5 wt.% in glass, which would force the elemental concentrations to be below the reportable limit. Per the DWPF Waste Form Compliance Plan,²³ components in the glass having an elemental concentration greater than 0.5 wt.% shall be reported. Limiting the minor oxide concentrations to less than 0.5 wt.% in glass eliminated the possibility of identifying glass compositions in the ComPro™ database that have unique minor oxides (e.g., Nb₂O₅), which are not representative of previous DWPF sludge batches. The results of each review, for coupled operation with ARP-MCU and coupled operation with SWPF, are presented in the following sections.

4.1 Coupled Operation with ARP-MCU

Forty “model” entries were found to have compositions that simultaneously satisfy the oxide intervals of the search criteria for coupled operation with ARP-MCU.^e A list of the glasses is shown in Table 4-1 and

^d Based on the assumption of 66 Ci/gal of Cs-137 in the SE, Cs could become a reportable element in glass (greater than 0.5 wt.%). At 36% WL, the nominal concentration of Cs in glass is ~0.53-0.57 wt.% for the baseline single MST strike (Case #1).

^e “Model” entries are results from studies that were conducted under quality assurance criteria that were RW-0333P compliant or criteria determined to be RW-0333P equivalent.

includes compositions from the Sludge Batch 7a (SB7a),³⁰⁻³² SB8,²⁷ and SB9¹ variability studies. The compositions may represent target or measured compositions, or both.

Table 4-1. Previous Glasses Identified in the Anticipated Compositional Region for Coupled Operation with ARP-MCU

SB7aVS-01	VSL-SB8-11
SB7aVS-05	VSL-SB8-12
VSL-SB7a-01	VSL-SB8-13
VSL-SB7a-05	VSL-SB8-14
VSL-SB7a-14	VSL-SB8-15
VSL-SB7a-15	VSL-SB8-16
VSL-SB7a-17	VSL-SB8-17
VSL-SB7aNM-01	VSL-SB8-18
VSL-SB7aNM-05	VSL-SB8-19
VSL-SB7aNM-15	VSL-SB8-20
VSL-SB8-01	VSL-SB8-21
VSL-SB8-02	VSL-SB8-22
VSL-SB8-03	SB9VS01
VSL-SB8-04	SB9VS02
VSL-SB8-05	SB9VS03
VSL-SB8-06	SB9VS04
VSL-SB8-07	SB9VS05
VSL-SB8-08	SB9VS06
VSL-SB8-09	SB9VS07
VSL-SB8-10	SB9VS08

Each of these glasses identified from the variability studies underwent a heat treatment representing canister centerline cooling (CCC). For each composition, samples of both the quenched glass (cooled in air) and glass subjected to the CCC were evaluated by the PCT. The normalized concentrations (NC_i) of B, Li, Na, and Si were calculated using both the target and measured compositions. These results were reported previously and will not be repeated in this report.

Figure 4-1 provides plots of the DWPF durability models⁸ that relate the normalized concentrations for each element of interest to a linear function of a free energy of hydration term (ΔG_p , kcal/100 g glass). Prediction limits at a 95% confidence for an individual PCT result (---) are plotted along with the linear fit (—).

All the variability study glasses are predictable with respect to the revised PCCS models for durability except for the following six glasses (shown by a ● in Figure 4-1), which are slightly outside of the lower 95% confidence band.

- NC_B for glasses SB7aVS-01 (measured-CCC), VSL-SB7a-01 (measured-quenched and measured-CCC), VSL-SB8-19 (targeted-quenched and targeted-CCC), VSL-SB8-22 (targeted-quenched, targeted-CCC, measured-quenched, and measured-CCC), SB9VS05 (measured-quenched and measured-CCC), and SB9VS08 (targeted-CCC, measured-quenched, and measured-CCC)
- NC_{Li} for glasses SB7aVS-01 (measured-quenched), VSL-SB8-22 (targeted-quenched and targeted-CCC), and SB9VS08 (targeted-CCC, measured-quenched, and measured-CCC)
- NC_{Na} for glass SB7aVS-01 (measured-CCC)

The durability models are conservative for the PCT responses of these six glasses since the actual results indicate better durability values than predicted by the models. Since the glass region for SB9 coupled operation with ARP-MCU and either Frit 803 or Frit 625 is already covered by previous glasses that are predictable by the current PCCS models for durability, no additional experiments are necessary to qualify this glass system.

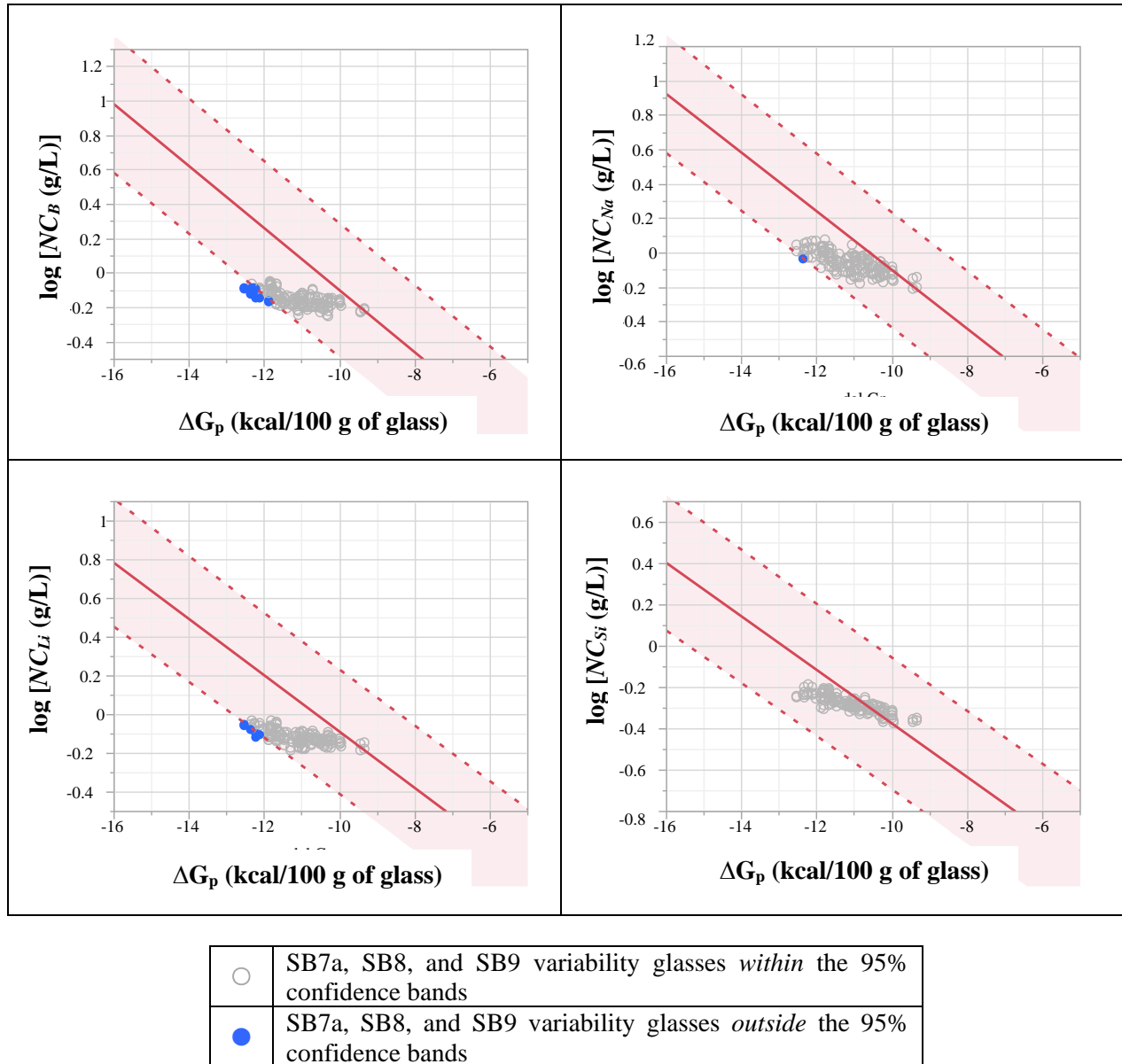


Figure 4-1. ΔG_p predictions (kcal/100 g of glass) versus the log of the normalized concentrations (g/L) of B, Li, Na, and Si.

4.2 Coupled Operation with SWPF

No “model” entries were found to have compositions that simultaneously satisfy the search criteria for coupled operation with SWPF. To widen the search, the TiO_2 criterion in Table 3-2 was ignored, and 27

“model” entries were found. A list of the glasses is shown in Table 4-2 and includes compositions from the SB8²⁷ and SB9¹ variability studies. The compositions may represent target or measured compositions, or both. All these compositions were also identified in Section 4.1 for coupled operation with ARP-MCU, which demonstrates the compositional overlap of these two glass systems, except for TiO₂ concentrations. Therefore, to confirm that the anticipated glass region for SB9 coupled operation with SWPF is predictable by the current PCCS models for durability,⁸ only a minimal number of glasses will need to be fabricated and tested via PCT at TiO₂ concentrations greater than 2 wt.% to supplement the previous variability study data.

Table 4-2. Previous Glasses Identified in the Anticipated Compositional Region for Coupled Operation with SWPF (Ignoring TiO₂ Criterion from Table 3-2)

VSL-SB8-01	VSL-SB8-16
VSL-SB8-02	VSL-SB8-17
VSL-SB8-03	VSL-SB8-18
VSL-SB8-04	VSL-SB8-19
VSL-SB8-05	VSL-SB8-20
VSL-SB8-06	VSL-SB8-21
VSL-SB8-07	VSL-SB8-22
VSL-SB8-08	SB9VS01
VSL-SB8-10	SB9VS02
VSL-SB8-11	SB9VS03
VSL-SB8-12	SB9VS04
VSL-SB8-13	SB9VS05
VSL-SB8-14	SB9VS06
VSL-SB8-15	SB9VS08

5.0 Glass Selection

Using the Space Filling routine of the Design of Experiments platform in JMP[®],¹⁶ 1000 compositions were generated within the oxide intervals shown in Table 3-2^f for the anticipated glass region for SB9 coupled operation with SWPF and Frit 803 and Frit 625. Each of the compositions was evaluated against the PCCS MAR criteria to determine whether the composition would pass the Slurry Mix Evaporator (SME) acceptability process. Of the original 1000 compositions, 919 compositions passed the MAR constraints. Compositions that failed the MAR constraints were excluded from further evaluation. Due to the compositional overlap of the glass systems for coupled operation with ARP-MCU and coupled operation with SWPF, only six major components were of interest to generate the variability study test matrix (Al₂O₃, Fe₂O₃, MnO, Na₂O, SiO₂, and TiO₂). The remaining components from Table 3-2 were not considered since there was minimal variation between the minimum and maximum oxide concentrations. Using the OPTEX routine in SAS[®],¹⁷ six glass compositions were D-optimally selected from the 919 compositions, where six is the minimum number of glasses that represents the compositional variation of the major components of interest (Al₂O₃, Fe₂O₃, MnO, Na₂O, SiO₂, and TiO₂).

Variation of the TiO₂ concentration between 2 and 6 wt.% is not expected to result in sporadic durability behavior, so it is not necessary to have glass compositions with TiO₂ concentrations throughout this interval.

^f An interval of 0.51-1.17 wt.% was used for the “Others,” which included BaO, Ce₂O₃, Cr₂O₃, CuO, K₂O, La₂O₃, Li₂O, MgO, PbO, SO₄²⁻, ZnO, and ZrO₂. The minimum and maximum concentrations of this interval were calculated using the method described in Section 3 for the major oxides listed in Table 3-2. Compositional variation of ±0.5 wt.% in sludge is included in these concentrations (as used for the MAR assessments).

Thus, the six glasses were developed using the extreme vertices, which trends the TiO₂ concentrations closer to the upper and lower concentration limits used to define the test matrix (2 and 6 wt.%).

Two additional glasses were manually selected to maximize the Na₂O and TiO₂ concentrations evaluated in this variability study, while still passing the MAR constraints. These glasses are based on the following scenarios^g that were previously evaluated by MAR assessments:¹⁰

- Maximum Na₂O concentration at 40% WL – Case #1 (single MST strike) with Frit 803 and a transfer volume of 3600 gallons from the Sludge Solids Receipt Tank (SSRT)
- Maximum TiO₂ concentration at 38% WL^h – Case #4 (double MST strike) with Frit 625 and an SSRT transfer volume of 4200 gallons

Target compositions of the eight variability study glasses are shown in Table 5-1. Glasses SB9b-01 through SB9b-06 are the D-optimally selected compositions, SB9b-07 maximizes the Na₂O concentration, and SB9b-08 maximizes the TiO₂ concentration.

Table 5-1. Recommended Glass Compositions (wt.%) for the Variability Study

Glass ID	SRNL-SB9b-01	SRNL-SB9b-02	SRNL-SB9b-03	SRNL-SB9b-04	SRNL-SB9b-05	SRNL-SB9b-06	SRNL-SB9b-07	SRNL-SB9b-08
Al ₂ O ₃	4.398	4.595	5.264	6.207	6.716	6.773	5.653	5.759
B ₂ O ₃	5.318	5.374	5.605	5.518	5.243	5.433	4.819	4.978
BaO	0.034	0.030	0.031	0.033	0.032	0.033	0.030	0.027
CaO	0.513	0.535	0.652	0.552	0.569	0.565	0.561	0.508
Ce ₂ O ₃	0.055	0.049	0.051	0.054	0.053	0.053	0.049	0.045
Cr ₂ O ₃	0.049	0.044	0.046	0.048	0.047	0.047	0.044	0.040
Cs ₂ O	0.572	0.589	0.737	0.561	0.533	0.623	0.626	0.566
CuO	0.030	0.026	0.028	0.029	0.028	0.028	0.026	0.024
Fe ₂ O ₃	7.447	7.200	9.447	7.814	7.172	11.000	9.700	8.779
K ₂ O	0.130	0.115	0.121	0.128	0.124	0.125	0.121	0.112
La ₂ O ₃	0.020	0.018	0.018	0.019	0.019	0.019	0.018	0.016
Li ₂ O	4.446	4.185	4.526	4.040	3.908	4.295	3.645	4.381
MgO	0.168	0.148	0.156	0.165	0.159	0.161	0.150	0.136
MnO	2.213	2.435	3.283	2.318	3.078	2.281	2.846	2.576
Na ₂ O	16.895	12.885	13.259	16.295	13.475	12.390	17.157	14.347
NiO	0.622	0.555	0.612	0.577	0.600	0.663	0.610	0.552
PbO	0.018	0.016	0.017	0.018	0.017	0.017	0.016	0.015
SO ₄ ²⁻	0.365	0.322	0.339	0.358	0.346	0.351	0.327	0.297
SiO ₂	52.674	53.822	47.983	48.137	53.987	50.562	47.948	49.399
ThO ₂	0.353	0.344	0.518	0.380	0.368	0.405	0.377	0.342
TiO ₂	2.104	5.358	5.528	5.318	2.107	2.575	3.727	5.702
U ₃ O ₈	1.531	1.318	1.736	1.388	1.378	1.556	1.508	1.364
ZnO	0.017	0.015	0.016	0.016	0.016	0.016	0.015	0.014
ZrO ₂	0.027	0.024	0.025	0.027	0.026	0.026	0.024	0.022

^g Both scenarios are based on the transfer of 5200 gallons of sludge slurry from Tank 40 per SRAT batch and SE containing the baseline BOBCalixC6 solvent.

^h At 39 and 40% WL, the PCCS constraint for the maximum TiO₂ concentration failed, which occurs when the TiO₂ concentration is greater than 6 wt.% minus measurement uncertainty. Thus, the WL was reduced to 38% WL so that the glass composition would pass the MAR constraints.

6.0 Recommendation

Except for TiO_2 concentrations, the glass regions for SB9 coupled operation with ARP-MCU and coupled operation with SWPF overlap for both Frit 803 and Frit 625. Thus, SRNL recommends that eight glasses be fabricated, tested, and analyzed to confirm that the glasses are acceptable relative to the chemical durability of the EA reference glass and predictable by the current PCCS models for durability. These eight glasses will have TiO_2 concentrations greater than 2 wt.% to represent single and double MST strike operation and will supplement the previous SB8 and SB9 variability study data.

For SB9 coupled operation with ARP-MCU and either Frit 803 or Frit 625, no additional experiments are required since 40 glasses from previous variability studies exist within the compositional region. Almost all the PCT results are well predicted by the durability models (i.e., the values fall within the 95% confidence band). Six of these variability study glasses exhibit some NC_i values that fall slightly outside of the lower 95% confidence band, which indicates that the models conservatively predicted the durability results. Thus, this document serves as the completion of the variability study for coupled operation with ARP-MCU and either Frit 803 or Frit 625.

7.0 References

1. W.K. Kot, I.L. Pegg, F.C. Johnson, and T.B. Edwards, "Final Report Sludge Batch 9 Variability Study with Frit 803," Vitreous State Laboratory, Washington, DC, VSL-16R3370-1, Rev. 0, 2016.
2. T.B. Edwards, F.C. Johnson, W.K. Kot, H. Gan, and I.L. Pegg, "Evaluation of Glass Density to Support the Estimation of Fissile Mass Loadings from Iron Concentrations in SB9 Glasses," Savannah River National Laboratory, Aiken, SC, SRNL-TR-2016-00071, Rev. 0, 2016.
3. F.C. Johnson and T.B. Edwards, "Assessment of the SB9 Variability Study Recommendation Based on the January 2016 Reprojection," Savannah River National Laboratory, Aiken, SC, SRNL-L3100-2016-00011, Rev. 0, 2016.
4. F.C. Johnson and T.B. Edwards, "February 2016 SB9 Projection Representing an SB8 Tank 40 Heel of 40 inches - MAR Assessment Results," Savannah River National Laboratory, Aiken, SC, SRNL-L3100-2016-00071, Rev. 0, 2016.
5. F.C. Johnson, "Recommendation for the Sludge Batch 9 Sulfate Solubility Limit," Savannah River National Laboratory, Aiken, SC, SRNL-L3100-2016-00044, Rev. 0, 2016.
6. T.B. Edwards, "SME Acceptability Determination for DWPF Process Control," Savannah River National Laboratory, Aiken, SC, WSRC-TR-95-00364, Rev. 5, 2006.
7. A. Samadi, H.B. Shah, J.D. Ledbetter, J.W. Ray, K.M. Brotherton, R. McNew, and T.L. Fellingner, "Integration of the Defense Waste Processing Facility (DWPF) and Salt Waste Processing Facility (SWPF): Assumptions and Guidance to Support Measurement Acceptance Region (MAR) Assessments for Sludge Batch 9 (SB9)," Savannah River Remediation, Aiken, SC, SRR-WSE-2018-00025, Rev. 0, 2018.
8. T.B. Edwards, "SME Acceptability Determination for DWPF Process Control," Savannah River National Laboratory, Aiken, SC, WSRC-TR-95-00364, Rev. 6, 2017.
9. F.C. Johnson and T.B. Edwards, "Evaluation of the Sludge Batch 9 - Frit 803 Variability Study Glasses with the Revised Defense Waste Processing Facility Product Composition Control System," Savannah River National Laboratory, Aiken, SC, SRNL-STI-2018-00189, Rev. 0, 2018.

10. F.C. Johnson and T.B. Edwards, "Frit Recommendation for Sludge Batch 9 Coupled Operation with the Salt Waste Processing Facility," Savannah River National Laboratory, Aiken, SC, SRNL-STI-2019-00004, Rev. 0, 2019.
11. A. Samadi-Dezfouli, "Variability Study for Sludge Batch 9 Coupled Operation with the Salt Waste Processing Facility," Savannah River Remediation, Aiken, SC, X-TTR-S-00070, Rev. 0, 2018.
12. "Standard Test Methods for Determining Chemical Durability of Nuclear, Hazardous, and Mixed Waste Glasses and Multiphase Glass Ceramics: The Product Consistent Test (PCT)," ASTM International, West Conshohocken, PA, C1285 - 14, 2014.
13. J.W. Ray, B.H. Culbertson, S.L. Marra, C.M. Jantzen, T.B. Edwards, and A.A. Ramsey, "Technical Bases for the DWPF Glass Product Control Program," Savannah River Remediation, Aiken, SC, WSRC-IM-91-116-5, Rev. 4, 2018.
14. C.M. Jantzen, N.E. Bibler, D.C. Beam, C.L. Crawford, and M.A. Pickett, "Characterization of the Defense Waste Processing Facility (DWPF) Environmental Assessment (EA) Glass Standard Reference Material," Westinghouse Savannah River Company, Aiken, SC, WSRC-TR-92-346, Rev. 1, 1993.
15. F.C. Johnson, "Task Technical and Quality Assurance Plan for Variability Study for Sludge Batch 9 Coupled Operation with the Salt Waste Processing Facility," Savannah River National Laboratory, Aiken, SC, SRNL-RP-2018-01085, Rev. 0, 2018.
16. "JMP^(R) Pro Version 11.2.1," SAS Institute Inc., Cary, NC, Software Classification Document Number B-SWCD-W-00023, Rev. 0, 2014.
17. "SAS^(R) Version 8.2," SAS Institute Inc., Cary, NC, Software Classification Document Number B-SWCD-A-00083, Rev. 6, 2014.
18. R.A. Baker, T.B. Edwards, A.D. Elizondo, S.P. Harris, E.P. Shine, and H.L. Watson, "Verification & Validation for Commercial Statistical Packages Utilized by SRNL Statisticians," Savannah River National Laboratory, Aiken, SC, B-VVR-A-00002, Rev. 3, 2014.
19. "Technical Reviews," Savannah River Site, Aiken, SC, Manual E7, Procedure 2.60, Rev. 17, 2016.
20. "Savannah River National Laboratory Technical Report Design Check Guidelines," Westinghouse Savannah River Company, Aiken, SC, WSRC-IM-2002-00011, Rev. 2, 2004.
21. C.J. Martino, "PRFT Composition for Sludge Batch 9 MAR Assessment," Savannah River National Laboratory, Aiken, SC, SRNL-L3100-2014-00223, Rev. 1, 2015.
22. M.E. Stone, "SSRT Effluent Composition Estimate for SB9/SB10 MAR Assessments," Savannah River National Laboratory, Aiken, SC, SRNL-L3300-2018-00063, Rev. 1, 2018.
23. "DWPF Waste Form Compliance Plan," Savannah River Remediation, Aiken, SC, WSRC-IM-91-116-0, Rev. 12, 2018.

24. T.B. Edwards, F.C. Johnson, and K.M. Fox, "Data Qualification Report: SRNL Glass Composition-Properties (ComPro™) Database," Savannah River National Laboratory, Aiken, SC, SRNL-STI-2009-00094, Rev. 1, 2013.
25. F.C. Johnson and T.B. Edwards, "Metrics for Revision 2 of the ComPro™ Database," Savannah River National Laboratory, Aiken, SC, SRNL-L3100-2013-00164, Rev. 0, 2013.
26. F.C. Johnson, T.B. Edwards, and K.M. Fox, "The User Guide for the ComPro™ Database," Savannah River National Laboratory, Aiken, SC, SRNL-STI-2009-00093, Rev. 1, 2013.
27. W.K. Kot, I.L. Pegg, D.K. Peeler, and T.B. Edwards, "Final Report Sludge Batch 8 Variability Study with Frit 803," Vitreous State Laboratory, Washington, D.C., VSL-13R2580-1, Rev. 0, 2013.
28. D.K. Peeler and T.B. Edwards, "Integration of SWPF into the DWPF Flowsheet: Gap Analysis and Test Matrix Development," Savannah River National Laboratory, Aiken, SC, SRNL-STI-2014-00578, Rev. 0, 2014.
29. T.B. Edwards and K.M. Fox, "Evaluations of the Measurements of Chemical Composition, Viscosity, and Density of Glasses with High Concentrations of Titanium," Savannah River National Laboratory, Aiken, SC, SRNL-TR-2016-00094, Rev. 0, 2016.
30. D.K. Peeler and T.B. Edwards, "The Sludge Batch 7a Glass Variability Study with Frit 418 and Frit 702," Savannah River National Laboratory, Aiken, SC, SRNL-STI-2011-00063, Rev. 0, 2011.
31. W.K. Kot, I.L. Pegg, D.K. Peeler, and T.B. Edwards, "Final Report Sludge Batch 7a Glass Study with Noble Metals," Vitreous State Laboratory, Washington, DC, VSL-12R2580-2, Rev. 0, 2012.
32. W.K. Kot, I.L. Pegg, D.K. Peeler, and T.B. Edwards, "Final Report Sludge Batch 7a Glass Variability Study," Vitreous State Laboratory, Washington, D.C., VSL-11R2580-1, Rev. 0, 2012.