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Selection of Glasses in Support of the Sludge Batch 9 Sulfate Solubility Limit for Coupled Operation with the Salt Waste Processing Facility

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EXECUTIVE SUMMARY

For Sludge Batches 3 through 8, the sulfate (SO_4^{2-}) solubility limit for the Defense Waste Processing Facility (DWPF) has been determined by laboratory-scale crucible testing. In preparation for Sludge Batch 9 (SB9) processing, a comparison demonstrated that minor compositional differences existed between the Sludge Batch 8 (SB8)-Frit 803 and SB9-Frit 803 glass composition regions for sludge-only and coupled operations with the Actinide Removal Process (ARP) and Modular Caustic Side Solvent Extraction Unit (MCU). Thus, no experimental testing was necessary and the SB8 SO_4^{2-} limit of 0.65 wt.% was recommended for SB9 processing. This previous SB9 assessment did not address coupled processing with streams from the Salt Waste Processing Facility (SWPF), which is anticipated to start operations in November 2019. These high activity streams will 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 TiO_2 concentrations in glass greater than 2 wt.% based on single and double MST strike scenarios.

In support of coupled operation with SWPF, the DWPF Product Composition Control System was revised and allows a TiO_2 concentration of up to 6 wt.% (minus measurement uncertainty) in glass. For the SB8-Frit 803 SO_4^{2-} solubility study, the maximum TiO_2 concentration evaluated was 0.94 wt.%. Since the influence of increased TiO_2 on the retention of SO_4^{2-} in the SB9 glass region is unknown, a test matrix of ten glass compositions has been proposed to determine whether the 0.65 wt.% SO_4^{2-} limit is still appropriate for SB9 coupled operation with SWPF. This report documents the development of a test matrix that will support this study.

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LIST OF ABBREVIATIONS

ARP	Actinide Removal Process
DWPF	Defense Waste Processing Facility
g	gram
L	liter
MAR	Measurement Acceptance Region
MCU	Modular Caustic Side Solvent Extraction Unit
MST	monosodium titanate
PCCS	Product Composition Control System
SB3	Sludge Batch 3
SB4	Sludge Batch 4
SB7b	Sludge Batch 7b
SB8	Sludge Batch 8
SB9	Sludge Batch 9
SE	Strip Effluent
SME	Slurry Mix Evaporator
SMRF	Slurry-Fed Melt Rate Furnace
SRAT	Sludge Receipt and Adjustment Tank
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation
SS	sludge solids
SSRT	Sludge Solids Receipt Tank
SWPF	Salt Waste Processing Facility
TTR	Technical Task Request
WL	waste loading
wt.%	weight percent

1.0 Introduction

To support initial operations at the Defense Waste Processing Facility (DWPF), the original sulfate (SO_4^{2-}) solubility limit for Product Composition Control System (PCCS) Slurry Mix Evaporator (SME) acceptability was defined at 0.4 weight percent (wt.%) in glass based on pilot-scale melter testing.[1-3] This limit signified that 0.4 wt.% SO_4^{2-} could be retained in the glass without the formation of a sulfate phase. The utilization of a 0.4 wt.% SO_4^{2-} limit in glass for SME acceptability was challenged for Sludge Batch 3 (SB3), which included a Np-based stream projected to contain a significant fraction of ferrous sulfamate.[4] Laboratory-scale crucible testing with both batch chemicals and simulated Sludge Receipt and Adjustment Tank (SRAT) product was performed and a new PCCS SME acceptability limit for SO_4^{2-} was established at 0.6 wt.% for SB3, which was confirmed by supplementary Slurry-Fed Melt Rate Furnace (SMRF) testing with simulated SME product.[4] While 0.6 wt.% SO_4^{2-} was allowed in the melter feed, it was anticipated that less than 0.6 wt.% would be retained in the glass based on SO_4^{2-} volatility during DWPF melter processing, which provides some conservatism with respect to the formation of a sulfate phase. PCCS was not revised to reflect the updated SO_4^{2-} limit and DWPF imposed this constraint administratively outside of PCCS.

The 0.6 wt.% SO_4^{2-} limit was confirmed for Sludge Batch 4 (SB4) through Sludge Batch 7b (SB7b) by laboratory-scale crucible testing with batch chemicals.[5-10] For Sludge Batch 8 (SB8), the limit was defined at 0.65 wt.%.[11,12] In preparation for SB9 processing, a comparison demonstrated that minor compositional differences existed between the SB8-Frit 803 and SB9-Frit 803 glass composition regions for sludge-only and coupled operations with the Actinide Removal Process (ARP) and Modular Caustic Side Solvent Extraction Unit (MCU).[13] Thus, no experimental testing was necessary and the 0.65 wt.% SO_4^{2-} limit was recommended for SB9 processing.

This previous SB9 assessment did not address coupled processing with streams from the Salt Waste Processing Facility (SWPF), which is anticipated to start operations in November 2019. These SWPF streams will 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 TiO_2 concentrations in glass greater than 2 wt.% based on single and double MST strike scenarios.[14]

In support of coupled operation with SWPF, PCCS was revised and allows a TiO_2 concentration of up to 6 wt.% (minus measurement uncertainty) in glass.[3] For the SB8-Frit 803 SO_4^{2-} solubility study, the maximum targeted TiO_2 concentration evaluated was 0.94 wt.%.[11,12] Since the impact of increased TiO_2 on the retention of SO_4^{2-} in the SB9 glass region is unknown, experimental testing has been proposed to determine whether the 0.65 wt.% SO_4^{2-} limit is still appropriate for SB9 coupled operation with SWPF. This report documents the development of a test matrix that will support this study.

2.0 Quality Assurance

This work was requested via a Technical Task Request (TTR)[15] and directed by a Task Technical and Quality Assurance Plan.[16] The TTR indicated the portion of the work scope covered by this report is classified as Safety Class and not subject to RW-0333P requirements. Requirements for performing reviews of technical reports and the extent of review are established in Manual E7, Procedure 2.60.[17] 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.[18]

3.0 Glass Selection

Using the SB9 Tank 40 blend projection on a calcine basis received from Savannah River Remediation (SRR),[14] the elemental concentrations were converted to oxides and normalized to 100 wt.% as shown in Table 3-1.

Table 3-1. Normalized SB9 Tank 40 Blend Projection

Oxide	Concentration (wt.%)	Oxide	Concentration (wt.%)
Al_2O_3	17.50	MnO	9.42
B_2O_3	0.06	Na_2O	24.40
BaO	0.10	NiO	2.02
CaO	1.86	PbO	0.05
Ce_2O_3	0.16	SO_4^{2-}	1.02
Cr_2O_3	0.15	SiO_2	3.80
CuO	0.09	ThO_2	1.25
Fe_2O_3	32.11	TiO_2	0.05
K_2O	0.13	U_3O_8	4.99
La_2O_3	0.06	ZnO	0.05
Li_2O	0.15	ZrO_2	0.08
MgO	0.50		

Based on the guidance and assumptions provided by SRR,[14,19] SRNL performed subsequent calculations to estimate compositions of SE[20] and the SSRT effluent stream for the following two cases:[21,22]

- Case 1: Single MST strike operation (nominal 0.4 g MST/L of salt solution). This case represents the baseline.
- Case 4: Double MST strike operation (i.e., two sequential contactings of salt solution in SWPF with a nominal 0.4 g MST/L of salt solution in each).

Other pertinent assumptions from SRR-WSE-2018-00025 include:

- 0.7M Na (total Na) wash endpoint for the SSRT stream
- DWPF receives 5700 gallons of sludge slurry from Tank 40 per SRAT batch
- DWPF receives 12,800 gallons of SE per SRAT batch based on the baseline BOBCalixC6 solvent[a]
- DWPF receives 2800 gallons of the SSRT effluent stream (MST and sludge solids (SS)) per SRAT batch for single strike operation and 4200 gallons for double strike operation

Estimates for the composition in the SRAT resulting from the addition of streams from SWPF that represent single and double MST strike scenarios are shown in Table 3-2. Using the compositions in Table 3-2, the SO_4^{2-} concentration was fixed at 0.65 wt.% in glass at 32% and 40% waste loading (WL). The TiO_2 concentration was also held constant and the remainder of the oxides in Table 3-2 were renormalized.

Glass compositions were developed using both Frit 803 and Frit 625.[b] Frit 803 was recommended for SB9 coupled operation with ARP-MCU and could be used during initial SWPF startup operations at lower processing rates.[22-24] Frit 625 was recommended for operational flexibility during coupled operation with SWPF at design-basis processing rates.[22]

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

[b] The composition of Frit 803 is $8B_2O_3$-$6Li_2O$-$8Na_2O$-$78SiO_2$ (wt.%) and the composition of Frit 625 is $1Al_2O_3$-$8B_2O_3$-$7Li_2O$-$6Na_2O$-$78SiO_2$ (wt.%).

An additional glass composition was selected from the variability study to maximize the TiO_2 concentration.[c,22] At 40% WL, the PCCS constraint for maximum TiO_2 concentration failed, which occurs when the TiO_2 concentration in glass is greater than 6 wt.% minus measurement uncertainty. Thus, the WL for this glass was reduced to 38% WL so that the glass composition would pass the PCCS measurement acceptance region (MAR) constraints.

Target compositions for the recommended glass compositions are shown in Table 3-3.

Table 3-2. SRAT Composition (wt.%) Based on Single and Double MST Strike Scenarios

	Case #1 2800 gallons MST/SS Single MST Strike 12,800 gallons SE	Case #4 4200 gallons MST/SS Double MST Strike 12,800 gallons SE
Al_2O_3	15.207	13.939
B_2O_3	0.053	0.048
BaO	0.083	0.075
CaO	1.538	1.386
Ce_2O_3	0.136	0.122
Cr_2O_3	0.121	0.109
Cs_2O	1.564	1.410
CuO	0.072	0.065
Fe_2O_3	26.594	23.958
K_2O	0.291	0.288
La_2O_3	0.048	0.044
Li_2O	0.125	0.112
MgO	0.411	0.371
MnO	7.803	7.030
Na_2O	27.669	28.054
NiO	1.673	1.507
PbO	0.045	0.040
SO_4^{2-}	0.880	0.805
SiO_2	3.148	2.836
ThO_2	1.035	0.932
TiO_2	7.263	13.048
U_3O_8	4.133	3.724
ZnO	0.041	0.037
ZrO_2	0.067	0.060

[c] The variability study glass identification is SRNL-SB9b-08.

Table 3-3. Recommended Glass Compositions (wt.%) for the Sulfate Solubility Study

Glass ID	SB9b-S10	SB9b-S11	SB9b-S12	SB9b-S13	SB9b-S14	SB9b-S15	SB9b-S16	SB9b-S17	SB9b-S18	SB9b-S19
Case	#1	#1	#1	#1	#4	#4	#4	#4	Max TiO_2	Max TiO_2
WL	32%	40%	32%	40%	32%	40%	32%	40%	38%	38%
Frit ID	625	625	803	803	625	625	803	803	625	803
Al_2O_3	5.485	6.633	4.805	6.033	5.077	6.123	4.397	5.523	5.702	5.082
B_2O_3	5.457	4.821	5.457	4.821	5.455	4.819	5.455	4.819	4.977	4.977
BaO	0.026	0.033	0.026	0.033	0.024	0.030	0.024	0.030	0.027	0.027
CaO	0.486	0.610	0.486	0.610	0.437	0.549	0.437	0.549	0.502	0.502
Ce_2O_3	0.043	0.054	0.043	0.054	0.039	0.048	0.039	0.048	0.044	0.044
Cr_2O_3	0.038	0.048	0.038	0.048	0.034	0.043	0.034	0.043	0.039	0.039
Cs_2O	0.494	0.621	0.494	0.621	0.445	0.559	0.445	0.559	0.560	0.560
CuO	0.023	0.029	0.023	0.029	0.021	0.026	0.021	0.026	0.024	0.024
Fe_2O_3	8.403	10.551	8.403	10.551	7.557	9.492	7.557	9.492	8.682	8.682
K_2O	0.092	0.115	0.092	0.115	0.091	0.114	0.091	0.114	0.111	0.111
La_2O_3	0.015	0.019	0.015	0.019	0.014	0.017	0.014	0.017	0.016	0.016
Li_2O	4.799	4.249	4.119	3.649	4.795	4.244	4.115	3.644	4.381	3.761
MgO	0.130	0.163	0.130	0.163	0.117	0.147	0.117	0.147	0.134	0.134
MnO	2.466	3.096	2.466	3.096	2.217	2.785	2.217	2.785	2.547	2.547
Na_2O	12.823	14.578	14.183	15.778	12.930	14.715	14.290	15.915	14.230	15.470
NiO	0.529	0.664	0.529	0.664	0.475	0.597	0.475	0.597	0.546	0.546
PbO	0.014	0.018	0.014	0.018	0.013	0.016	0.013	0.016	0.015	0.015
SO_4^{2-}	0.650	0.650	0.650	0.650	0.650	0.650	0.650	0.650	0.650	0.650
SiO_2	54.035	48.049	54.035	48.049	53.935	47.924	53.935	47.924	49.388	49.388
ThO_2	0.327	0.411	0.327	0.411	0.294	0.369	0.294	0.369	0.338	0.338
TiO_2	2.324	2.905	2.324	2.905	4.176	5.219	4.176	5.219	5.702	5.702
U_3O_8	1.306	1.640	1.306	1.640	1.175	1.475	1.175	1.475	1.349	1.349
ZnO	0.013	0.016	0.013	0.016	0.012	0.015	0.012	0.015	0.013	0.013
ZrO_2	0.021	0.027	0.021	0.027	0.019	0.024	0.019	0.024	0.022	0.022

4.0 Recommendation

Since the influence of increased TiO_2 concentrations on the retention of SO_4^{2-} in the SB9 glass region is unknown, a test matrix of ten glass compositions has been proposed to determine whether the 0.65 wt.% SO_4^{2-} limit is still appropriate for SB9 coupled operation with SWPF.

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