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Reconfirmation of Frit 803 Based on the January 2016 Sludge Batch 9 Reprojection

Summary

On January 11, 2016, Savannah River Remediation (SRR) provided the Savannah River National Laboratory (SRNL) with a Sludge Batch 9 (SB9) reprojection that was developed from the analyzed composition of a Tank 51 sample. This sample was collected after field washing had been completed in Tank 51 to support the alternate reductant task. Based on this reprojection, Frit 803 is still a viable option for the processing of SB9 under sludge-only operations and coupled (Actinide Removal Process (ARP) product with and without monosodium titanate (MST)) operations. The maximum projected volumes of ARP product that can be transferred from the Precipitate Reactor Feed Tank (PRFT) per Sludge Receipt and Adjustment Tank (SRAT) batch and the resulting Na_2O concentrations in the SRAT are as follows for coupled operations:

Volume of ARP Product (gallons)	Na_2O Concentration (wt%) (based on January 2016 projections)	Na_2O Concentration (wt%) (based on August 2015 projections)
1750 gallons (with MST)	28.4	28.3
1500 gallons (without MST)	28.1	27.8

The Na_2O concentrations in the SRAT resulting from the maximum projected ARP product transfer volumes are consistent with those from the previous assessments that were based on the August 2015 projections. Regardless of the presence or absence of MST in the ARP product, the contribution of Na_2O to the resulting glass will be similar at the same waste loading (WL). These projected volumes of ARP product are not anticipated to be an issue for SB9. The actual transfer volumes from the PRFT to the SRAT are determined based upon the analyzed

Na_2O concentrations in the PRFT samples, which has resulted in larger transfer volumes than those allowed by the projections for Sludge Batch 8 (SB8).

An operating window of 32-40% WL around the nominal WL of 36% is achievable for both sludge-only and coupled operations; however, each of the glass systems studied does become limited by waste form affecting constraints (durability) at higher volumes of ARP product and WLs of 41-42%.

1.0 Introduction

While Frit 803 was previously confirmed for SB9 processing[1], SRR provided SRNL with an additional SB9 projection[2] on January 11, 2016 based on the analysis[3] of a Tank 51 sample. This sample was collected after field washing had been completed to support the alternate reductant task. On a calcine basis, the most significant compositional shift was the SB9 Tank 51 Na reprojection, which was 1.57 wt% less than the original projection that was developed using the analyzed composition of the qualification sample.[2] In order to verify that Frit 803 can still be used for SB9 processing, SRR requested that SRNL perform assessments of the projections using the current Defense Waste Processing Facility (DWPF) Product Composition Control System (PCCS) models and their associated Measurement Acceptability Region (MAR) constraints. The intent of this memorandum is to present the results of the MAR assessments from these projections and confirm the viability of Frit 803 for both sludge-only and coupled operations.

This assessment does not provide any insight into (i) the impact of the additional boron from the strip effluent used in the Modular Caustic-Side Solvent Extraction Unit (MCU), (ii) melter feed preparation in the Chemical Processing Cell (CPC), and (iii) SB9 melting rate and canister production rates. MAR assessments to determine the impact of the additional boron from the strip effluent used in MCU on the viability of Frit 803 to meet DWPF operating goals for SB9 will be completed and documented separately.

This work was directed by a Task Technical and Quality Assurance Plan and was supported by the use of JMP Pro Version 11.2.1.[4,5]

2.0 Sludge Projections

The nominal SB9 sludge-only projection received from SRR on January 11, 2016 was converted to oxides and normalized to 100 wt% as shown in Table 1.[2] As in previous SB9 MAR studies, ARP product additions were included in these assessments, utilizing compositions with and without[a] MST that were based on analytical data from the PRFT in DWPF.[6] Nominal (calcine) compositions of ARP product with and without MST are shown in Table 2. In order to generate the coupled operations projections (ARP product with and without MST), the following assumptions were made:

- ARP product additions per SRAT batch – 250-2000 gallons in 250 gallon increments
- SRAT batch size – 6000 gallons
- SRAT receipt total solids content – 17.21 wt%[7]
- ARP calcine solids – 3.82 wt% (with MST) and 3.13 wt% (without MST)[6]
- SRAT receipt calcine factor – 0.763 grams oxide/grams dried solids[7]
- ARP density – 1.03 kg/L[8]
- SRAT receipt density – 1.16 kg/L[7]

The inputs for the SRAT receipt total solids content, SRAT receipt calcine factor, and SRAT receipt density were updated from those used for the previous SB9-Frit 803 assessment[1] based on the analytical results of the SB8 Tank 40 sample.[7] Table 3 presents the sludge-only and coupled projections with up to 2000 gallons of ARP

[a] If the salt batch meets the Saltstone Waste Acceptance Criteria limits for strontium and actinides, then there will be an alternative processing option to not strike the salt batch with MST.

product (with and without MST). As will be discussed in Section 3.0, some of the minor oxides were grouped into an "Others" component, and are shaded blue in Table 3.

Table 1. Normalized Nominal Sludge-Only SB9 Projection

Oxide	Concentration (wt%)
Al_2O_3	17.46
B_2O_3	0.06
BaO	0.11
CaO	1.84
Ce_2O_3	0.19
Cr_2O_3	0.15
CuO	0.09
Fe_2O_3	32.03
K_2O	0.14
La_2O_3	0.06
Li_2O	0.13
MgO	0.50
MnO	9.37
Na_2O	24.47
NiO	2.08
PbO	0.05
SO_4^{2-}	1.05
SiO_2	3.74
ThO_2	1.24
TiO_2	0.05
U_3O_8	5.06
ZnO	0.05
ZrO_2	0.08

Table 2. Nominal Composition of ARP Product With and Without MST[6]

Oxide	ARP Product with MST (wt%)	ARP Product Without MST (wt%)
Na_2O	80.3	97.2
SO_4^{2-}	2.3	2.8
TiO_2	17.4	---

Table 3. SB9 Sludge-only and Coupled Operations Projections

Volume of ARP Product (gal)		Al_2O_3	B_2O_3	BaO	CaO	Ce_2O_3	Cr_2O_3	CuO	Fe_2O_3	K_2O	La_2O_3	Li_2O	MgO
0	Sludge-only	17.46	0.06	0.11	1.84	0.19	0.15	0.09	32.03	0.14	0.06	0.13	0.50
250	without MST	17.31	0.06	0.11	1.83	0.19	0.14	0.09	31.75	0.14	0.06	0.13	0.49
500		17.16	0.06	0.11	1.81	0.18	0.14	0.09	31.48	0.14	0.06	0.13	0.49
750		17.01	0.06	0.11	1.80	0.18	0.14	0.09	31.21	0.14	0.06	0.13	0.48
1000		16.87	0.06	0.11	1.78	0.18	0.14	0.08	30.94	0.14	0.06	0.12	0.48
1250		16.72	0.06	0.11	1.77	0.18	0.14	0.08	30.68	0.14	0.06	0.12	0.48
1500		16.58	0.06	0.11	1.75	0.18	0.14	0.08	30.42	0.14	0.06	0.12	0.47
1750		16.45	0.06	0.10	1.74	0.18	0.14	0.08	30.17	0.14	0.06	0.12	0.47
2000		16.31	0.06	0.10	1.72	0.17	0.14	0.08	29.92	0.13	0.05	0.12	0.46
250	with MST	17.28	0.06	0.11	1.82	0.19	0.14	0.09	31.69	0.14	0.06	0.13	0.49
500		17.09	0.06	0.11	1.80	0.18	0.14	0.09	31.36	0.14	0.06	0.13	0.49
750		16.92	0.06	0.11	1.79	0.18	0.14	0.08	31.03	0.14	0.06	0.12	0.48
1000		16.74	0.06	0.11	1.77	0.18	0.14	0.08	30.71	0.14	0.06	0.12	0.48
1250		16.57	0.06	0.11	1.75	0.18	0.14	0.08	30.40	0.14	0.06	0.12	0.47
1500		16.40	0.06	0.10	1.73	0.18	0.14	0.08	30.09	0.14	0.05	0.12	0.47
1750		16.24	0.06	0.10	1.71	0.17	0.14	0.08	29.79	0.13	0.05	0.12	0.46
2000		16.08	0.06	0.10	1.70	0.17	0.13	0.08	29.49	0.13	0.05	0.12	0.46

Table 3 cont. SB9 Sludge-only and Coupled Operations Projections

Volume of ARP Product (gal)		MnO	Na_2O	NiO	PbO	SO_4^{2-}	SiO_2	ThO_2	TiO_2	U_3O_8	ZnO	ZrO_2
0	Sludge-only	9.37	24.47	2.08	0.05	1.05	3.74	1.24	0.05	5.06	0.05	0.08
250	without MST	9.29	25.11	2.06	0.05	1.06	3.70	1.23	0.05	5.02	0.05	0.08
500		9.21	25.73	2.05	0.05	1.08	3.67	1.22	0.05	4.97	0.05	0.08
750		9.13	26.35	2.03	0.05	1.09	3.64	1.21	0.05	4.93	0.05	0.08
1000		9.05	26.95	2.01	0.05	1.11	3.61	1.20	0.05	4.89	0.05	0.08
1250		8.97	27.54	1.99	0.05	1.12	3.58	1.19	0.05	4.85	0.05	0.08
1500		8.90	28.13	1.98	0.05	1.13	3.55	1.18	0.05	4.81	0.05	0.08
1750		8.82	28.70	1.96	0.05	1.15	3.52	1.17	0.05	4.77	0.05	0.08
2000		8.75	29.26	1.95	0.05	1.16	3.49	1.16	0.05	4.73	0.05	0.08
250	with MST	9.27	25.07	2.06	0.05	1.06	3.70	1.22	0.23	5.01	0.05	0.08
500		9.17	25.65	2.04	0.05	1.07	3.66	1.21	0.42	4.95	0.05	0.08
750		9.08	26.22	2.02	0.05	1.09	3.62	1.20	0.59	4.90	0.05	0.08
1000		8.98	26.78	2.00	0.05	1.10	3.58	1.19	0.77	4.85	0.05	0.08
1250		8.89	27.32	1.98	0.05	1.11	3.55	1.17	0.94	4.80	0.05	0.08
1500		8.80	27.86	1.96	0.05	1.12	3.51	1.16	1.10	4.75	0.05	0.08
1750		8.71	28.38	1.94	0.05	1.13	3.47	1.15	1.27	4.71	0.05	0.08
2000		8.63	28.90	1.92	0.05	1.15	3.44	1.14	1.43	4.66	0.05	0.07

The addition of ARP product with MST increases the TiO_2 concentration of the projected compositions. At 40% WL and 2000 gallons of ARP product, the maximum nominal projected TiO_2 content in glass is 0.57 wt%, which is lower than the maximum TiO_2 concentration determined from the previous projections (~0.72 wt%).[1] This shift in TiO_2 concentration is due to the updated inputs that were used to generate the coupled operations projections for the current assessment. Based on the PCCS limit of 2 wt% TiO_2 in glass (without measurement uncertainty applied), none of these amounts of ARP product with MST will exceed the PCCS limit for a target WL up to 40%.[9]

As expected, increased volumes of ARP product have higher SO_4^{2-} concentrations. At 40% WL and 2000 gallons of ARP product, the maximum nominal projected SO_4^{2-} content in glass is 0.46 wt%, which is consistent with the maximum SO_4^{2-} concentration determined with the previous projections.[1] The maximum projected SO_4^{2-} concentrations in glass based on other volumes of ARP product (with and without MST) are within the range of 0.42-0.46 wt%.

3.0 Methodology for the Variation Stage MAR Assessment

The approach taken for the Variation Stage MAR assessment was to evaluate how robust Frit 803 is relative to variation in the composition of the SB9 SRAT product and the uncertainty in targeting the nominal 36% WL during the blending process. These variations and uncertainties come into play as DWPF (i) conducts the blending process[b] to target the desired WL for the next Slurry Mix Evaporator (SME) batch and, (ii) subsequently judges the new SME batch for MAR acceptability via the PCCS process, which is driven by the analyses of samples of the new SME batch. The Variation Stage MAR assessments were conducted using JMP Pro Version 11.2.1 to evaluate the performance of Frit 803 for the SB9 projections provided in Table 3.[5,10]

Compositional variation (±) around the nominal projections is introduced into the MAR assessments to account for likely, but not necessarily bounding, differences that may be seen in the sludge that is transferred from Tank 40 into the SRAT during the processing of SB9. The compositional variation around the nominal concentration was represented by the larger of 0.5 wt% or 7.5% of the nominal concentration for each of the individually-tracked oxides in the sludge-only and coupled operations projections shown in Table 3. The exception was SO_4^{2-} for which a 0.1 wt% variation was applied. Those oxides not tracked individually were grouped into an "Others" component. These oxides are shaded blue in Table 3. If no MST is present in the ARP product, then TiO_2 is grouped into the "Others" component; however, TiO_2 becomes an individually tracked oxide when MST is included in the ARP product.

An example of the resulting sludge oxide concentration intervals for the sludge-only flowsheet is provided in Table 4. In this example TiO_2 is an individually tracked oxide, which indicates that the coupled operations version of this composition will include MST.

Table 4. Sludge Oxide Intervals (wt%) for the Sludge-only Flowsheet

Al_2O_3	CaO	Fe_2O_3	MnO	Na_2O	NiO
16.152	1.343	29.630	8.666	22.636	1.583
18.772	2.343	34.435	10.071	26.307	2.583

SO_4^{2-}	SiO_2	ThO_2	TiO_2	U_3O_8	Others
0.946	3.236	0.738	0.000	4.560	1.109
1.146	4.236	1.738	0.550	5.560	2.109

The sludge oxide intervals were used to generate extreme vertices (EVs) of sludge compositions for each flowsheet of interest using the Design of Experiments platform for mixtures available in JMP. The EVs are the

[b] Combining SRAT product with frit and the heel of the SME.

corner-points of the sludge compositional region defined by each set of the sludge oxide intervals such as that given in Table 4. A set of sludge oxide intervals was developed for each sludge projection of interest:

- Sludge-only (0 gallons of ARP product added)
- ARP product additions (250-2000 gallons) with and without MST (in increments of 250 gallons)

For a given projection, all of the EVs were combined with Frit 803 at WLs in the range of 30-42%, and each of the resulting glass compositions was evaluated against the PCCS MAR criteria to determine if the composition would pass the SME acceptability process.[9] Since the nominal targeted WL is 36% for SB9, an operating window of 36 ± 4% WL (at least 32-40% WL) was the primary success metric used to evaluate increasing additions of ARP product.[c] As WLs were increased, glass compositions that were durability limited (e.g., free energy of hydration (ΔG_p)) were considered less desirable options as these limitations would be waste form affecting.

4.0 Variation Stage MAR Assessment Results

Table 5 provides the results of the Variation Stage MAR assessments of the EVs based on the sludge-only and coupled operations projections. The WL operating window for each volume of ARP product in the range of 0-2000 gallons is provided and the constraint(s) limiting higher WLs is listed, as well as the number of sludge EVs failing the constraint (shown in parentheses). The options in which all EVs are acceptable based on the success criterion (at least 32-40% WL window) are highlighted in blue. For each of the glass systems being evaluated, the proportion of failing EVs to the total number of EVs should not be interpreted as a measure of the likelihood of an issue during DWPF operation, but instead as a *qualitative assessment* to which the glass system fails to meet the success criterion discussed in Section 0.

Table 5. Variation Stage MAR Assessment Results

ARP (gal)	Na_2O (wt%)	#EVs	WL Window	Limiting Constraints
0	24.47	2040	30-42	---
250	25.11	1910	30-42	---
500	25.73	2090	30-42	---
750	26.35	2090	30-42	---
1000	26.95	2120	30-42	---
1250	27.54	2120	30-41	lv (2)
1500	28.13	2156	30-40	ΔG_p (14)
1750	28.7	2156	30-39	ΔG_p (87)
2000	29.26	2156	30-37	ΔG_p (13)

Case: ARP product without MST

ARP (gal)	Na_2O (wt%)	#EVs	WL Window	Limiting Constraints
0	24.47	4282	30-42	---
250	25.07	4408	30-42	---
500	25.65	4464	30-42	---
750	26.22	4512	30-42	---
1000	26.78	4428	30-42	---
1250	27.32	4372	30-42	---
1500	27.86	4372	30-41	lv(82); ΔG_p (19)
1750	28.38	4372	30-40	ΔG_p (85)
2000	28.9	4372	30-39	ΔG_p (176)

Case: ARP product with MST

ΔG_p – durability and lv – low viscosity

Consider the coupled operations case (ARP product without MST) as an example for the interpretation of the information provided in Table 5. For the sludge-only option, the Na_2O content in the sludge is 24.47 wt% and the number of EVs representing the compositional region is 2040. The WL interval over which all glass compositions pass the SME acceptability process is 30-42%.[d] When 1500 gallons of ARP product are added (without MST), the WL interval is reduced to 30-40% due to the higher Na_2O content (28.13 wt% in sludge). At 41% WL, 14 compositions fail the ΔG_p constraint for durability out of 2156 EV compositions. As the ARP

[c] The ±4% WL around the nominal 36% WL is used to account for any uncertainty in targeting this nominal WL.
[d] 30-42% WL is the full range over which MAR assessments were performed.

product volume is increased to 1750 gallons (28.7 wt% Na_2O in sludge), the WL range is further reduced to 30-39%, which does not meet the operating window success criterion of at least 32-40% WL as discussed in Section 3.0.

Based on these compositional projections, the projected volumes of ARP product that can be transferred from the PRFT per SRAT batch while maintaining an operating window of 32-40% WL are as follows for coupled operations:

- 1750 gallons of ARP product with MST
- 1500 gallons of ARP without MST

Note that these volumes of ARP product have increased with respect to the original Frit 803 assessment[1] due to updated inputs for the SRAT receipt total solids content, SRAT density, and the SRAT receipt calcine factor shown in Section 2.0 for the ARP product calculations; however, the resulting Na_2O concentration in the SRAT at which the systems become limited is consistent with the previous MAR assessments based on the August 2015 projections as shown in Table 6.

Table 6. Maximum Na_2O Concentrations in the SRAT for the Coupled Operations Projections

Volume of ARP Product (gallons)	Na_2O Concentration (wt%) (based on January 2016 projections)	Na_2O Concentration (wt%) (based on August 2015 projections)
1750 gallons (with MST)	28.4	28.3
1500 gallons (without MST)	28.1	27.8

These projected volumes of ARP product are not anticipated to be an issue for SB9. The actual transfer volumes from the PRFT to the SRAT are determined based upon the analyzed Na_2O concentrations in the PRFT samples, which has resulted in larger transfer volumes than those allowed by the projections for SB8. Each of the glass systems does become limited by waste form affecting constraints (durability) at higher volumes of ARP product and WLs of 41-42%.

5.0 Conclusions

Based on the January 2016 projections, Frit 803 is still a viable option for both sludge-only and coupled operations (with and without MST) for SB9 processing at WLs of 32-40%. The maximum volumes of ARP product that can be added to each SRAT batch are 1750 gallons of ARP product with MST and 1500 gallons of ARP product without MST, which corresponds to Na_2O concentrations in the SRAT of 28.4 and 28.1 wt%, respectively. Regardless of the presence or absence of MST in the ARP product, the contribution of Na_2O from ARP product in the resulting glass will be similar at the same WL.

6.0 Future Work

In support of SB9 qualification, these remaining tasks will be completed:

- MAR assessments to determine the impact of the additional boron from the strip effluent used in the MCU on the viability of Frit 803 to meet DWPF operating goals for SB9
- Recommendation for the SB9 sulfate solubility study

Due to the SB9 reprojection and the experimental work already underway, the following tasks will be completed:

- Assessment and subsequent recommendations related to the impact of the reprojected compositional region on the applicability of the initial glasses for the variability and fissile loading studies

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