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# **Evaluation of Sludge Solids Returns Impacts on Sludge Batch 10 Flammability, Glass Quality, and Glass Processability**

**W. H. Woodham**

February 2022

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## EXECUTIVE SUMMARY

The Savannah River National Laboratory (SRNL) is currently preparing to return  $\leq 20$  kgs of sludge solids collected over time from Tank Farm characterization activities and demonstrations of the Defense Waste Processing Facility (DWPF) flowsheets (nitric-formic and nitric-glycolic). These sludge solids will be transported and added to Tank 51 which is currently preparing Sludge Batch (SB) 10. DWPF plans to operate the under the nitric-glycolic flowsheet for the processing of SB10. The hydrogen generation rate for the nitric-glycolic flowsheet is  $0.024 \text{ lb h}^{-1}$ . The addition of  $\leq 20$  kg of sludge solids returns to SB 10 does not have an impact on flammability in the DWPF Chemical Process Cell (CPC) or glass quality and processability. The relatively low mass of the addition ( $\leq 20$  kg) is insufficient to detect a significant analytical change to the expected SB 10 compositions. The following bounding assumptions are employed in this assessment:

### *General Bounding Assumptions*

- A range of 20 kg to 40 kg of returns are assumed to be added to Tank 51. The actual amount of returns is expected to be lower than 20 kg and partially composed of non-reactive water (which will be dried).
- 20 kg of returns are assumed to be added to Tank 51 at the conclusion of SB 10 washing. If the returns are added prior to the completion of washing, many components are expected to be washed away, further diluting the impact of sludge solids.

### *CPC Flammability Bounding Assumptions*

- 20 kg of returns are assumed to be added as rhodium metal when the composition is comprised of various cations. The actual composition of returns is expected to have a rhodium concentration much less than 0.1 wt%.
- 20 kg of returns are assumed to be added as formic acid when the composition is comprised of various cations and anions. The actual composition of returns is expected to have a minor formate concentration. The full mass of sludge returns (planned 20 kg) is increased to 40 kg. The 40 kg is divided equally between rhodium and formate.
- The most active components in catalytic hydrogen production (rhodium and formate) have been selected for this assessment, thus assessing the impact of individual anions (hydroxide, carbonate, nitrate, nitrite, and oxalate) outside of formate is ignored.
- The full mass of sludge returns is assumed to contribute to the rhodium-catalyzed formate dehydrogenation mechanism. In reality, a fraction of the returns would contribute to the less-reactive ruthenium- and palladium-catalyzed reactions.
- The mass of aluminum containers ( $\sim 1.7$  kg) is negligible because aluminum is not involved in the catalytic dehydrogenation of formic acid.

### *Glass Quality and Processability Bounding Assumptions*

- 20 kg of returns are assumed to be added as pure metals (one type of metal for each addition scenario for all metals except aluminum). The actual returns are expected to be a blend of many metal compounds.
- The amount of aluminum metal in the sludge returns is assumed to be less than 18.3 kg, yielding a total of 20 kg of aluminum when combined with the  $\sim 1.7$  kg of aluminum present in the waste containers

The following conclusions are made as a result of this work:

- The addition of  $\leq 20$  kg of waste from SRNL can be made to Tank 51 prior to the Tank 51 to Tank 40 SB 10 transfer without risk to flammability of CPC vessels, glass quality, and glass processability.
- Future additions to sludge batches should be assessed to demonstrate compliance with the flammability limits in the CPC. These assessments may reflect the evaluation performed in this document or employ an alternative methodology, if necessary.
  - The evaluation performed in this document utilizes several overly conservative assumptions. Future assessments may ease these assumptions as necessary (e.g., purity and composition of 20 kg sludge returns).
- The glass qualification process is robust enough to avoid perturbation by the addition of  $\leq 20$  kg:
  - In cases where a sludge batch has not been qualified, any potential offset to calcined composition will be assessed as a part of the sludge batch qualification process.
  - In cases where a sludge batch has been partially or fully qualified, 20 kg additions are insufficient to change calcined compositions from compositions previously evaluated with Product Composition Control System (PCCS) Measurement Acceptance Region (MAR) assessments.

It is recommended that any existing lines of inquiry regarding the impact of the addition of 20 kg of sludge solids returns to SB 10 Tank 51 on Waste Acceptance Criteria such as the flammability of CPC vessels or glass quality and glass processability during SB 10 processing be closed with the understanding that potential impacts have been assessed and are well within existing facility constraints.

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## **LIST OF ABBREVIATIONS**

CPC	Chemical Processing Cell
CSTF	Concentration, Storage, and Transfer Facilities
DWPF	Defense Waste Processing Facility
MAR	Measurement Acceptance Region
PCCS	Product Composition Control System
SB	Sludge Batch
SME	Slurry Mix Evaporator
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation
SRS	Savannah River Site
SWPF	Salt Waste Processing Facility

## 1.0 Introduction

Savannah River National Laboratory (SRNL) has recently been requested by Savannah River Remediation (SRR) to assess the impact of the addition of  $\leq 20$  kg of sludge solids on processing during Sludge Batch (SB) 10 at the Defense Waste Processing Facility (DWPF). The  $\leq 20$  kg of sludge solids in question represent waste solids to be returned from the SRNL Shielded Cells to Tank 51 in the Concentration, Storage, and Transfer Facilities (CSTF) at the Savannah River Site (SRS) in Aiken, SC. Tank 51 is designated as the SB preparation tank and is currently being used to wash sludge slurry to a target supernatant sodium concentration of  $\sim 1$  M. Once SB 10 washing is completed, sludge will be transferred from Tank 51 to Tank 40. This combined material represents the blend of SB 10 sludge that will be sent to the DWPF for processing.

The purpose of this document is to assess the potential impact of  $\leq 20$  kg of sludge solids on 1) the flammability of gases generated during SB 10 processing and 2) glass quality and processability. Other potential impacts (e.g., increased cycle time, rheological adjustments, etc.) are beyond the scope of this document.

## 2.0 Evaluation Methodology

### 2.1 Flammability Assessment

The flammability of SB 10 waste processing during Chemical Process Cell (CPC) operations is expected to be well-described by hydrogen concentrations observed during SB 10 simulant testing.<sup>1</sup> The maximum hydrogen generation rate observed during this testing ( $6.04 \times 10^{-4}$  lb h<sup>-1</sup> on a 6,000 gallon sludge volume basis) is used to estimate the anticipated hydrogen generation during SB 10 processing at the DWPF. The mechanism for hydrogen evolution in the CPC is believed to be due to the catalytic dehydrogenation of formate due to dissolved rhodium, ruthenium, and palladium catalysts.<sup>2</sup> The most active catalyst of these has been shown to be rhodium.<sup>3</sup> Therefore, the greatest possible impact on hydrogen generation and resulting flammability would be an increase in rhodium and formate due to the addition of sludge solids returns to Tank 51. This flammability assessment examines the bounding case where the  $\leq 20$  kg of sludge solids returns are assumed to be added as 20 kg of formic acid and 20 kg of rhodium metal, totaling 40 kg of waste in the hypothetical case.

### 2.2 Glass Quality and Processability Assessment

The expected compositions of glass produced during SB 10 operations are well known based on previous evaluations of projections of the calcined solids in SB 10 Tank 51 batch waste, SB 9 Tank 40 heel waste, waste streams from Salt Waste Processing Facility (SWPF) processing, and glass frit added during CPC operations.<sup>4-6</sup> Less than or equal to 20 kg of sludge solids returns will be added to Tank 51 SB 10 waste, which suggests that impact of sludge solids returns on DWPF glass composition is limited by the potential changes in the calcined solids of SB 10 Tank 40 blended waste due to the addition of these solids to SB 10 Tank 51 waste. This assessment examines multiple bounding cases where 20 kg of sludge solids returns are added as pure metals and the change in SB 10 Tank 40 blended waste calcined solids is calculated.

### 2.3 Quality Assurance

This document pertains to the impacts of sludge solids returns on hydrogen flammability and glass composition during SB 10 processing at the DWPF. Per X-TTR-S-00076, Rev. 2, data and conclusions applicable to these parameters are subject to a functional classification of Safety Class.<sup>7</sup> Per E7, 3.60,<sup>8</sup> a technical report supporting Safety Class functional classification must, at a minimum, be subjected to a technical review by Design Verification as specified in E7, 2.60.<sup>9</sup> This document and the calculations described herein have been subjected to a Design Verification by Document Review. The signatures of

technical reviewers at the beginning of this document indicate the completion of the Design Verification by Document Review.

SRNL documents the Design Verification using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2.<sup>10</sup> The Design Checklists for this report are stored in the Electronic Laboratory Notebook experiment L7748-00442-03.

### 3.0 Results and Discussion

#### 3.1 Assessment of CPC Flammability

Recent testing performed to support SB 10 flowsheet development indicated that hydrogen generation during CPC operations is expected to be below  $6.04 \times 10^{-4} \text{ lb h}^{-1}$ .<sup>1</sup> The proposed hydrogen generation limit for CPC processing under the nitric-glycolic flowsheet is  $2.4 \times 10^{-2} \text{ lb h}^{-1}$ ,<sup>7</sup> indicating that hydrogen generation can increase by a factor of ~40 before challenging operations at the DWPF. Hydrogen generation during CPC operations is believed to occur via the noble metal (Rh, Ru, Pd) catalyzed dehydrogenation of formic acid.<sup>3</sup> Of these noble metals, rhodium is believed to be the most reactive toward the generation of hydrogen gas. Therefore, it is reasonable to assume that the hydrogen generation reaction rate expression takes the form of a second order equation, given in Equation [1].

$$r = k [Rh] [HCO_2H] \quad [1]$$

where,

- $r$  is the reaction rate of hydrogen formation in  $\text{lb h}^{-1}$ ,
- $k$  is the reaction rate constant in  $\text{lb L}^2 \text{ mol}^{-2} \text{ h}^{-1}$ ,
- $[Rh]$  is the concentration of rhodium in  $\text{mol L}^{-1}$ , and
- $[HCO_2H]$  is the concentration of formate in  $\text{mol L}^{-1}$ .

Given that this reaction is expected to be the dominant source of hydrogen generation in the CPC, it is reasonable to assume that a bounding evaluation of the impact of sludge solids to Tank 51 on CPC flammability would include the scenario where all  $\leq 20 \text{ kg}$  of proposed solids are added as formic acid and rhodium. To this end, an evaluation was performed in which the concentrations of rhodium and formate in SB 10 CPC processing were increased proportional to the theoretical addition of 20 kg of rhodium and 20 kg of formic acid to Tank 51 before SB 10 transfer to Tank 40. This represents a gross excess of what is physically possible and is therefore considered a bounding case.

Projections provided by SRR indicate that 407552.6 kg of total solids will be present at the end of Tank 51 SB 10 washing.<sup>11</sup> The same projections estimate that the rhodium concentration within these solids is 0.0069 wt%. These values suggest that 28.1 kg of rhodium will be present in Tank 51 at the end of SB 10 washing. Projections suggest that 95% of Tank 51 solids will be transferred to Tank 40, which is projected to have a heel containing 90969 kg of total solids at a rhodium concentration of 0.0124 wt% of total solids. This indicates a final rhodium mass of ~38.0 kg in SB 10 Tank 40, 70.3% of which is expected to come from Tank 51. The addition of 20 kg of rhodium to Tank 51 before the transfer to Tank 40 would increase this final Tank 40 mass to 57.0 kg. This suggests a potential increase of 1.5x in the final concentration of rhodium in Tank 40 SB 10 sludge (assuming that all sludge returns sent to Tank 51 are pure rhodium metal).

Formate is not believed to be present in SB 9 or SB 10 waste in measurable amounts.<sup>11-12</sup> However, formate is expected to be present during CPC operations at measurable amounts due to the degradation of glycolate.<sup>13</sup> Recent testing reported Slurry Mix Evaporator (SME) product formate concentrations between 212 and 1240  $\text{mg kg}^{-1}$ .<sup>1</sup> Assuming that the 20 kg of sludge returns is added to Tank 51 as pure formic acid,

the increase in formate concentration during SME processing (the regime responsible for the highest H<sub>2</sub> generation during SB 10 processing) is limited to 7.3 mg kg<sup>-1</sup>. This represents an increase of 1.03x in the final concentration of formate relevant to hydrogen production.

Note that ~1.7 kg of aluminum will be added along with the ≤20 kg of anticipated sludge returns in the form of aluminum canisters containing the waste material.<sup>14</sup> Given that aluminum is 1) likely to be removed via sludge batch washing and 2) not involved in the catalytic dehydrogenation of formic acid in the DWPF, this additional mass of aluminum cannot be reasonably expected to increase hydrogen production in the DWPF.

Given that the maximum potential increase in rhodium is a factor of 1.5 and the maximum potential increase in formate is a factor of 1.03, the highest potential increase in catalytic hydrogen generation due to ≤20 kg of sludge returns to Tank 51 is expected to be limited to ~1.545. This is significantly less than the factor of 39.7 difference between the proposed H<sub>2</sub> limit in the DWPF and the highest H<sub>2</sub> observed during SB 10 testing. Therefore, it is reasonable to conclude that the addition of ≤20 kg of sludge to Tank 51 will not challenge the flammability controls within the DWPF during SB 10 operations.

### 3.2 Assessment of Glass Quality and Processability

In order to assess the impact of sludge solids returns addition to Tank 51 on DWPF glass compositions, the changes in Tank 51 calcined solids composition need to be understood. The projected composition of Tank 51 calcined solids at the end of Tank 51 washing is given in Table 3-1.<sup>11</sup> Additionally, the SB 10 Tank 51-Tank 40 transfer and the SB 9 Tank 40 heel masses and compositions are given for comparison.

**Table 3-1. Calcined Solids Profiles and Masses for SB 10 Tank 51 Batch and SB 9 Tank 40 Heel Wastes.**

Parameter	Tank 51 (SB 10 Batch)	Tank 51 (SB 10 Transfer)	Tank 40 (SB 9 Heel)
Calcined Solids (kg)	279,640	265,517	64,415
Al (wt%)	17.53		8.52
B	<0.01		0.04
Ba	0.06		0.10
Ca	0.74		1.40
Ce	0.12		0.30
Cr	0.22		0.11
Cu	0.05		0.04
Fe	11.91		21.46
K	0.08		0.13
La	0.03		0.05
Li	0.02		0.05
Mg	0.29		0.29
Mn	3.72		6.98
Na	24.44		20.53
Ni	0.38		1.42
Pb	0.02		0.05
S	0.54		0.58
Si	0.59		1.69
Th	2.42		1.09
Ti	0.02		0.03
U	3.08		3.95
Zn	0.02		0.04
Zr	0.16		0.04

The most conservative estimate that can be made is to assume that all 20 kg of sludge returns are added as a single metal (e.g., Al, B, etc.) or sulfur. The potential calcined compositions due to the addition of 20 kg of each possible element is given in Table 3-2. The projected sludge-only Tank 40 composition with no sludge solids returns is also provided for reference.<sup>11</sup>

**Table 3-2. Tank 40 Blend Calcined Solids Compositions of Possible Sludge Solids Returns Scenarios.**

Element Added	None	Al	B	Ba	Ca	Ce	Cr	Cu	Fe	K	La	Li	Mg
Calcined Species	None	Al <sub>2</sub> O <sub>3</sub>	B <sub>2</sub> O <sub>3</sub>	BaO	CaO	Ce <sub>2</sub> O <sub>3</sub>	Cr <sub>2</sub> O <sub>3</sub>	CuO	Fe <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O	La <sub>2</sub> O <sub>3</sub>	Li <sub>2</sub> O	MgO
Element Added (kg)	0	20	20	20	20	20	20	20	20	20	20	20	20
Calcined Mass Added (kg)	0	37.8	94.0	22.3	28.0	23.4	29.2	25.0	28.6	24.1	23.5	43.1	33.2
Al, wt%	15.77	15.78	15.77	15.77	15.77	15.77	15.77	15.77	15.77	15.77	15.77	15.77	15.77
B	0.01	0.01	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Ba	0.07	0.07	0.07	0.08	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07
Ca	0.87	0.87	0.87	0.87	0.88	0.87	0.87	0.87	0.87	0.87	0.87	0.87	0.87
Ce	0.16	0.16	0.16	0.16	0.16	0.17	0.16	0.16	0.16	0.16	0.16	0.16	0.16
Cr	0.20	0.20	0.20	0.20	0.20	0.20	0.21	0.20	0.20	0.20	0.20	0.20	0.20
Cu	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Fe	13.77	13.77	13.77	13.77	13.77	13.77	13.77	13.77	13.78	13.77	13.77	13.77	13.77
K	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.10	0.09	0.09	0.09
La	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04
Li	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.03	0.02
Mg	0.29	0.29	0.29	0.29	0.29	0.29	0.29	0.29	0.29	0.29	0.29	0.29	0.30
Mn	4.36	4.36	4.36	4.36	4.36	4.36	4.36	4.36	4.36	4.36	4.36	4.36	4.36
Na	23.68	23.67	23.67	23.67	23.67	23.67	23.67	23.67	23.67	23.67	23.67	23.67	23.67
Ni	0.59	0.59	0.59	0.59	0.59	0.59	0.59	0.59	0.59	0.59	0.59	0.59	0.59
Pb	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03
S	0.55	0.55	0.55	0.55	0.55	0.55	0.55	0.55	0.55	0.55	0.55	0.55	0.55
Si	0.81	0.81	0.81	0.81	0.81	0.81	0.81	0.81	0.81	0.81	0.81	0.81	0.81
Th	2.16	2.16	2.16	2.16	2.16	2.16	2.16	2.16	2.16	2.16	2.16	2.16	2.16
Ti	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02
U	3.25	3.25	3.25	3.25	3.25	3.25	3.25	3.25	3.25	3.25	3.25	3.25	3.25
Zn	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03
Zr	0.14	0.14	0.14	0.14	0.14	0.14	0.14	0.14	0.14	0.14	0.14	0.14	0.14

**Table 3-2. Tank 40 Blend Calcined Solids Compositions of Possible Sludge Solids Returns Scenarios (Continued).**

Element Added	None	Mn	Na	Ni	Pb	S	Si	Th	Ti	U	Zn	Zr
Calcined Species	None	MnO	Na <sub>2</sub> O	NiO	PbO	SO <sub>4</sub> <sup>2-</sup>	SiO <sub>2</sub>	ThO <sub>2</sub>	TiO <sub>2</sub>	U <sub>3</sub> O <sub>8</sub>	ZnO	ZrO <sub>2</sub>
Element Added (kg)	0	20	20	20	20	20	20	20	20	20	20	20
Calcined Mass Added (kg)	0	25.8	27.0	25.5	6.9	59.9	42.8	22.8	33.4	23.6	24.9	27.0
Al, wt%	15.77	15.77	15.77	15.77	15.77	15.77	15.77	15.77	15.77	15.77	15.77	15.77
B	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Ba	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07
Ca	0.87	0.87	0.87	0.87	0.87	0.87	0.87	0.87	0.87	0.87	0.87	0.87
Ce	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16
Cr	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20
Cu	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Fe	13.77	13.77	13.77	13.77	13.77	13.77	13.77	13.77	13.77	13.77	13.77	13.77
K	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09
La	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04
Li	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02
Mg	0.29	0.29	0.29	0.29	0.29	0.29	0.29	0.29	0.29	0.29	0.29	0.29
Mn	4.36	4.36	4.36	4.36	4.36	4.36	4.36	4.36	4.36	4.36	4.36	4.36
Na	23.68	23.67	23.68	23.67	23.68	23.67	23.67	23.67	23.67	23.67	23.67	23.67
Ni	0.59	0.59	0.59	0.59	0.59	0.59	0.59	0.59	0.59	0.59	0.59	0.59
Pb	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03
S	0.55	0.55	0.55	0.55	0.55	0.55	0.55	0.55	0.55	0.55	0.55	0.55
Si	0.81	0.81	0.81	0.81	0.81	0.81	0.81	0.81	0.81	0.81	0.81	0.81
Th	2.16	2.16	2.16	2.16	2.16	2.16	2.16	2.17	2.16	2.16	2.16	2.16
Ti	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02
U	3.25	3.25	3.25	3.25	3.25	3.25	3.25	3.25	3.25	3.25	3.25	3.25
Zn	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03
Zr	0.14	0.14	0.14	0.14	0.14	0.14	0.14	0.14	0.14	0.14	0.14	0.14



The data in Table 3-2 indicate that compositional changes in Tank 40 SB 10 blend due to the addition of 20 kg of any species has an undetectable impact on calcined concentrations, limited to a difference of  $\leq 0.01$  wt% (e.g., the concentration of Al is increased from 15.77 to 15.78 wt%). These Tank 40 blend compositions are within the composition region that has already been evaluated for SB 10 using the DWPF Product Composition Control System (PCCS) models and their associated Measurement Acceptance Region (MAR) constraints.<sup>4</sup> Thus, the addition of sludge solids to Tank 51 before the SB 10 transfer to Tank 40 will have no further impact on glass quality and processability beyond the SB 10 assessment. Note that the addition of  $\sim 1.7$  kg of aluminum (as containers for the sludge return waste) is adequately captured by the 20 kg assumption made above because the sludge returns cannot reasonably be expected to contribute more than 18.3 kg of aluminum metal in  $\leq 20$  kg of sludge return waste.

## 4.0 Conclusions

SRNL is currently preparing to return  $\leq 20$  kgs of sludge solids collected over time from Tank Farm characterization activities and demonstrations of the DWPF flowsheets (nitric-formic and nitric-glycolic). These sludge solids will be transported and added to Tank 51 which is currently preparing SB 10. DWPF plans to operate the under the nitric-glycolic flowsheet for the processing of SB10. The hydrogen generation rate for the nitric-glycolic flowsheet is  $0.024 \text{ lb h}^{-1}$ . The addition of  $\leq 20$  kg of sludge solids returns to SB 10 does not have an impact on flammability in the DWPF CPC or glass quality and processability. The relatively low mass of the addition ( $\leq 20$  kg) is insufficient to detect a significant analytical change to the expected SB 10 compositions. The following bounding assumptions are employed in this assessment:

### *General Bounding Assumptions*

- A range of 20 kg to 40 kg of returns are assumed to be added to Tank 51. The actual amount of returns is expected to be lower than 20 kg and partially composed of non-reactive water (which will be dried).
- 20 kg of returns are assumed to be added to Tank 51 at the conclusion of SB 10 washing. If the returns are added prior to the completion of washing, many components are expected to be washed away, further diluting the impact of sludge solids.

### *CPC Flammability Bounding Assumptions*

- 20 kg of returns are assumed to be added as rhodium metal when the composition is comprised of various cations. The actual composition of returns is expected to have a rhodium concentration much less than 0.1 wt%.
- 20 kg of returns are assumed to be added as formic acid when the composition is comprised of various cations and anions. The actual composition of returns is expected to have a minor formate concentration.
- The full mass of sludge returns (planned 20 kg) is increased to 40 kg. The 40 kg is divided equally between rhodium and formate.
- The most active components in catalytic hydrogen production (rhodium and formate) have been selected for this assessment, thus assessing the impact of individual anions (hydroxide, carbonate, nitrate, nitrite, and oxalate) outside of formate is ignored.
- The full mass of sludge returns is assumed to contribute to the rhodium-catalyzed formate dehydrogenation mechanism. In reality, a fraction of the returns would contribute to the less-reactive ruthenium- and palladium-catalyzed reactions.
- The mass of aluminum containers ( $\sim 1.7$  kg) is negligible because aluminum is not involved in the catalytic dehydrogenation of formic acid.

*Glass Quality and Processability Bounding Assumptions*

- 20 kg of returns are assumed to be added as pure metals (one type of metal for each addition scenario for all metals except aluminum). The actual returns are expected to be a blend of many metal compounds.
- The amount of aluminum metal in the sludge returns is assumed to be less than 18.3 kg, yielding a total of 20 kg of aluminum when combined with the ~1.7 kg of aluminum present in the waste containers.

The following conclusions are made as a result of this work:

- The addition of  $\leq 20$  kg of waste from SRNL can be made to Tank 51 prior to the Tank 51 to Tank 40 SB 10 transfer without risk to flammability of CPC vessels, glass quality, and glass processability.
- Future additions to sludge batches should be assessed to demonstrate compliance with the flammability limits in the CPC. These assessments may reflect the evaluation performed in this document or employ an alternative methodology, if necessary.
  - The evaluation performed in this document utilizes several overly conservative assumptions. Future assessments may ease these assumptions as necessary (e.g., purity and composition of 20 kg sludge returns).
- The glass qualification process is robust enough to avoid perturbation by the addition of  $\leq 20$  kg:
  - In cases where a sludge batch has not been qualified, any potential offset to calcined composition will be assessed as a part of the sludge batch qualification process.
  - In cases where a sludge batch has been partially or fully qualified, 20 kg additions are insufficient to change calcined compositions from compositions previously evaluated with PCCS MAR assessments.

**5.0 Recommendations**

It is recommended that any existing lines of inquiry regarding the impact of the addition of 20 kg of sludge solids returns to SB 10 Tank 51 on Waste Acceptance Criteria such as the flammability of CPC vessels or glass quality and glass processability during SB 10 processing be closed with the understanding that potential impacts have been assessed and are well within existing facility constraints.

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