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Preliminary Evaluation of DWPF Impacts of Boric Acid Use in Cesium Strip for SWPF and MCU

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EXECUTIVE SUMMARY

A new solvent system is being evaluated for use in the Modular Caustic-Side Solvent Extraction Unit (MCU) and in the Salt Waste Processing Facility (SWPF). The new system includes the option to replace the current dilute nitric acid strip solution with boric acid. To support this effort, the impact of using 0.01M, 0.1M, 0.25M and 0.5M boric acid in place of 0.001M nitric acid was evaluated for impacts on the DWPF facility. The evaluation only covered the impacts of boric acid in the strip effluent and does not address the other changes in solvents (i.e., the new extractant, called MaxCalix, or the new suppressor, guanidine).

Boric acid additions may lead to increased hydrogen generation during the SRAT and SME cycles as well as change the rheological properties of the feed. The boron in the strip effluent will impact glass composition and could require each SME batch to be trimmed with boric acid to account for any changes in the boron from strip effluent additions. Addition of boron with the strip effluent will require changes in the frit composition and could lead to changes in melt behavior. The severity of the impacts from the boric acid additions is dependent on the amount of boric acid added by the strip effluent. The use of 0.1M or higher concentrations of boric acid in the strip effluent was found to significantly impact DWPF operations while the impact of 0.01M boric acid is expected to be relatively minor.

Experimental testing is required to resolve the issues identified during the preliminary evaluation. The issues to be addressed by the testing are:

1. Impact on SRAT acid addition and hydrogen generation
2. Impact on melter feed rheology
3. Impact on glass composition control
4. Impact on frit production
5. Impact on melter offgas

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LIST OF ABBREVIATIONS

ARP	Actinide Removal Project
CPC	Chemical Process Cell
DWPF	Defense Waste Processing Facility
GPM	gallons per minute
MCU	Modular Caustic-Side Solvent Extraction Unit
MST	monosodium titanate
REDOX	REDuction/Oxidation potential
SE	Strip Effluent
SME	Slurry Mix Evaporator
SRAT	Sludge Receipt and Adjustment Tank
SRNL	Savannah River National Laboratory
SWPF	Salt Waste Processing Facility

1.0 Introduction

A new solvent system is being evaluated for use in the Modular Caustic-Side Solvent Extraction Unit (MCU) and in the Salt Waste Processing Facility (SWPF). The new system includes the option to replace the current dilute nitric acid strip solution with boric acid. To support this effort, the impact of using 0.01M, 0.1M, 0.25M and 0.5M boric acid in place of 0.001M nitric acid was evaluated for impacts on the DWPF facility. The evaluation only covered the impacts of boric acid in the strip effluent and does not address the other changes in solvents (i.e., the new extractant, called MaxCalix, or the new suppressor, guanidine). Experimental testing with the improved solvent is required to determine the impact of any changes in the entrained solvent on DWPF processing.

2.0 Experimental Procedure

N/A

3.0 Results and Discussion

The evaluation was performed assuming the nominal amount of strip effluent from MCU operation is 520 gallons per 27 hours (based on MCU operation at 6 GPM) and a maximum case of 520 gallons per 13 hours[1]. SWPF was assumed to have a nominal processing rate of 0.8 GPM of strip effluent and a maximum rate of 1.6 GPM; both cases assumed 75% attainment[2]. A minimum of 40 SRAT batches per year and a nominal of 73 batches per year were used for the evaluation. Table 1 shows the expected amounts of strip effluent for each processing condition.

Table 1. Strip Effluent Processing Volumes per SRAT Batch (Gallons / Liters)

Case	MCU-Nominal	MCU – Max	SWPF – Nominal	SWPF – Max
40 SRAT cycles per year	3,200 / 12,000	6,300 / 24,000	8,000 / 30,000	16,000 / 60,000
73 SRAT Cycles per year	1,750 / 6,500	3,500 / 13,000	4,300 / 16,000	8,600 / 33,000

The assumptions made for a typical SRAT batch are shown in Table 2 and Table 3. These parameters were based on typical processing. Inclusion of monosodium titanate (MST) from salt processing would increase the amounts of SRAT oxides in a batch, but not enough to significantly impact the conclusions in this preliminary study.

Table 2. Assumptions of Nominal CPC Batch for SWPF Evaluations

Amount of SRAT product transferred to SME per batch	4,500	gallons
Amount of SRAT product transferred to SME per batch	17,033	liters
SRAT Product Density	1.25	Kg/L
SRAT Nitric Acid Amount	50	gallons
SRAT Formic Acid Amount	350	gallons
Nitric Acid Concentration	10	Molar
Formic Acid Concentration	23.6	Molar
SRAT Product Calcine Solids	0.15	g oxide/g sludge
Waste Loading	42	%
Frit Boron Oxide Concentration	8	Wt%

Table 3. Calculated Nominal CPC Batch Parameters

Amount of SRAT product transferred per batch	21,291	Kg
SRAT Nitric Acid Amount	1,893	Moles
SRAT Formic Acid Amount	31,264	Moles
Total Acid Amount	33,157	Moles
Amount of SRAT product oxides	3,194	Kg sludge oxide
Amount of Glass Produced	7,604	Kg glass
Frit Added to SME cycle	4,410	Kg frit
Frit Added to SME cycle	9,702	lb frit
Boron Oxide in Frit	353	Kg B2O3 in frit
Boron in Frit	109	Kg B

The impacts to DWPF assuming 0.01M boric acid in the strip effluent are relatively minor as shown in Table 4. The maximum amount of boron from this scenario represents less than 7% of the boron contained in the process frit assuming 8 wt% boron oxide in the frit and 42% waste loading even when processing extremely high volumes of strip effluent. The amount of additional acid does not exceed 2.5% of the acid added during a typical SRAT cycle.

As the boric acid concentration is increased as shown in Table 5, Table 6, and Table 7, the amounts of boron added are not minor and significant impacts could be noted. The boron from the strip effluent could account for up to 76% of the boron currently added by the frit at 0.1M and greater than 100% at higher boric acid concentrations. The additional acid added to the system could account for 21% of the acid added during the SRAT cycle at 0.1M and would be correspondingly higher as boric acid concentration is increased. Several impacts from these levels of additional acid and boron in the system should be evaluated with experimental testing prior to implementation of the new solvent at ARP-MCU/SWPF.

Acid is added during the SRAT cycle to reduce mercury, control melter REDOX, and control melter feed rheology. Boric acid is a very weak acid and cannot be used to perform all the functions of the current acid addition. Therefore, the boric acid in the strip effluent would likely not replace the current acid additions in the SRAT cycle. Flowsheet testing is necessary to determine if the addition of boric acid leads to higher hydrogen emissions and if the boric acid must be counted in the acid addition calculation.

The melter feed rheology is targeted to be thick enough to allow frit to remain suspended in the slurry during processing, but not too thick to be pumpable. The pH buffering expected from the boric acid would impact rheological properties of the melter feed as would the change in the solids concentrations from replacement of a frit component with a batch chemical. Experimental testing is necessary to evaluate the changes in melter feed rheology caused by the boric acid addition.

The amount of boron added could significantly change the glass composition; however the boron could be removed from the frit to account for the boron from the strip effluent. The amount of boron removed would have to accommodate the maximum expected amount of boron to be received in the strip effluent. Since the maximum amount of strip effluent would not likely be used for each batch, each batch would likely require a trim addition (presumably boric acid) to achieve a constant glass composition. Although the tanks and transfer lines are in place to perform this trim, they have been placed out-of-service and are not covered by the current facility baseline for safety documentation.

The removal of boron from the frit would make it more refractory and increase the temperature required during frit production. The increased temperature requirements could increase the price of the frit or reduce the number of vendors that can prepare the frit.

The boric acid will generate additional offgas in the melter from water emitted as the boric acid is converted to boron oxide and the melting characteristics of the batch will be different. In addition, boron volatility could be increased. Tests are required to determine if the melt rate of the process would be negatively impacted and to determine the magnitude of boron volatility.

Table 4. Calculations for 0.01M Boric Acid

Strip Effluent Added per SRAT Batch	5,000	10,000	15,000	20,000	25,000	30,000	40,000	50,000	60,000	70,000	liters
Strip Effluent Added per SRAT Batch	1321	2642	3963	5284	6605	7926	10568	13210	15852	18494	gallons
Amount of Boron in Strip Effluent	50	100	150	200	250	300	400	500	600	700	moles
Amount of Boron in Strip Effluent	1	1	2	2	3	3	4	5	6	8	kg
Percentage of Boron in frit contained in SE	0.5	1.0	1.5	2.0	2.5	3.0	3.9	4.9	5.9	6.9	%
Percentage of Acid Added to SRAT in SE	0.2	0.3	0.5	0.6	0.8	0.9	1.2	1.5	1.8	2.1	%

Table 5. Calculations for 0.1M Boric Acid

Strip Effluent Added per SRAT Batch	5,000	10,000	15,000	20,000	25,000	30,000	40,000	50,000	60,000	70,000	liters
Strip Effluent Added per SRAT Batch	1321	2642	3963	5284	6605	7926	10568	13210	15852	18494	gallons
Amount of Boron in Strip Effluent	500	1000	1500	2000	2500	3000	4000	5000	6000	7000	moles
Amount of Boron in Strip Effluent	5	11	16	22	27	32	43	54	65	76	kg
Percentage of Boron in frit contained in SE	4.9	9.9	14.8	19.7	24.7	29.6	39.5	49.3	59.2	69.0	%
Percentage of Acid Added to SRAT in SE	1.5	3.0	4.5	6.0	7.5	9.0	12.1	15.1	18.1	21.1	%

Table 6. Calculations for 0.25M Boric Acid

Strip Effluent Added per SRAT Batch	5,000	10,000	15,000	20,000	25,000	30,000	40,000	50,000	60,000	70,000	liters
Strip Effluent Added per SRAT Batch	1321	2642	3963	5284	6605	7926	10568	13210	15852	18494	gallons
Amount of Boron in Strip Effluent	1250	2500	3750	5000	6250	7500	10000	12500	15000	17500	moles
Amount of Boron in Strip Effluent	14	27	41	54	68	81	108	135	162	189	kg
Percentage of Boron in frit contained in SE	12.3	24.7	37.0	49.3	61.6	74.0	98.6	123.3	148.0	172.6	%
Percentage of Acid Added to SRAT in SE	3.8	7.5	11.3	15.1	18.8	22.6	30.2	37.7	45.2	52.8	%

Table 7. Calculations for 0.5M Boric Acid

Strip Effluent Added per SRAT Batch	5,000	10,000	15,000	20,000	25,000	30,000	40,000	50,000	60,000	70,000	liters
Strip Effluent Added per SRAT Batch	1321	2642	3963	5284	6605	7926	10568	13210	15852	18494	gallons
Amount of Boron in Strip Effluent	2500	5000	7500	10000	12500	15000	20000	25000	30000	35000	moles
Amount of Boron in Strip Effluent	27	54	81	108	135	162	216	270	324	378	kg
Percentage of Boron in frit contained in SE	24.7	49.3	74.0	98.6	123.3	148.0	197.3	246.6	295.9	345.2	%
Percentage of Acid Added to SRAT in SE	7.5	15.1	22.6	30.2	37.7	45.2	60.3	75.4	90.5	105.6	%

4.0 Conclusions

The use of boric acid in the strip effluent is expected to have minor impacts to DWPF at 0.01M and significantly impact DWPF operations at 0.1M or higher concentrations. Experimental testing is required to resolve the issues identified during the preliminary evaluation. The issues to be addressed by the testing are:

1. Impact on SRAT acid addition
2. Impact on melter feed rheology
3. Impact on glass composition control
4. Impact on frit production
5. Impact on melter offgas

5.0 Recommendations, Path Forward or Future Work

The following experimental work is recommended to further evaluate the impact of boric acid on the DWPF. Experimental testing for evaluation of the changes in solvent is also shown.

1. *CPC flowsheet demonstration*
   Description - Simulant testing using the current DWPF flowsheet and operating parameters shall be performed with associated by-product stream from MCU. The stream shall contain the new solvent and strip acid at the anticipated (or bounding) concentrations. The analyses typically included for flowsheet testing shall be performed; however, particular attention shall be placed upon changes in off-gas generation (specifically, the effect of boric acid on hydrogen generation), the effect of boric acid additions (from strip effluent and from bulk additions) on melter feed rheology and mercury removal. In addition, the testing will evaluate the partitioning of the new solvents in the CPC process and the amounts of organic residue accumulation in offgas components.

2. *Solvent stability*
   Description - Tests shall be performed to investigate the stability of the solvent in DWPF radiolytic and chemical conditions. Specifically, solvent shall be exposed to nitric acid and formic acid at a bounding pH for SRAT operation to determine what by-products, if any, are formed from the new solvent. Similarly, the new solvent shall be exposed to a radiation field (similar to that expected from DWPF processing of SWPF material) to determine stability to radiation.

3. *Glass formulation studies*
   Description - Paper studies shall be performed to determine the impact of changes in the strip effluent stream to DWPF glass formulation. Included in this study shall be an evaluation of the practicality of boron-free frit.

4. *Melt rate testing*
   Description - Testing shall be performed to determine the impact of a more refractory frit (due to removal of boron) on melting characteristics. The testing will evaluate impacts to melt rate and amount of boron volatility. The testing should be performed assuming a bounding case for the amount of boron added by the strip effluent as well as a nominal case.

6.0 References

1. Fink, S.D.,“Evaluation of NG-CSSX Solvent Impacts on DWPF”,e-mail dated 6-8-2010.
2. Fellinger, T. L., phone conversation, 7-13-2010.

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