Contract No:

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Anion Analysis of Sludge Batch 10 with Sodium Reactor Experiment Material Solubility Test Slurries

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REVIEWS AND APPROVALS

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C.J. Martino, Chemical Flowsheet Development Date

TECHNICAL REVIEW:

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M.S. Williams, Chemical Flowsheet Development, Reviewed per E7 2.60 Date

APPROVAL:

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F.M. Pennebaker, Customer Manager, Chemical Processing Sciences Date

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S.D. Fink, Director, Chemical Processing Sciences Date

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T.H. Huff, Manager, DWPF/Saltstone Facility Engineering Date

EXECUTIVE SUMMARY

Anion concentrations are reported for the product slurries from the solubility testing of Sludge Batch 10 material with added Sodium Reactor Experiment material. A mass balance was performed to show the gain and loss of nitrite, nitrate, glycolate, and oxalate during solubility testing.

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LIST OF ABBREVIATIONS

DWPF	Defense Waste Processing Facility
IC	Ion Chromatography
KMA	Koopman Minimum Acid
NCSE	Nuclear Criticality Safety Evaluation
RSD	relative standard deviation
SB10	Sludge Batch 10
SRE	Sodium Reactor Experiment
SRNL	Savannah River National Laboratory
TIC	Total Inorganic Carbon

1.0 Introduction

To support the Defense Waste Processing Facility (DWPF) Nuclear Criticality Safety Evaluation (NCSE), the Savannah River National Laboratory (SRNL) performed a series of solubility tests on the Sludge Batch 10 (SB10) Tank 51 sample with added Sodium Reactor Experiment (SRE) material.[1-3] During the solubility testing, three tests with different nitric and glycolic acid additions were performed and samples were heated to 95 °C for 10 hours.[1]

Invoking a clause in the Technical Task Request,[2] Savannah River Remediation (SRR) requested by email that anion analysis be performed for the three product slurries from the solubility testing. The email request is contained in the Appendix. This report details the anion results for the solubility testing product slurries and augments the information contained in the solubility test report.[1]

2.0 Experimental Procedure

Product slurry samples were prepared in triplicate with an approximately 55-times dilution (by volume) with deionized water. The anion analysis included Ion Chromatography (IC) for nitrate, nitrite, sulfate, glycolate, oxalate, formate, phosphate, chloride, fluoride, and bromide and Total Inorganic Carbon (TIC) analysis for carbonate. A caustic quench preparation was not performed.

2.1 Quality Assurance

The functional classification of this activity is Production Support (see the Appendix). Requirements for performing reviews of technical reports and the extent of review are established in manual E7 2.60.[4] SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2.[5]

3.0 Results and Discussion

Table 3-1 contains the analytical results for the three product slurry sample analyses, in mg/kg of slurry. Results for analytes that were below detectable levels are preceded by "<". The averages and relative standard deviations (RSD) of the three measurements are reported for each product slurry. The Hsu and Koopman Minimum Acid (KMA) acid addition stoichiometries and the measured pH are included for reference.[1] Other information and analyses for these slurries are contained in the solubility test report.[1] A portion of the carbonate analyses may be anomalous, especially a high outlier in the low acid product slurry (which was not included in the average) and the above detectable level in the high acid, low pH case where carbonate is not expected. It is recommended that these carbonate data are not used.

Mass balances were performed considering the components in the feed slurry, the added acids, and the product slurries. Table 3-2 contains information on the gain (positive) or loss (negative) of components during the three acid addition conditions during the solubility test. Nitrate, nitrite, glycolate, and oxalate, were the components that were observed to increase or decrease during testing. Sulfate and several elemental components are included in Table 3-2 to demonstrate the overall uncertainty in the mass balance for components that are not being created or destroyed during solubility testing. Carbonate could not be evaluated.

As expected, the nitrate and glycolate concentrations in the product slurries increased with increasing acid addition. At the low and moderate acid addition concentrations, partial nitrite decomposition was observed (approximately 11 and 35 percent nitrite decomposition, respectively). At the high acid addition concentration, nitrite was decomposed to less than 480 mg/kg (greater than 95% nitrite decomposition). Oxalate concentration also increased with increasing acid addition.

Table 3-1. Results for the Anion Analysis of SB10/SRE Solubility Test Slurries (mg/kg)

	SB10/SRE Feed		Low Acid		Moderate Acid		High Acid	
	Average	RSD	Average	RSD	Average	RSD	Average	RSD
Hsu	0%		70%		100%		140%	
KMA	0%		65%		92%		129%	
pH	>13 estimated		7.9		6.4		4.2	
NO_3^-	8.29E+03	2.3%	1.93E+04	2.0%	3.03E+04	1.3%	4.67E+04	1.7%
NO_2^-	1.14E+04	1.2%	9.60E+03	2.0%	6.87E+03	1.2%	< 4.8E+02	--
CO_3^{2-}	2.79E+03	1.1%	2.74E+03*	11%	< 2.4E+03	--	3.29E+03	4.0%
SO_4^{2-}	1.62E+03	0.9%	1.41E+03	1.2%	1.39E+03	1.3%	1.36E+03	0.7%
$C_2H_3O_3^-$	--	--	2.52E+04	1.6%	2.94E+04	5.5%	3.31E+04	1.2%
$C_2O_4^{2-}$	4.27E+02	1.4%	6.07E+02	8.0%	1.64E+03	1.9%	2.25E+03	1.9%
CHO_2^-	< 2.8E+02	--	< 5.0E+02	--	< 4.8E+02	--	< 4.8E+02	--
PO_4^{3-}	< 2.8E+02	--	< 5.0E+03	--	< 4.8E+03	--	< 4.8E+03	--
F^-	< 2.8E+02	--	< 5.0E+02	--	< 4.8E+02	--	< 4.8E+02	--
Cl^-	< 2.8E+02	--	< 5.0E+02	--	< 4.8E+02	--	< 4.8E+02	--
Br^-	< 1.4E+03	--	< 2.5E+03	--	< 2.4E+03	--	< 2.4E+03	--

* One carbonate measurement high outlier was excluded from this average

Table 3-2. Mass Balance for the Gain (positive) or Loss (negative) of Anions and Select Elements

Hsu Acid	70%	100%	140%
NO_3^-	0.35 mmol 5%	1.55 mmol 15%	3.96 mmol 30%
NO_2^-	-0.58 mmol -11%	-1.94 mmol -35%	<-4.85 mmol <-95%
$C_2H_3O_3^-$	0.04 mmol 0%	-0.52 mmol -5%	-1.47 mmol -13%
$C_2O_4^{2-}$	0.06 mmol 52%	0.34 mmol 314%	0.48 mmol 489%
SO_4^{2-}	-7%	-8%	-7%
Al	0%	-6%	-3%
Fe	3%	0%	2%
Mn	2%	0%	2%
Na	7%	6%	8%
U	1%	0%	1%

There are several general differences in the anion results and mass balance compared to flowsheet testing of the nitric-glycolic acid flowsheet.[6] These solubility tests exhibited lower levels of nitrite and glycolate decomposition and, of the quantity decomposed, larger fractions of nitrite conversion to nitrate and glycolate conversion to oxalate. Several differences exist between these smaller scale solubility tests and the larger scale flowsheet tests, including lower temperature, shorter duration, lack of non-condensable purge, and lack of steam stripping.

The differences in nitrite and oxalate concentrations are not expected to have a major influence on the solubility testing components of interest, which are primarily uranium and manganese. Two more important factors that were achieved during testing are expected to have a larger influence on the solubility test results. First, a wide pH range (4.2 to 7.9) was achieved to allow for various levels of partial dissolution of metals. Second, ample glycolic acid was present to provide the potential for metal complexes to form.

4.0 Conclusions

Anion concentrations are reported for the product slurries from the solubility testing of SB10 material with added SRE. A mass balance was performed to show the gain and loss of nitrite, nitrate, glycolate, and oxalate during solubility testing.

5.0 References

[1] Martino, C. J. and Coleman, C. J., "Solubility Testing to Support the Addition of Sodium Reactor Experiment Material to Sludge Batch 10", SRNL-STI-2020-00294, Revision 0, August 2020.

[2] Russell, K. J., "Delta Scope to Support SRE Addition to Sludge Batch 10", X-TTR-S-00079, Revision 1, August 18, 2020.

[3] Pareizs, J. M. and Martino, C. J., "Task Technical and Quality Assurance Plan for Sludge Batch 10 Sample Analysis and Qualification", SRNL-RP-2019-00658, Revision 1, May 4, 2020.

[4] Conduct of Engineering Technical Reviews, Manual E7, Procedure 2.60, Revision 18. Savannah River Site: Aiken, SC, 2019.

[5] "Savannah River National Laboratory Technical Report Design Check Guidelines", WSRC-IM-2002-00011, Revision 2, August 2004.

[6] Lambert, D. P.; Williams, M. S.; Brandenburg, C. H.; Luther, M. C.; Newell, J. D.; and Woodham, W. H., "Sludge Batch 9 Simulant Runs Using the Nitric-Glycolic Acid Flowsheet", SRNL-STI-2016-00319, Revision 0, November 2016.

Appendix A.

From: Kirk Russell
Sent: Thursday, August 20, 2020 9:14 AM
To: Chris Martino; Frank Pennebaker
Cc: Jeff Ray; Azadeh Samadi-Dezfouli; Terri Fellinger
Subject: X-TTR-S-00079 - Metals Solubility Testing - Anion Analysis

Chris,

SRR is invoking the e-mail clause statement that is included in X-TTR-S-00079, Rev.1. The e-mail clause allows for additions/deletions to be made to the TTR. DWPF Engineering has determined that there is a need for additional sample analysis based on the results of Task 1.

Using the products of Task 1 (if there is enough sample), perform an IC anion analysis (glycolate, nitrate, nitrite, fluoride, chloride, phosphate, oxalate, formate, and sulfate) and TIC analysis for each of the three acid stoichiometries studied (70%, 100%, and 140%).

The functional classification of the analysis requested in this email is Production Support.

Please place a copy of this electronic request in your laboratory notebook. If you have any questions, please let me know.

Thank you,
Kirk Russell

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