Background

Melter feed preparation at the Defense Waste Processing Facility (DWPF) includes pretreatment in the process flowsheet to:

- Destroy nitrite and carbonate by acidification
- Remove mercury by chemical reduction using formic acid and steam stripping
- Balance redox of glass melt to prevent foaming and metal precipitation
- Control rheology of melter feed

The Sludge Receipt Adjustment Tank (SRAT) process is used to:

- Acidify waste sludge with 10 M HNO_3, followed by 23 M HCOOH
- Dewater to reduce the final volume
- Reflux (> 30h) to remove mercury

The Slurry Mix Evaporator (SME) process is used to:

- Receive SRAT product
- Add glass frit as a dilute formic acid slurry (in 2 batches)
- Concentrate melter feed by boiling

Objectives

Reduce feed-preparation cycle times at DWPF to support higher glass production rates with improved waste loading

- Minimize the amount of formic acid to reduce hydrogen generation during SRAT, allowing increased boil-up rate
- Replace the balance of the formic acid with sugar to control glass melt redox
- Characterize the chemistry of the SRAT/SME process, provide component analysis and specify control parameters
- Perform small scale melter tests using melter feed prepared with alternate flowsheet to support flammability modeling
- Assess the feasibility of a sugar-nitric acid only flowsheet (no formic acid)

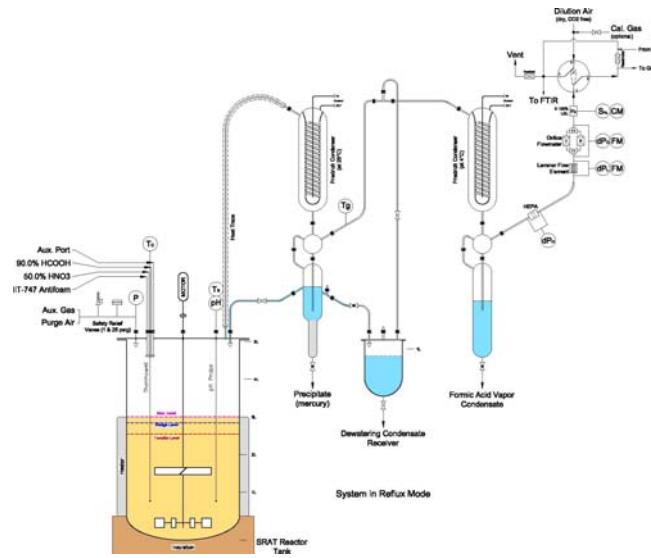

Figure 1. Schematic of Experimental Setup

Experimental

- Bench-scale equipment (≈ 1/10,000 scale) replicates functionally the process vessels found in DWPF SRAT/SME flowsheet
- Baseline run used current DWPF flowsheet and Sludge Batch 6 (SB6) simulant
- Trim chemicals included HgO, noble metals (Ag, Pd, Rh, and Ru) and RCRA metals (Ba, Cd, and Cr)

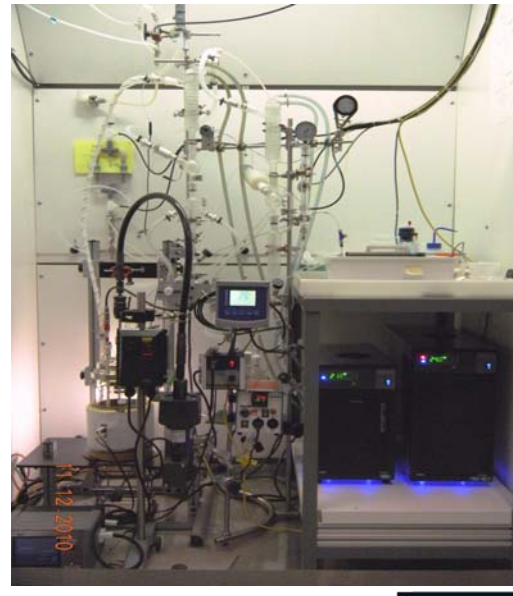

Figure 2. Photograph of Experim Setup

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Sugar-Based Alternate Reductant Flowsheet for DWPF

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Experimental (continued)

- Off-gases monitored with GC (H_2, N_2, and O_2) and FTIR (CO_2 and NO_x)
- Reduced formic-acid use studied (20% - 40% compared to DWPF baseline flowsheet)
- Both 2-cycle (nitric, formic) and 3-cycle (nitric, formic, nitric) acid additions investigated to reach final target pH of 3, 4, or 5; 3-cycle addition may minimize reactions between the 2 acids (denitration)
- Sugar solution added at the end of SME cycle
- Redox of glasses prepared from SME product characterized with Mössbauer spectroscopy

Results and Discussion

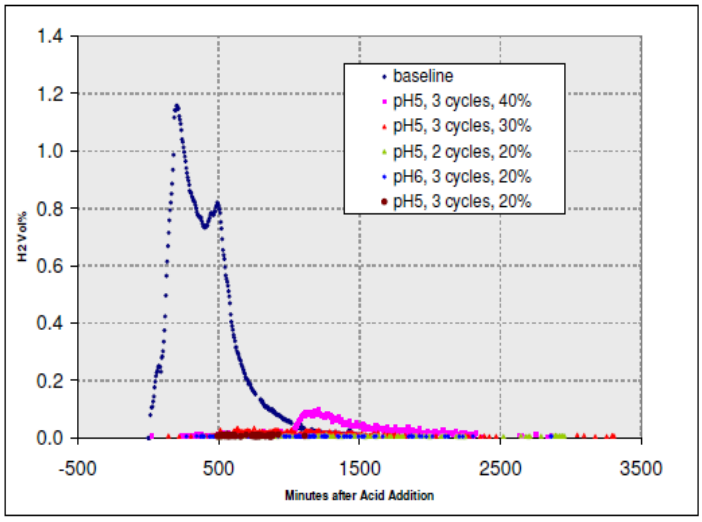
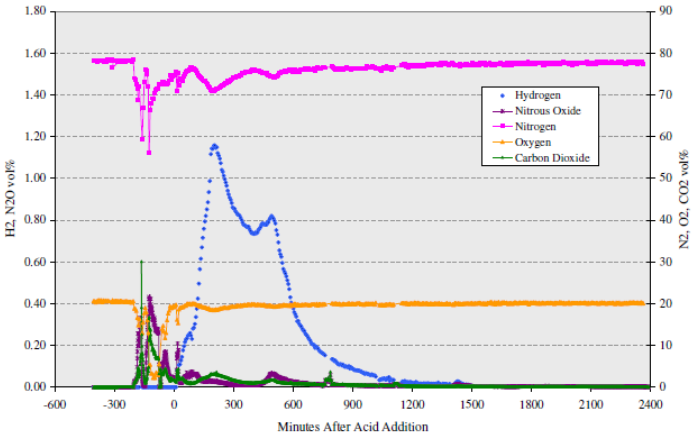


Figure 3. Hydrogen generation during SRAT/SME runs (H_2 not observed for pH 4 run or no-formic acid run)

- Significant reduction in hydrogen generation observed in all alternate runs (Figure 3) as compared to the baseline run
- Major off-gases included CO_2 and NO_x (Figure 4)
- Selected primary reactions:

$$HCOO^- + Hg^{2+} \rightarrow CO_2 + Hg + H^+$$
$$3HCOO^- + 2NO_3^- + H2O \rightarrow 3CO_2 + 2NO + 5OH^-$$
$$HCOO^- + 2NO_2^- + H2O \rightarrow CO_2 + 2NO + 3\ OH^-$$

- Amounts of mercury that remained un-stripped in selected runs comparable to baseline run (Table 1)



4. Off-gas composition during baseline run

Figure 5. Mercury metal recovered from SRAT cycle

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Mercury	SRAT Product	SME Product
Baseline Run	0.98%	0.25%
pH 5 Run (3 acid cycles, 20% HCOOH)	0.82%	0.39%
pH 4 Run (3 cycles, 20%)	2.11%	1.11%
pH 6 Run (3 cycles, 20%)	0.90%	0.30%
pH 5 Run (2 cycles, 20%)	0.68%	0.82%
pH 5 Run (3 cycles, 30%)	1.31%	0.50%
pH 5 Run (3 cycles, 40%)	1.14%	0.30%

Table 1. Mercury analytical data

- Based on nitrate/nitrite contents in feed, sugar added as a reductant to control redox at various ratios (Figure 6)

  $C_{12}H_{22}O_{11} + 8NaNO_3 \rightarrow 8CO_2 + 4CO + 4N_2 + 11H_2O + 4Na_2O$ (sugar ratio =1)
- Sugar ratio of ~ 0.9 is required to achieve a target redox of $Fe^{2+}/\Sigma Fe = 0.2$ (Figure 7)
- Rheology of SRAT and SME products characterized (Figure 8)
- pH 5 run (20% formic acid, 3 acid cycles) selected for melter testing

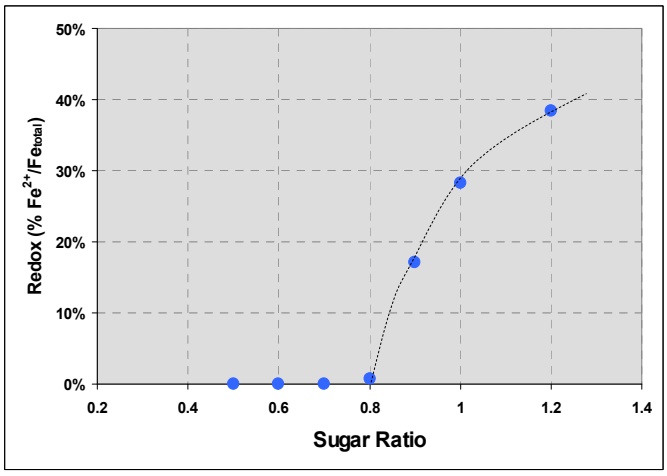

Figure 6. Variation of glass redox with sugar ratio

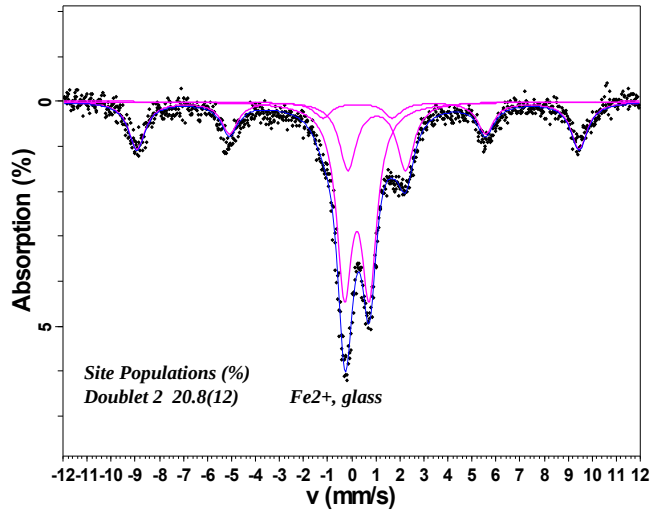

Figure 7. Mössbauer spectrum of product glass that meets the target redox state ($Fe^{2+}/\Sigma Fe = 20\%$) by sugar addition

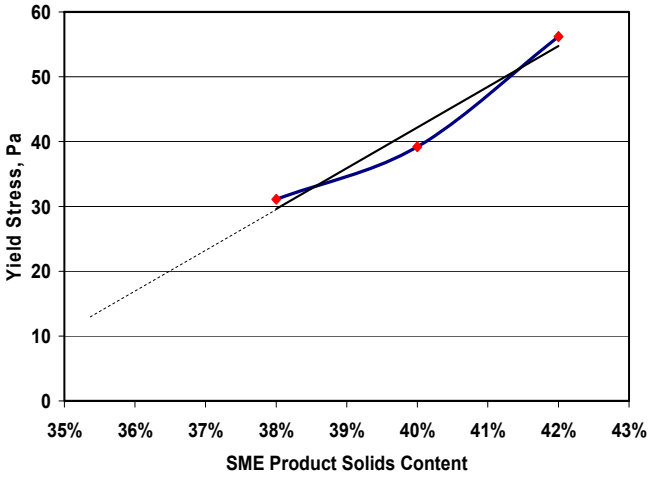

Figure 8. Effects of solids content on SME product yield stress

Summary

The main objectives of the project have been achieved:

- Demonstrated that the amount of formic acid needed to reduce mercury in the sludge can be decreased considerably
- Formic acid can be replaced with sugar for the control of the melt redox to meet the target of 0.2 (Fe^{2+}/Fe_{total})
- Decreasing the amount of formic acid results in substantial decrease in hydrogen generation, allowing shorter feed preparation cycle
- The pH 5, 3-acid cycle, 20% formic acid alternate flowsheet has been selected for subsequent melter testing
- Small-scale melter tests using alternate flowsheet melter feed in preparation