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# **IMPLEMENTATION OF FLOWSHEET CHANGE TO MINIMIZE HYDROGEN AND AMMONIA GENERATION DURING CHEMICAL PROCESSING OF HIGH LEVEL WASTE IN THE DEFENSE WASTE PROCESSING FACILITY**

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## **Abstract**

Testing was completed to develop a chemical processing flowsheet for the Defense Waste Processing Facility (DWPF), designed to vitrify and stabilize high level radioactive waste. DWPF processing uses a reducing acid (formic acid) and an oxidizing acid (nitric acid) to rheologically thin the slurry and complete the necessary acid base and reduction reactions (primarily mercury and manganese). Formic acid reduces mercuric oxide to elemental mercury, allowing the mercury to be removed during the boiling phase of processing through steam stripping. In runs with active catalysts, formic acid can decompose to hydrogen and nitrate can be reduced to ammonia, both flammable gases, due to rhodium and ruthenium catalysis. Replacement of formic acid with glycolic acid eliminates the generation of rhodium- and ruthenium-catalyzed hydrogen and ammonia. In addition, mercury reduction is still effective with glycolic acid. Hydrogen, ammonia and mercury are discussed in the body of the report.

Ten abbreviated tests were completed to develop the operating window for implementation of the flowsheet and determine the impact of changes in acid stoichiometry and the blend of nitric and glycolic acid as it impacts various processing variables over a wide processing region. Three full-length 4-L lab-scale simulations demonstrated the viability of the flowsheet under planned operating conditions. The flowsheet is planned for implementation in early 2017.

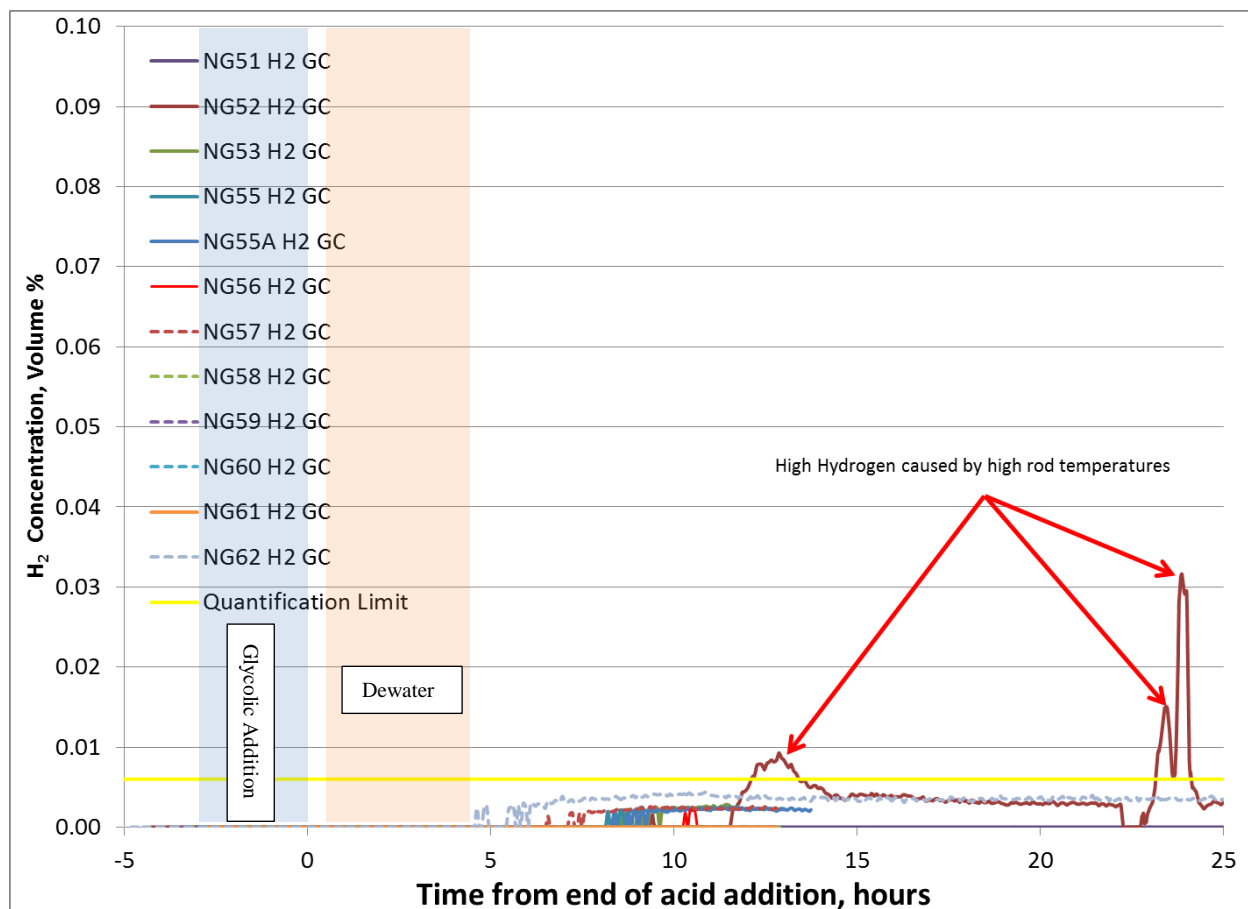
## **Hydrogen**

The offgas was monitored by a gas chromatograph and mass spectrometer for hydrogen. Hydrogen is generated in nitric-glycolic acid processing; however its concentration is almost always below the 0.006 volume % quantification limit of the gas chromatograph. In runs where hydrogen was detected but was below the quantification limit, the results will be reported. In runs where no hydrogen was detected, the results will be reported as less than the quantification limit. Two of the runs had thick rheology, fouling, and excessive heating rod temperatures. In these two runs where significant hydrogen was quantified, a note will be added saying the hydrogen data was collected at rod temperatures in excess of DWPF steam coils. Peak hydrogen generation data are summarized in Table 1. The hydrogen concentration profile is shown in Figure 1.

**Table 1 Peak Hydrogen Concentration and Generation Rates**

Experiment #	Acid Stoichiometry	Percent Reducing Acid	H <sub>2</sub> Peak mmol/min	H <sub>2</sub> Peak vol %	H <sub>2</sub> Total mmol
51	83.7	58.36	<0.0018	<0.006	N/A
52*	116	54.1	0.0048	0.032	0.6
53	83.6	62.62	0.0005	0.003	0.4
54*	117	58.36	0.0410	0.227	1.5
55	100	58.36	0.0004	0.003	0.3
55A	100	52.34	0.0004	0.002	0.3
56	100	64.39	0.0004	0.003	0.2
57	99.9	62.62	0.0005	0.003	0.5
58	76.9	62.62	<0.0018	<0.006	N/A
59	123	62.62	<0.0018	<0.006	N/A
60	100	62.62	<0.0018	<0.006	N/A
61	100	54.1	<0.0018	<0.006	N/A
62	97.4	58.36	0.0007	0.004	0.9

\* Hydrogen data generated while heating rod temperatures exceeded 160 °C.



## Figure 1 Hydrogen Concentration All Runs, Volume %

### Ammonia

Ammonia scrubbers are operated to scrub ammonia from the offgas use the acidic condensate to prevent the formation of ammonium nitrate (an explosive hazard) solids in the offgas piping. Ammonia can be generated during chemical processing and is released to the offgas when the ammonia/ammonium equilibrium favors ammonia (slurry pH >7). If the slurry pH is acidic, the ammonia is retained in the slurry as ammonium. The offgas was monitored by a Fourier transform infrared spectrometer (FTIR), and mass spectrometer.

In addition to the offgas, other sources for ammonia are the products and the ammonia scrubber solution. The concentrations of ammonium in the scrubber solutions and the concentrations of ammonium in the products are summarized in Table 2. Note that no ammonium was detected in the ammonia scrubber solutions. This indicates that if ammonium is being produced, the ammonia/ammonium equilibrium is preventing the release of ammonia to the offgas. Note also that a low concentration of ammonium was detected in runs 61 and 62. Since the slurry pH was acidic, no detectable ammonium was adsorbed by the ammonia scrubber. It is also interesting that the runs that lasted longer, runs 61 and 62, produced more ammonium.

**Table 2 Ammonium in Ammonia Scrubber Solution and Products, mg/L**

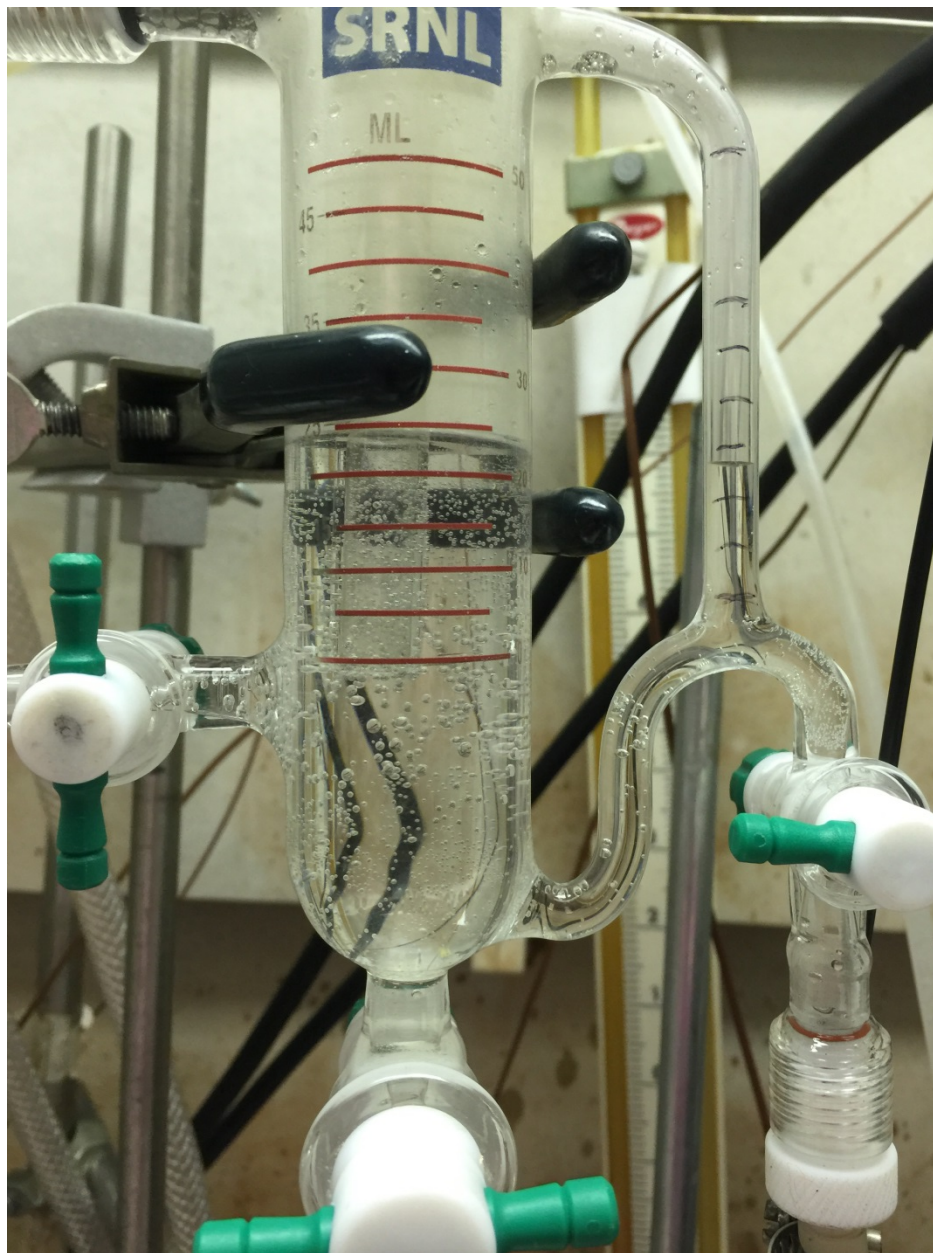
	51	52	60	61	62
Post Acid Scrub Solution	NA	NA	<5	<5	<5
Post Processing Scrub Solution	NA	NA	<5	<5	<5
Post Processing Slurry	NA	NA	<5	6.39	11.5
Post Processing Slurry pH	7.45	4.36	5.00	4.93	5.93

The result is that little ammonia is produced during simulant testing and the ammonia is retained as ammonium by the slurry since it is acidic. Thus, the main function of the scrubbers under the glycolic-nitric flowsheet is to remove NO<sub>2</sub> gas as nitric acid, as well as scrub other volatile species (such as mercury) from offgas streams. Because the pH of the scrubber need not be regulated to optimize ammonia removal under the nitric—glycolic flowsheet, the pH of the scrub solution may be changed to improve scrubbing efficiencies of the alternate species.”

### Mercury

DWPF is designed to be the purge point for mercury in high level waste processing. For this to succeed the mercury needs to be reduced, steam stripped, coalesced, and collected in the mercury decanter or condensate tank. In addition, once the elemental mercury is collected, it can't be dissolved or reoxidized or it will be reprocessed at a later date as the condensate is processed. The recovery of mercury in the mercury decanter has been extremely poor in DWPF. During this testing, mercury stripping and recovery were quantified for each run. In an attempt to increase the mercury recovery, all runs maintained an agitator speed of 700 revolutions per minute (rpm). In addition, all runs except 61 used the maximum boilup rate of 5,000 lb/hr.

The mercury decanter is not an ideal decanter (slow liquid flows yielding sufficient residence times for the mercury to coalesce). Instead, it is a busy vessel where  $\text{NO}_x$  is scrubbed, mercury is dissolved, other reactions occur, and water is continually flowing (dropping) during conflux. A photo of the mercury decanter used in this testing during the evaporation phase of processing is shown in Figure 2.

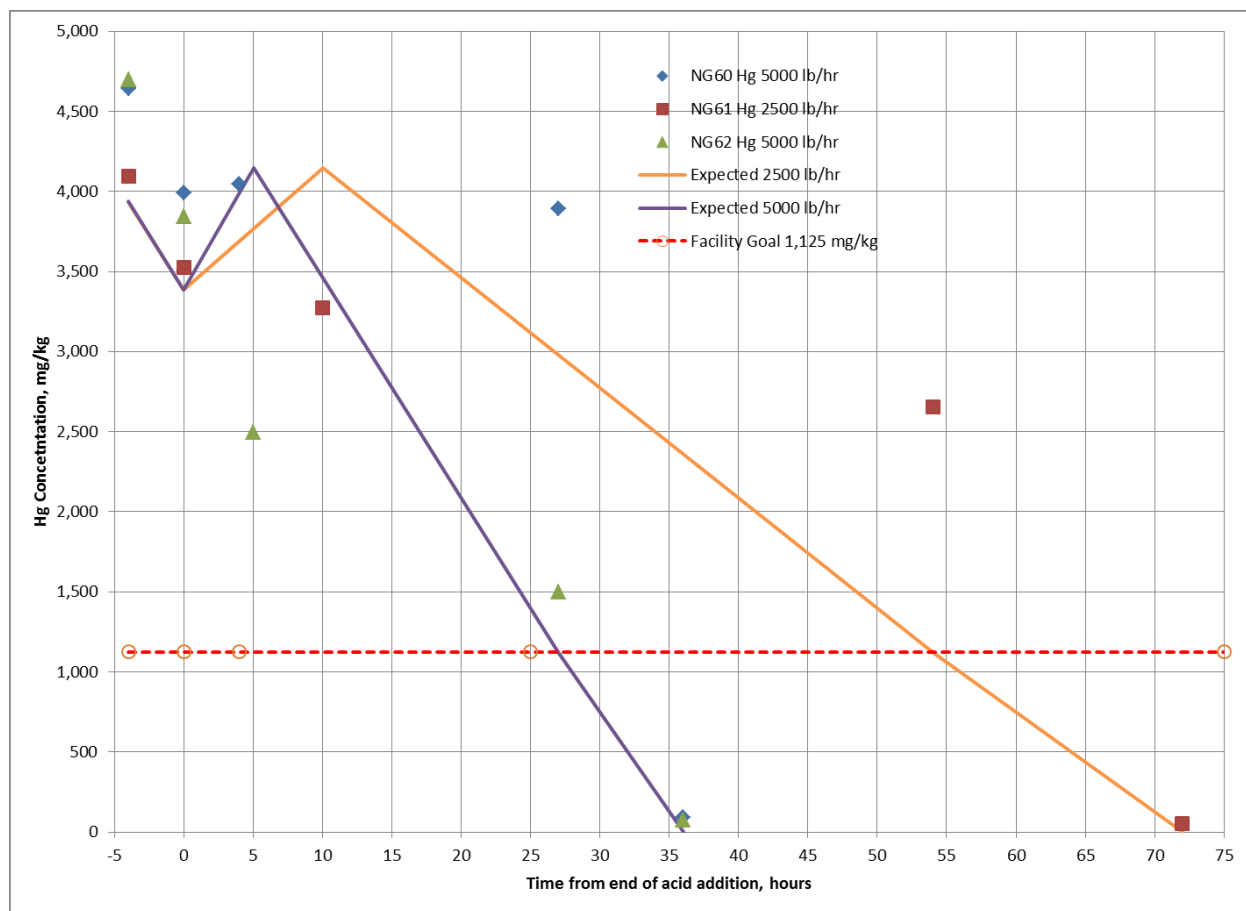


**Figure 2 Mercury Decanter during Dewater**

In each of the thirteen experiments, approximately 14.7 g of mercuric oxide (equivalent to 13.6 g of elemental mercury) was added to target a mercury concentration of 2.48 wt% total solids basis in the sludge simulant. One goal of the processing is to reduce the mercury loading by steam stripping the mercury to less than 0.45 wt % total solids basis in the product. In order to reach this product

mercury target, steam stripping (time at boiling or conflux) is planned for approximately 36 hours at a scaled boilup rate of 5,000 lb/hr condensate or 72 hours at a scaled boilup rate of 2,500 lb/hr, assuming it takes 750 g of steam to strip 1 g elemental Hg.

Slurry samples were pulled throughout the testing. Mercury is only stripped during boiling. During evaporation segment of processing, the stripping rate is constant but the mercury concentration increases due to evaporation of water. So although mercury is being stripped (between 0 and 5 hours for 5000 lb/hr scaled steam flow or between 0 and 10 hours for 2500 lb/hr scaled steam flow), the mercury concentration increases from about 3300 mg/kg to 4200 mg/kg. Once evaporation is complete, the condensate is returned to the reactor and the mercury concentration is expected to decrease linearly until boiling is complete (targeting a final mercury concentration of 1125 mg/kg or 0.45 wt %). A projected mercury stripping line for the maximum boilup runs (60 and 62, purple line for 5000 lb/hr scaled steam flow) and for the prototypic boilup run (61, orange line for 2500 lb/hr scaled steam flow) showing the mercury concentration versus time at boiling for Runs 60, 61 and 62 is summarized in Figure 3.



**Figure 3 Mercury Concentration during Processing**

At the completion of each run, the mercury decanter contents were drained to a sample bottle. The aqueous liquid in the sample bottle was transferred to a second sample bottle, leaving the mercury (and a small amount of water) in the first sample bottle, which was placed in a desiccator for at least a week. The dried mercury was weighed. The mercury added, the mercury collected from the decanter,

the % of mercury recovered in the decanter, the measured mercury in the product, and the calculated mercury from each run is summarized in Table 3. The mercury in the product was calculated assuming any mercury not collected in the mercury decanter is still in the product. The runs are ordered top to bottom from the lowest acid stoichiometry to the highest acid stoichiometry.

**Table 3 Mercury Added, recovered, and calculated mercury concentration in Product**

Run	Boilup Rate, lb/hr DWPF Scale	Hg Added, g	% Recovered in mercury decanter	Measured Hg in Product		Calculated Hg In Product, mg/kg
				mg/kg*	wt % TS	
58	5000	13.58	53.9	64	0.021	4,380
51	5000	13.58	30.7	170	0.055	2,719
53	5000	13.58	39.6	270	0.090	3,724
55	5000	13.58	80.8	213	0.062	3,122
55A	5000	13.53	57.8	82	0.041	1,305
56	5000	13.58	81.0	432	0.140	1,682
57	5000	13.59	60.9	135	0.044	1,161
60	5000	13.57	73.9	269	0.105	2,430
61	2500	13.58	22.8	274	0.102	2,942
62	5000	13.58	29.2	108	0.042	632
52	5000	13.58	50.3	1,610	0.610	1,358
54	5000	13.58	43.5	NA	NA	4,127
59	5000	13.58	82.2	195	0.104	3,153

\* Aqua Regia digestion of entire sample followed by ICP-AES analysis for Hg

The mercury recovery was much higher than expected (typical mercury recovery is ~30%). In these runs, the mercury recovery was as high as 81%. What is particularly noteworthy is the difference in mercury collection between runs 60 and 61, with the only difference being the boilup rate. Run 60 had 3x higher mercury recovery than 61. This may demonstrate the importance of high steam flow on mercury recovery. It is also expected that agitation speed is key to improved mercury recovery, although this was not varied in these runs. Good mixing and high boilup rates should work together to disperse the mercury more uniformly and should lead to better steam stripping. One other surprise was the lower mercury recovery in 62. Little testing has been done with the two additional waste streams that were added during run 62. More testing is recommended to determine the repeatability of the lowered mercury recovery under this type of processing.

Elemental mercury is the assumed form of mercury collected in the mercury decanter. If other forms or other impurities are present, they could change the reported mercury recovery. The mercury from runs 51 and 52 were completely digested and analyzed by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES). The results are reported in Table 4. Si was the only metal reported above the 10 mg/kg level. The sample collected from the mercury decanter was measured and reported as 1.00E6 mg/kg Hg and was therefore determined to be primarily elemental mercury.



**Table 4 Impurities in Mercury, mg/kg**

Element	BLANK		51 Mercury		52 Mercury	
	Result	Uncertainty	Result	Uncertainty	Result	Uncertainty
Ag	< 0.735	(N/A %RSD)	3.77	(13.8 %RSD)	< 0.726	(N/A %RSD)
<b>Al</b>	<b>&lt; 1.52</b>	<b>(N/A %RSD)</b>	<b>1.44</b>	<b>(110 %RSD)</b>	<b>3.84</b>	<b>(13.6 %RSD)</b>
B	< 0.53	(N/A %RSD)	< 0.483	(N/A %RSD)	< 0.524	(N/A %RSD)
Ba	< 0.083	(N/A %RSD)	< 0.076	(N/A %RSD)	< 0.082	(N/A %RSD)
<b>Ca</b>	<b>&lt; 0.119</b>	<b>(N/A %RSD)</b>	<b>0.336</b>	<b>(10 %RSD)</b>	<b>0.387</b>	<b>(13 %RSD)</b>
Cd	< 0.144	(N/A %RSD)	< 0.131	(N/A %RSD)	< 0.142	(N/A %RSD)
Ce	< 2.29	(N/A %RSD)	< 2.09	(N/A %RSD)	< 2.26	(N/A %RSD)
Co	< 0.19	(N/A %RSD)	< 0.173	(N/A %RSD)	< 0.187	(N/A %RSD)
Cr	< 0.083	(N/A %RSD)	< 0.076	(N/A %RSD)	< 0.082	(N/A %RSD)
Cu	10.9	(11 %RSD)	5.82	(14.3 %RSD)	0.761	(115 %RSD)
<b>Fe</b>	<b>&lt; 0.096</b>	<b>(N/A %RSD)</b>	<b>1.85</b>	<b>(10.3 %RSD)</b>	<b>5.53</b>	<b>(10.3 %RSD)</b>
K	< 12.1	(N/A %RSD)	< 11	(N/A %RSD)	< 11.9	(N/A %RSD)
La	< 0.332	(N/A %RSD)	< 0.303	(N/A %RSD)	< 0.328	(N/A %RSD)
Li	< 0.16	(N/A %RSD)	< 0.146	(N/A %RSD)	< 0.158	(N/A %RSD)
Mg	< 0.051	(N/A %RSD)	< 0.046	(N/A %RSD)	< 0.05	(N/A %RSD)
Mn	< 0.206	(N/A %RSD)	< 0.204	(N/A %RSD)	< 0.204	(N/A %RSD)
Mo	< 0.663	(N/A %RSD)	< 0.604	(N/A %RSD)	< 0.655	(N/A %RSD)
Na	< 1.18	(N/A %RSD)	< 1.08	(N/A %RSD)	< 1.17	(N/A %RSD)
Nb	< 0.475	(N/A %RSD)	< 0.433	(N/A %RSD)	< 0.469	(N/A %RSD)
Nd	< 0.804	(N/A %RSD)	< 0.734	(N/A %RSD)	< 0.795	(N/A %RSD)
Ni	< 0.156	(N/A %RSD)	< 0.142	(N/A %RSD)	< 0.154	(N/A %RSD)
P	< 0.896	(N/A %RSD)	< 0.817	(N/A %RSD)	< 0.885	(N/A %RSD)
Pb	< 0.373	(N/A %RSD)	< 10	(N/A %RSD)	< 10	(N/A %RSD)
Re	< 0.51	(N/A %RSD)	< 0.465	(N/A %RSD)	< 0.504	(N/A %RSD)
S	< 0.677	(N/A %RSD)	< 0.618	(N/A %RSD)	< 0.669	(N/A %RSD)
<b>Si</b>	<b>6.2</b>	<b>(26.5 %RSD)</b>	<b>25.1</b>	<b>(10.3 %RSD)</b>	<b>28</b>	<b>(10.5 %RSD)</b>
Sn	< 2.72	(N/A %RSD)	< 2.48	(N/A %RSD)	< 2.69	(N/A %RSD)
Sr	< 4.9	(N/A %RSD)	< 4.47	(N/A %RSD)	< 4.84	(N/A %RSD)
Ti	< 0.156	(N/A %RSD)	< 0.143	(N/A %RSD)	< 0.154	(N/A %RSD)
V	< 0.261	(N/A %RSD)	< 0.238	(N/A %RSD)	< 0.258	(N/A %RSD)
Zn	< 0.326	(N/A %RSD)	< 0.297	(N/A %RSD)	< 0.322	(N/A %RSD)
Zr	< 0.227	(N/A %RSD)	< 0.207	(N/A %RSD)	0.364	(23 %RSD)

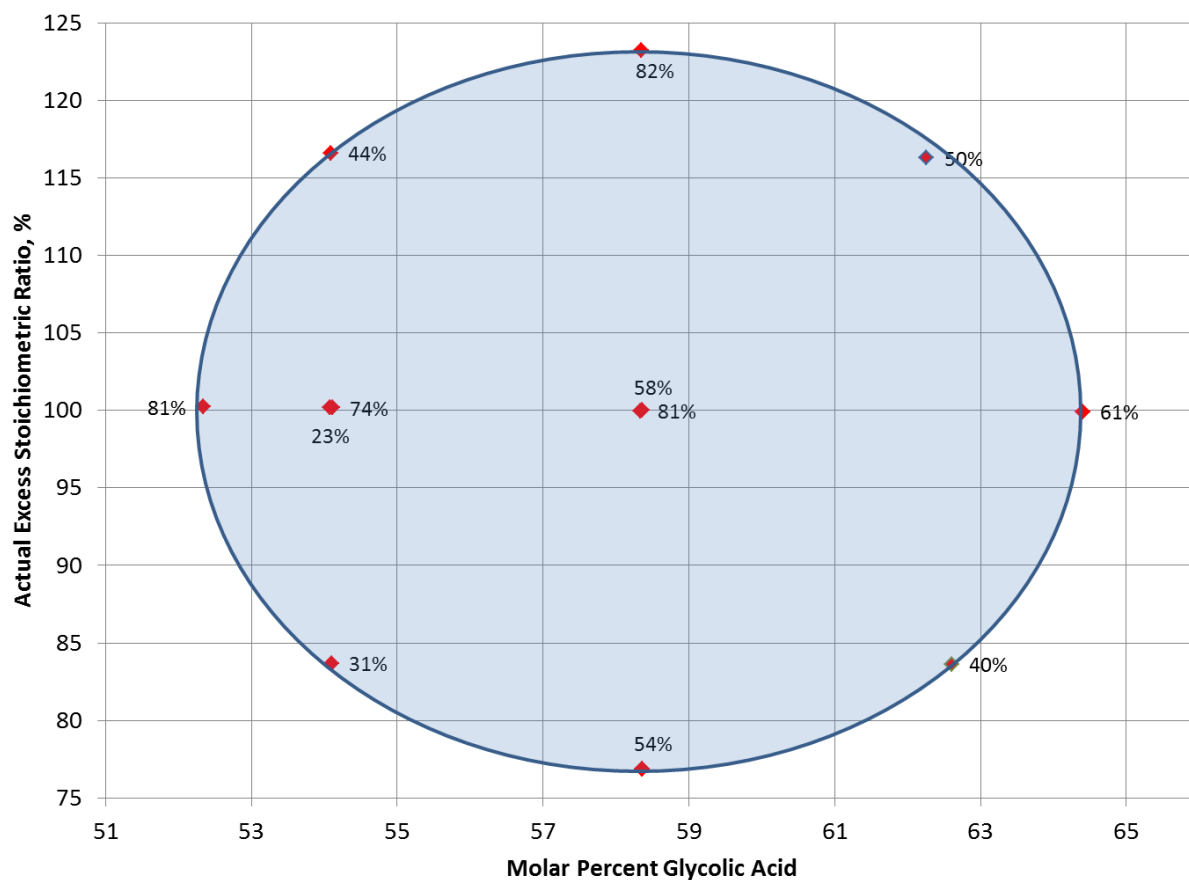
In some of the later runs, the product slurry was carefully poured out in an attempt to recover any unstripped elemental mercury. In Run 61 (a run with poor mercury recovery), 6.22 g of elemental mercury was recovered from the product. This confirms the poor mercury recovery in this run. Contrast this to Run 55, a run with excellent mercury recovery where only 1.22 g of mercury was recovered from the product. This suggests that the rate limiting step for mercury removal is physical and not chemical. A mercury mass balance was completed for all the runs and the results are summarized in Table 5.

**Table 5 Mercury Mass Balance**

<b>Run</b>	<b>Elemental Hg Added, g</b>	<b>Mercury collected - mercury decanter, g</b>	<b>Mercury Collected - Product, g</b>	<b>Mercury in Empty Kettle, g</b>	<b>Total Out, g</b>	<b>% Hg Balance</b>
<b>58</b>	13.58	7.32	0.14	NA	7.46	54.9%
<b>51</b>	13.58	4.17	0.37	NA	4.54	33.4%
<b>53</b>	13.58	5.38	0.59	NA	5.97	44.0%
<b>55</b>	13.58	10.98	0.42	1.09*	12.50	92.0%
<b>55A</b>	13.53	7.82	0.28	NA	8.10	59.9%
<b>56</b>	13.58	11.00	0.96	0.87*	12.83	94.5%
<b>57</b>	13.59	8.28	0.29	NA	8.57	63.1%
<b>60</b>	13.57	10.03	0.70	NA	10.73	79.1%
<b>61</b>	13.58	3.10	0.70	6.22*	10.02	73.8%
<b>62</b>	13.58	3.97	0.33	NA	4.30	31.7%
<b>52</b>	13.58	6.83	4.00	NA	10.83	79.7%
<b>54</b>	13.58	5.91	NA	NA	5.91	43.5%
<b>59</b>	13.58	11.16	0.75	NA	11.91	87.7%

\* In some of the runs the product contents were poured out slowly, leaving elemental Hg behind. This Hg was weighed and the mass included.

The impact of acid stoichiometry and percent reducing acid on process chemistry and rheology were two of the objectives of this testing. A graph showing the concentration of mercury in the products is included as Figure 3. The higher acid stoichiometry leads to higher mercury recovery. The two high acid runs with low Hg recovery were 52 and 54, both with very thick rheology which likely hindered steam stripping. Note that the highest acid stoichiometry run (59) had similar recovery to the mid acid runs but had to be processed at 20 wt % total solids target to eliminate the problems with high rheology. This suggests that processing the slurry at the optimum acid stoichiometry and total solids should lead to higher mercury recovery.



**Figure 4 Percent Mercury Recovery as a Function of Acid Stoichiometry and Molar Percent Glycolic Acid**

### Conclusions

Testing was completed to develop a chemical process flowsheet for DWPF. Simulations were completed using simulants and radioactive waste. As has been demonstrated in over 100 simulations, the replacement of formic acid with glycolic acid virtually eliminates the largest flammability hazards, hydrogen and ammonia.

Implementation of the nitric-glycolic acid flowsheet in DWPF is recommended. This flowsheet not only eliminates the hydrogen and ammonia hazards but also will lead to shorter processing times, higher elemental mercury recovery.