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### **Results of Initial Ammonia Oxidation Testing**

This memo presents an experimental survey of aqueous phase chemical processes to remove aqueous ammonia from waste process streams. Ammonia is generated in both the current Hanford waste flowsheet and in future waste processing. Much ammonia will be generated in the Low Activity Waste (LAW) melters.<sup>i</sup> Testing with simulants in glass melters at Catholic University has demonstrated the significant ammonia production.<sup>ii</sup> The primary reaction there is the reducing action of sugar on nitrate in the melter cold cap. Ammonia has been found to be a problem in secondary waste stabilization. Ammonia vapors are noxious and destruction of ammonia could reduce hazards to waste treatment process personnel. It is easily evolved especially when ammonia-bearing solutions are adjusted to high pH.

In the current operation of the Effluent Treatment Facility (ETF) at the Hanford Site, an ammonia laden waste stream is processed through a thin film dryer and disposed of as a granular salt (primarily ammonium sulfate) for disposal in drums.<sup>iii</sup> A stabilization and solidification treatment process is needed to provide a more leach resistant waste form for disposal in Hanford's Integrated Disposal Facility (IDF).

This work was performed in support of waste form development for liquid secondary waste from Hanford's ETF. It found and demonstrated a very effective process to remove ammonium ion from a simulant of Hanford ETF evaporator bottoms liquid (3.2 M ammonium ion).<sup>iv</sup> The process showed effectiveness in both batch flask and a small bench-scale reactor setting. The reaction of ammonium and nitrite ion proceeded cleanly and efficiently. Measured efficiencies of reagent use were 90 to 95%.

All chemical reactions in this work occurred in aqueous liquid phases. Three general categories of process were examined in the laboratory. Examples of all three (nitrite, catalyzed peroxide, and peroxydisulfate) were found to eliminate ammonia from aqueous solution. The ammonium / nitrite reaction in particular appears to be practical in many respects. The 3.2M concentration of ammonium ion in the chemical reactor feed, combined with high levels of oxidizing reagent (sodium nitrite) allowed the observation of nitrogen gas release and significant temperature rise. Manual pH control was effective in maintaining good reaction rates. Raman data on offgas composition was available in the second of the two runs. It showed almost exclusive production of nitrogen gas when nitrite reacts with ammonia in solution.

This work follows a literature survey which focused on ammonia oxidation in the liquid phase under moderate conditions.<sup>v</sup> By moderate it is meant that temperature is between room temperature and the boiling point of water,

and that pressure is to always be 1 atmosphere absolute. The literature survey looked at chemistries mainly within the three categories tested here (nitrite, catalyzed peroxide, and peroxydisulfate), but also reviewed processes that are considered less practical for Hanford liquid secondary waste treatment. It also listed heats of reactions.

Liquid phase ammonia oxidation processes were studied with the intention of demonstrating practical applications for use in evaporators or process tanks at atmospheric pressure. Such equipment would most likely be available or easily obtained for implementation of ammonia oxidation. A reaction using nitrite looks practical for use within evaporators such as the Hanford ETF evaporator, or separately treating evaporator bottoms liquids.

This work also provides awareness of some chemical reactions that could occur in the current flowsheet. For example, streams that contain both ammonium ion and nitrite together will self-react under certain conditions of pH and temperature. One example might be the point in the Direct Feed Low Activity Waste (DFLAW) flowsheet where melter offgas condensate contains significant amounts of both ammonium and nitrite. While pH may be higher than that required to drive the reaction, potential exists for the reaction to occur if the pH and temperature are not carefully controlled. Knowledge of such chemistry could enhance understanding of the DFLAW flowsheet outside of ammonia removal needs that can be applied in the ETF evaporator.

## EXPERIMENTAL

The laboratory testing was conducted in two phases. Phase I was an experimental scoping survey of chemistries, with each chemistry and set of conditions maintained in 125 mL Erlenmeyer flasks for several hours. Samples were taken primarily to measure removal of ammonium ion. Liquid temperature was  $42 \pm 2$  °C in most cases.

Phase II consisted of two campaigns using a glass laboratory scale reactor and a feed containing 3.2 M ammonium ion that is typical of a postulated Hanford Site ETF evaporator bottoms product concentrate. The nitrite process was run in both lab scale campaigns. Reactor pH was in the 4.75 to 6 range during operations. The primary reaction there was:



The initial feed, which represented a concentrated bottoms solution from the Hanford Site ETF evaporator, contained mostly dissolved ammonium sulfate. The use of the sodium nitrite oxidant in the ETF evaporator would convert ammonium sulfate to sodium sulfate in the aqueous solution.

### Simulants

Phase I testing used “242-A Evaporator Brine” simulant, diluted to about 0.4 M ammonium ion for safety reasons in initial reaction testing. The primary reference for the recipe was a report by Russell et al. at the Pacific Northwest National Lab (PNNL). The recipe is intended to represent ETF evaporator brine (bottoms) that would be generated while processing 242-A evaporator concentrate through the ETF.<sup>iv</sup> Separately a simulant of similar ammonium concentration was also made using a chromate-bearing concentrate solution from evaporator tests specified by a TTQAP.<sup>vi</sup>

Diluted (to ~0.4 M  $\text{NH}_4^+$ ) 242-A Evaporator simulant and its analysis are given in Table 1 below. The “Target Concentration” column uses values that are in proportion to what Russell provided in Section 2.1 of his work.<sup>iv</sup> The target for sodium was set to be an average sodium concentration as found in the diluted batches. The density of Batch 1 was not measured but Batch 2 density was measured to be 1.018 g/mL. It is not known why Batch 1 ammonium is relatively low, but its measurements were consistent over time and feed ammonium concentrations were thus used for respective Phase I test calculations. Batch 1 was depleted after use in a no-catalyst control plus

iron, copper, and cobalt flask tests. Batch 2 was used for Phase I testing after that. Sulfate and sodium could vary upward later as these simulants had to be pH-adjusted with sulfuric acid and sodium hydroxide for various processes being studied.

**Table 1. Composition of 242-A Evaporator Simulant Batches after Dilution**

	<b>Target Concentration, mg/L</b>	<b>Batch 1 Measured Average, mg/L*</b>	<b>%RSD*</b>	<b>Batch 2 Measured Average, mg/L**</b>	<b>%RSD**</b>
<b>Sodium</b>	1340	1317	7.5	1368	0.7
<b>Ammonium</b>	7570	6370	0.8	7613	1.4
<b>Potassium</b>	91	67	6.5	62	2.8
<b>Sulfate</b>	24200	31100	6.9	27550	6.2
<b>Chloride</b>	358	426	10.8	293	0.9
<b>Calcium</b>	716	422	6.4	445	0.3
<b>Magnesium</b>	170	332	5.1	90	2.7
<b>Silicon</b>	240	125	2.8	62	4.2

\*These are based on three replicate measurements.

\*\*These are based on four replicate measurements.

The chromate bearing simulant was made from reconstituted lab scale evaporator concentrate. Ammonium ion was below detection in that product, so ammonium sulfate was added to the solution. The ammonium ion concentration was to be close to that of the simulant of Table 1. The resulting material analysis for the chromate bearing simulant is in Table 2. It is clearly a complex simulant. It was used primarily to see if chromate would change process chemistry. The other species as well might inhibit or catalyze reactions seen in simpler simulants. Analytical measurements for Table 2 are stated to have a one-sigma uncertainty of 10%.

**Table 2. Evaporator Simulant with Chromate and added Ammonium Ion**

<b>Species</b>	<b>Measured Concentration, mg/L</b>		<b>Species</b>	<b>Measured Concentration, mg/L</b>
<b>Ammonium</b>	6930		<b>Boron</b>	1090
<b>Sodium</b>	8690		<b>Chromium</b>	41.7
<b>Potassium</b>	3070		<b>Lithium</b>	34.7
<b>Calcium</b>	0.8		<b>Zinc</b>	111
<b>Magnesium</b>	<0.05		<b>Fluoride</b>	350
<b>Silicon</b>	2.44		<b>Density</b>	1.035 g/mL
<b>Chloride</b>	2150		<b>pH</b>	10 (initial)
<b>Sulfate</b>	29500			
<b>Nitrate</b>	1100			
<b>Nitrite</b>	7250			

Phase II tests used a 3.2M ammonium ion solution representing a Hanford Site ETF evaporator bottoms product as calculated by Halgren.<sup>vii</sup> The Hanford ETF receives aqueous solutions from several site sources such as the 242-A evaporator overheads. The Direct Feed Low Activity Waste (DFLAW) process will contribute aqueous ammonia streams in the future. While the ETF bottoms is currently dried to a granular product for the Hanford Environmental Restoration Disposal Facility (ERDF), regulatory constraints may prevent such powdered solids disposal in the future. The same 3.2 M ammonium ion (ETF bottoms liquid) simulant recipe was used by Cozzi for FY 2016 Liquid Secondary Waste Formulation Development and Waste Form Qualification Testing.<sup>viii</sup> This simulant was used at full strength since Phase I experience and lab equipment design were considered sufficient for safe operation with the more concentrated reagents.

The 3.2M ammonium simulant target and measured compositions come from the “DFLAW EMF-CS” sheet of Halgren’s ETF mass balance calculations. For simplicity, only species exceeding a concentration of 1.0E+04 mg/L in the Halgren calculation were included in this simulant. Table 3 gives the target and experimentally measured composition of this aqueous solution that was used in reactor testing.

**Table 3. “DFLAW EMF-CS” Simulant with 3.2M Ammonium Ion**

<b>Target</b>	<b>Concentration, mg/L</b>	<b>Measured Average, mg/L*</b>	<b>%RSD*</b>
<b>Sodium</b>	45800	46800	3.6
<b>Ammonium</b>	58100	55300	1.9
<b>Nitrate</b>	19100	18400	3.8
<b>Sulfate</b>	238000	241000	0.0
<b>density</b>	1.2	1.211 g/mL	
<b>pH</b>	5.5	5.5	

\*Calculated from two sets of measurements.

#### Reagents – Hydrogen Peroxide

Roughly 30 wt% hydrogen peroxide was available and was used for the Phase I testing. Its density was measured at various points in the program, with an average of 1.115 g/mL with a %RSD of less than 0.2%, based on three measurements. This reagent density corresponded with a concentration of 28.5 wt%.<sup>ix</sup> Density of the source reagent did not change measurably with time.

#### Reagents – Sodium Nitrite

Sodium nitrite in concentrated liquid solution was needed for Phase II reactor testing. Solution at 7.5 M was chosen to be a practical concentration that is below the saturation at room temperature. This strength is also available commercially. Its density was measured to be  $1.2878 \pm 0.02\%$  g/mL at room temperature, based on two measurements.

Sodium nitrite was added as a solid salt to Phase I reaction flasks to minimize volume changes there. The amount chosen matched the molar amount of ammonia to oxidize. The reagent sodium nitrite salt did not contain anti-caking agents. The assay of the reagent was 99.7% or better.

#### Reagents – Catalysts

Use of hydrogen peroxide to oxidize ammonia likely required catalysts, and the literature survey reviewed possibilities. The Phase I results list the catalysts used with each flask. One nitrite test used a piece of platinum / 6% rhodium wire (62 cm long, 0.038 cm diameter) as a catalytic surface. The Omega catalog number for that wire was CF-000-J-3-96-1. The peroxydisulfate test did not use catalysts but required external heat to operate.

### Phase I Experiments

Phase I tests consisted of ~100 mL batch tests where 242-A Evaporator Brine simulant was first diluted to about 0.4 M ammonium ion with DI water. It was mixed with nitrite, peroxide/catalyst, or sodium peroxydisulfate, depending on the test. Each flask was stirred continuously during a test. Samples were taken 1 and 2 hours into each test. The temperature target was  $42 \pm 2$  °C for most batches (peroxydisulfate required >70 °C), though it was recognized that things like heat of reaction may affect actual temperature. Up to three reaction flasks were used in one temperature controlled water bath and one flask in the set had continuous temperature monitoring and recording.

Peroxide experiments used 90 grams of the ~0.4 M ammonium ion simulant, which is 88.4 mL. Peroxide tests were started by pipetting 8 mL of the hydrogen peroxide reagent into the flask.

Nitrite tests used the same simulant and amount, and 2.5 grams of solid sodium nitrite salt was added to commence each test. One run had a 62-cm long platinum/rhodium wire, coiled, in the flask to see if any catalysis of that reaction could be measured.

There was only one peroxydisulfate test, and 13.5 grams of sodium peroxydisulfate were added as a solid reagent to start that test. The test started after 90 grams of simulant were preheated to about 80 °C. External heating was maintained for that test since chemical reaction heat would not have been enough to sustain temperature at this small scale. This is the only flask that was heated directly on a hot plate and not in a water bath.

Samples had to be quenched to stop the reaction being studied. Peroxide samples were quenched by adding sufficient sodium sulfite salt, which removes hydrogen peroxide and forms water and sodium sulfate. Removal of the reactant hydrogen peroxide with no effect on ammonium ion was the goal for that sample treatment. Ammonium/nitrite samples were quenched by adding potassium carbonate to raise the pH. The ammonium nitrite reaction is very sensitive to pH. Alkali carbonate would raise pH to 8 or more, effectively stopping the reaction. Anhydrous potassium carbonate was used at the rate of 0.1 to 0.2 g for a 15 mL sample. Sodium peroxydisulfate samples were simply cooled to room temperature since that reaction requires high temperature to proceed.

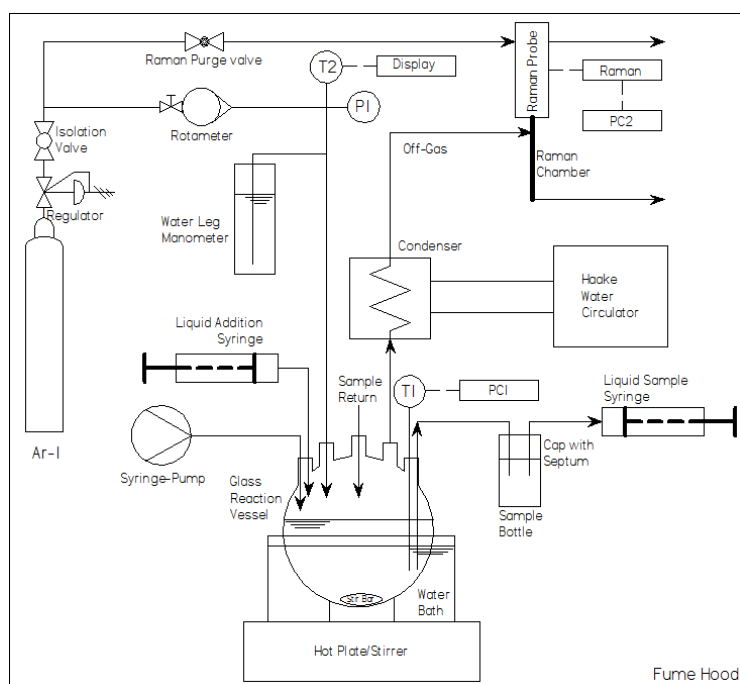
### Phase II Experiments

#### *System Description*

The experimental setup of the test apparatus is shown in Figure 1. All of the components shown, except for the data acquisition systems, were contained in a fume hood for personnel protection. The primary component is a round-bottom 1000-ml glass reaction vessel with multiple ports. The reaction vessel was partially submerged in a water bath which sat on a hot plate. Both the reactor vessel and the water bath had magnetic stirrer bars which operated off the same magnetic drive. The water bath provided a thermal mass to help stabilize the reaction temperature. The hot plate was mainly used for initial heat-up; the heat of chemical reaction maintained the temperature, which could rise from the initial point. Rubber stoppers or flask fittings were used in the ports to isolate the vessel vapor space from the atmosphere.

The primary oxidation liquid reagent was added to the reaction vessel with a Cole-Parmer, Catalog # 780200C syringe pump using 60 ml plastic syringes. The vessel head space was purged with argon during a test using a low-flow rotameter (F1). Argon temperature (T2) and pressure (P1) were measured after the rotameter for correction to standard conditions (14.696 psig, 21.1 °C). A branch off of the argon line leading to the vessel was submerged in a column of water to provide pressure protection for the vessel (manometer). Off-gas from the reaction vessel flowed into a condenser to remove moisture and then to a chamber for Raman Spectroscopy. A second argon line was used to purge the Raman probe to remove signals that would be caused by air and moisture in that location. Reaction temperature in the vessel was measured with a type K thermocouple (T1).

**Figure 1. Test Apparatus for Ammonium Oxidation**



Chilled water for the condenser was provided by a Haake® DC 10 water circulator filled with ice water. Liquid samples were extracted from the reaction vessel into a sample vial using a plastic syringe. Liquid additions, such as sulfuric acid for pH adjustment, were manually injected into the vessel with a 5 or 10-mL plastic syringe. A laptop PC (PC1) with Wonderware® data acquisition software recorded the temperature reading at a rate of once per minute. The Raman data was recorded on a separate PC (PC2) at a rate of approximately twice per minute.

The Raman unit was a ChemLogix GasRaman NOCH-532 (TSI, Inc., Irvine, CA). It had a CCD detector thermoelectrically cooled to -60 °C. The spectrometer had a range of 0-4200 cm<sup>-1</sup> with 8 cm<sup>-1</sup> resolution. Gas in front of the laser probe was excited by a 532 nm, 50 mW DPSS laser and a fiber optic imaging probe with a 10 mm focal length coupled into a quartz gas flow cell. The cell is located downstream of the ice water-cooled condenser but the gas stream was not otherwise filtered before monitoring.

### Preparations for Testing

Portions of the simulant (DFLAW EMF-CS) and reagent (7.5M sodium nitrite solution) were prepared prior to testing. Approximately 300 ml of simulant was used for each test. The mass of simulant used was recorded. The pH of the simulant was adjusted down to  $4.5 \pm 0.2$  by adding 3M (6 N) sulfuric acid before it was added to the

reaction vessel. The simulant in the vessel was heated to an initial test temperature of  $42 \pm 2^\circ\text{C}$  using the hot plate prior to reagent addition.

Approximately 128 ml of reagent was used for each test. This would have provided the same number of moles of sodium nitrite that would match the total ammonium ion moles in the reactor (approximately 1 mole  $\text{NH}_4^+$  for each test). Two 60 ml syringes were prepared for each test (filled to approximately 50 ml), which required a refill of one syringe to complete the test. The mass of the reagent in each syringe were recorded. The syringe pump was programmed for the required injection rate and volume to be injected prior to the start of each test. Syringe change-out was accomplished by stopping the pump, replacing the syringe and restarting the pump. The residual reagent left in the syringe was accounted for through weighing.

The electronic test equipment was started and allowed to warm up prior to testing. The two PCs, associated equipment, and data acquisition software were also started and prepared for logging. The chilled water circulator and argon purges for the reaction vessel and Raman probe were also started prior to reagent addition.

#### *Test Operation*

A test was started when reactor contents reached a desired temperature range. The test commenced by energizing the syringe pump. The timer on the reaction was started when the reagent travelled through the injection tube and dropped into the vessel. The reaction was visually monitored during testing by the production of gaseous microbubbles and by an increased solution temperature. Liquid samples were periodically taken (usually every 30 minutes up to 2-1/2 hours) by using the sample syringe, extracting solution from the reaction vessel to the sample bottle. 15 ml of solution were drawn for each sample. If the pH of the solution was high then sulfuric acid was injected into the reaction vessel to lower the pH closer to the target value.

The syringe pump was stopped when the prescribed amount of reagent was injected. The reaction continued and was monitored for a period of time after the pump was stopped. The test equipment and data acquisition systems were de-energized once the reaction had reduced to a safe condition. A final liquid sample was taken after the reaction was complete (usually the next working day).

#### *Liquid Sampling*

Most liquid samples were taken at half-hour intervals during the test. Each sample was immediately cooled in the circulator ice bath for about 15 seconds and then the pH of the sample was measured. A small amount of potassium carbonate was added to the sample bottle to quench the reaction, making the sample safe for storage. Potassium carbonate would raise the pH. The ammonium nitrite reaction is sensitive to pH and would effectively stop at pH 8 or so.

### RESULTS – Phase I

#### *Hydrogen Peroxide Tests*

The tables below show the catalysts used and the results obtained for each of two samples. The first sample was taken 1.5 hours after hydrogen peroxide addition, and the second sample was 3 hours after that test start.

Acid-side testing used simulant initially adjusted to  $\text{pH } 3 \pm 0.5$  with drops of 6 N sulfuric acid (5 M NaOH used if there was an overshoot). pH was checked using narrow range pH papers and sometimes with a pH probe. Table 4 contains the “metal found” data in mg/L, which is the ICP-ES measurement for concentration of catalyst actually found in solution for the samples.



The reasoning for testing potassium iodide was that iodide would be oxidized to iodine, a free halogen, and the author believed that iodine would oxidize ammonia and return to iodide to continue a catalytic cycle. This testing disproved that reasoning despite some appearance of brown iodine color in solution. The mildly acidic pH apparently inhibited any further usefulness of iodine.

**Table 4. Acidic Hydrogen Peroxide Results**

Test Metal Catalyst and Reagent	Salt mass added, grams	Catalyst Element added, mg	1.5 hr	1.5 hr	3 hr	3 hr
			Metal Found mg/L	% NH <sub>3</sub> removed	Metal Found mg/L	% NH <sub>3</sub> removed
Control						
No catalyst	zero	zero	zero	1.9%	zero	1.9%
Cobalt						
Co(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	0.492	99.6	899	3.8%	964	4.5%
Copper						
Cu(NO <sub>3</sub> ) <sub>2</sub> ·2.5H <sub>2</sub> O	0.069	18.9	179	4.1%	107	1.7%
Iron						
FeSO <sub>4</sub> ·7H <sub>2</sub> O	0.502	100.8	142	2.1%	149	2.4%
Iodide						
KI	0.032	24.5	**	0.4%	**	3.6%
Nickel						
Ni(SO <sub>4</sub> ) <sup>*</sup>	0.310	28.0	933	2.4%	939	0.7%
Manganese						
Mn(NO <sub>3</sub> ) <sub>2</sub> <sup>*</sup>	0.311	47.7	860	2.4%	876	-2.0%

<sup>\*</sup>added as 2 M solution (Ni), 50 wt% solution (Mn); only salt masses are given here.

<sup>\*\*</sup>No analysis for iodine was performed

Iron is the classic Fenton catalyst. The literature search cited earlier in this work pointed out that ammonia is refractory to treatment by Fenton chemistry. That was shown to be the case in this study.

The transition metals copper, nickel and manganese did not show promise as useful catalysts on the acid side. Overall, none of the acid side hydrogen peroxide chemistries tested appear to be promising.

Alkaline side testing results are in Table 5. Testing used simulant initially adjusted to pH 9 ± 0.5 with drops of 5 M NaOH (6N sulfuric acid used if there was an overshoot). Iron and manganese were excluded from alkaline side testing because there is no chemistry mechanism to keep them soluble. In contrast, there is some ammonia complexation that may keep nickel, copper, and cobalt soluble. These transition metals are known to complex ammonia, boosting their solubility. Dissolved metal ion concentrations are given in Table 5 under “Metal Found”. Formation of hydroxide solids in some cases (like iron) would provide catalytic surfaces that decompose

hydrogen peroxide to oxygen, wasting the reagent. Temperature in these tests remained in the range of  $42 \pm 2^\circ\text{C}$ . The copper and nickel test pH ranges as monitored were 8.1 to 8.4, and 8.3 to 8.7, respectively.

**Table 5. Alkaline Hydrogen Peroxide Results**

Test Metal and Reagent	Salt mass added, grams	Catalyst Element added, mg	1.5 hr	1.5 hr	3 hr	3 hr
			Metal Found mg/L	% NH <sub>3</sub> removed	Metal Found mg/L	% NH <sub>3</sub> removed
Nickel						
Ni(SO <sub>4</sub> )*	0.0365	3.3	90.2	18.6%	89.9	21.9%
Cobalt						
Co(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	0.4893	99.7	68.8	11.3%	81.7	11.3%
Copper						
Cu(NO <sub>3</sub> ) <sub>2</sub> ·2.5H <sub>2</sub> O	0.0706	19.3	160	21.1%	166	25.9%
Molybdenum +I						
Na <sub>2</sub> MoO <sub>4</sub> ·2H <sub>2</sub> O	0.2415	95.8	962	2.0%	986	4.2%
KI***	0.031					
Chromate	41.7 mg/L	3.8				
(in simulant)	as Cr		22.8	11.0%	22.8	12.4%

\*added as 2 M solution; only salt mass is given here

\*\*Iodine in solution not measured

\*\*\* Iodide and molybdate were tested together at pH 9

Alkaline catalysis of hydrogen peroxide showed initial promise for some tests since easily measureable reductions in ammonia were seen. The fact that the 1.5 and 3 hour sample ammonia remaining for the tests are not much different from each other suggests that some hydrogen peroxide has been wasted (depleted) by decomposition to oxygen and water. Copper appears to be the best of the catalysts tested, though nickel was not far behind. If alkaline conditions are the best situation for ammonia removal by peroxide, further work would be needed to refine such processing. One disadvantage to alkaline side processing is that if gas is evolved (either nitrogen or oxygen are likely), such gas will contain ammonia stripped out of the alkaline solution. Such ammonia would potentially require abatement.

#### *Sodium Nitrite Tests*

Table 1 simulant, simulant with the platinum/rhodium wire in the flask, and the chromium-bearing simulant of Table 2 were tested using the sodium nitrite salt chemistry. Table 6 below provides the results. No effect of the platinum wire was seen. The first two test outcomes in the table do not look significantly different from each other. The chromate simulant showed better ammonia removal than the others, but that simulant also started with nitrite content (see Table 2), and the nitrite addition to start the test was still 2.5 g. Adding 2.5 g sodium nitrite to

88.4 mL of simulant boosts the nitrite concentration by 0.41 M. The concentration of nitrite in that simulant was not known at the time of the test, but its kinetic effect to improve results is clear.

Overall, the results of the Phase I nitrite tests show that this process would be an excellent candidate for further study. The process would have an advantage of no ammonia release because of the acidic nature of the solution. The amount of ammonia removal in 3-hour testing was very good as well.

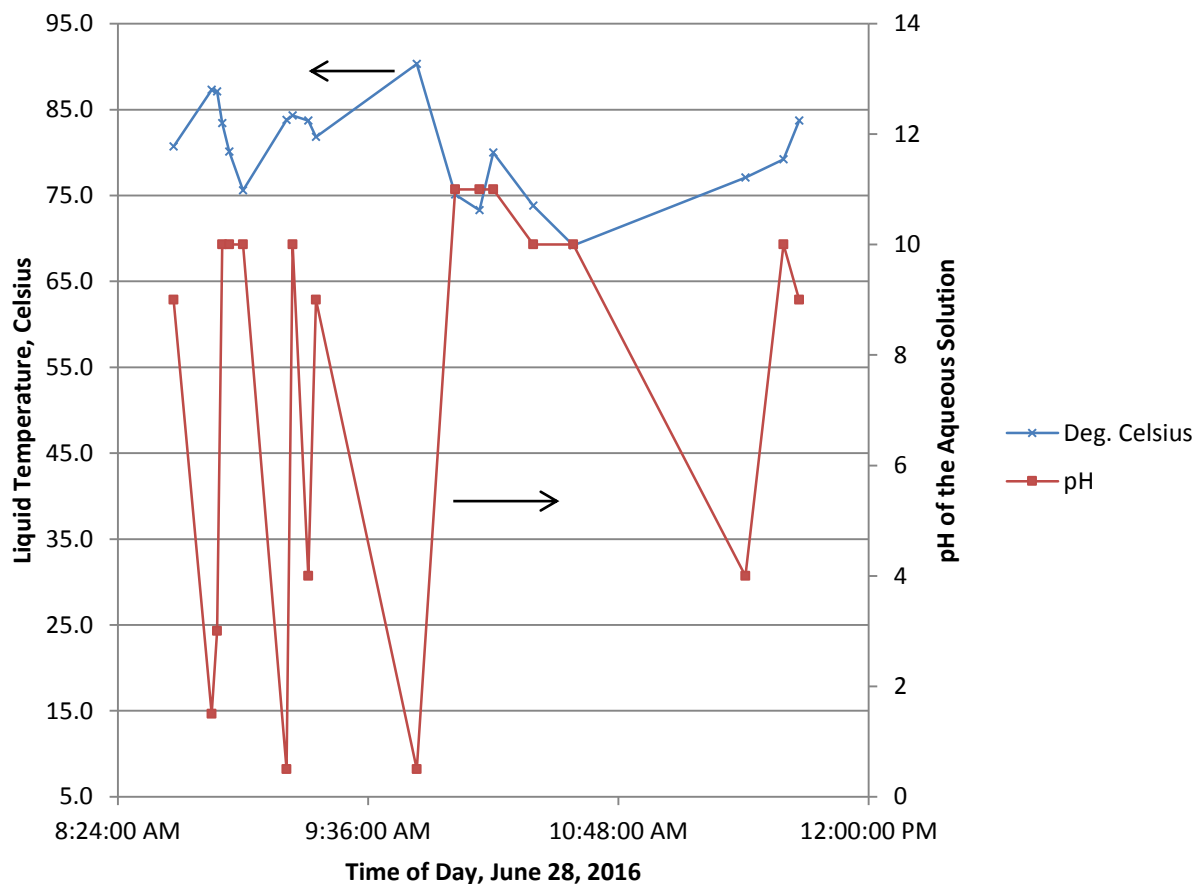
**Table 6. Nitrite Reaction Results**

Nitrite Test	1.5 hr	3 hr
	% NH <sub>3</sub> removed	% NH <sub>3</sub> removed
Sodium nitrite		
No catalyst	44.7%	43.1%
Sodium nitrite		
Pt/Rh wire	42.2%	41.5%
Sodium nitrite		
Table 2 simulant (contains Cr)	63.0%	69.8%

#### *Peroxydisulfate Test*

The one peroxydisulfate test demonstrated excellent oxidation of ammonia. No catalyst was used. The test was started with simulant at pH 9. Temperature and pH were controlled manually (5 M NaOH was added as needed given the tendency for pH to drop). Figure 2 shows the temperature history and pH excursions. The rate of pH excursions was faster than expected and manual control with pH paper checking could not keep the process steady. When ammonium sulfate is oxidized by this process, this salt converts to sulfuric acid (ammonium ion is removed, leaving the sulfate). This drops the pH. The manual additions of sodium hydroxide were needed to neutralize the acid produced. A positive outcome observed here is that the pH excursions were initial evidence that the ammonia destruction reaction was actively operating.

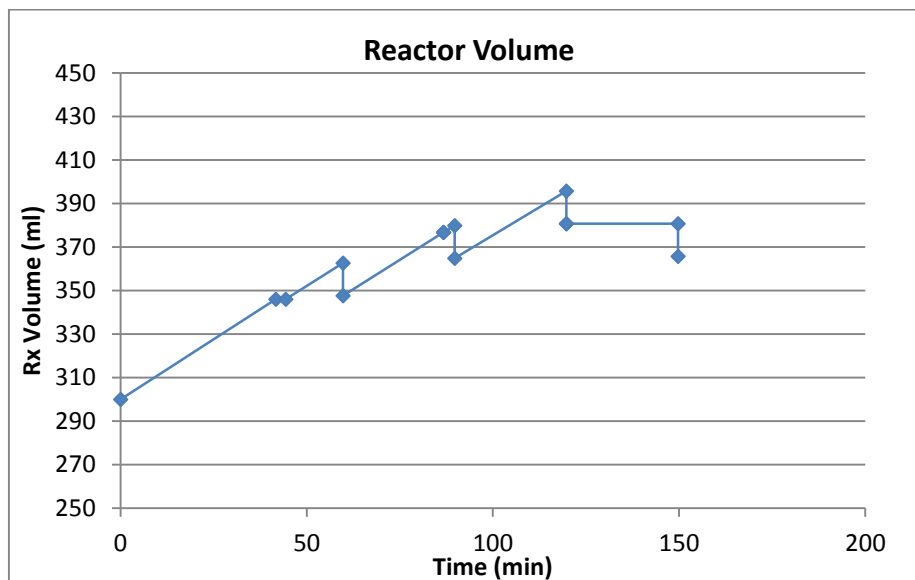
The results of the test were that 67.6% of the ammonia was removed after 1.5 hours, and 79.2% in total was gone after 3 hours. Removal was thus rapid. In calculating these removals the initial solution volume was adjusted for reagent salt volume added (13.5 grams is 5.6 mL of salt volume, effectively diluting the ammonia in the initial 88.4 mL of feed).

**Figure 2. Temperature and pH History for the Peroxydisulfate Test**

## RESULTS – Phase II

Two reactor tests demonstrated ease of processing and a clean, efficient reaction between ammonium ion and nitrite. The first test, labeled Rx1 below, was started cautiously with no initial spike of nitrite, and nitrite reagent was added at a relatively slow linear rate (about 1.06 mL/min for 120 minutes). The second test, labeled Rx2, started with a fast initial spike of 43.8 g of the nitrite solution at time zero. The goal of this was to get the reaction processing underway at a faster rate. In addition, nitrite solution was added at a faster rate than that of Rx1. The nominal rate of linear addition was 1.6 mL/min for Rx2.

Figure 3 shows reactor volume as a function of time. Time for this and following figures is in minutes after nitrite is first added to start the reaction. Sudden decreases reflect the removal of 15 mL samples. The samples were cooled, pH measured, and then they were quenched with potassium carbonate before being submitted for analyses. Results of the analyses are plotted in Figure 4. The data on the right side of Figure 4 represent a sampling after the reactor sat at room temperature over a weekend. The reactor contents were highly effervescent in the initial hour of operation as shown in Figure 5.

**Figure 3. Reaction Liquid Volume for Rx1**

An important result shown in Figure 4 is that at the end of the test, ammonia and nitrite concentrations were equal. Since the test was designed to have the same mole contents of these two reagents, the equivalence at the end shows the high one-to-one efficiency of the reaction. In other words, the initial moles of ammonium ion were equal to the final total of added nitrite. Side reactions such as those that would waste nitrite and perhaps release NO<sub>x</sub> were thus minimal.

Figure 4 shows how the reaction was slow initially. Sodium and nitrite concentrations both increased together in the first 50 minutes while ammonium ion declined slowly (probably because of dilution). Nitrite and ammonium ion then both show declines after that. A second Test Rx2 described later was thus started with an initial fast charge of sodium nitrite to get the reaction underway more quickly.

Figure 4. Composition History for Rx1

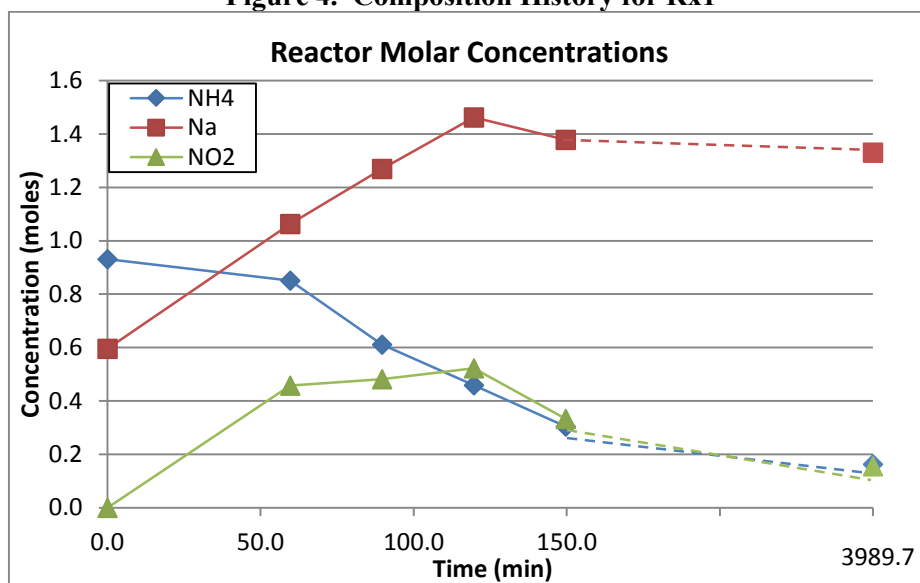


Figure 5. Evolution of Nitrogen Gas in Rx1

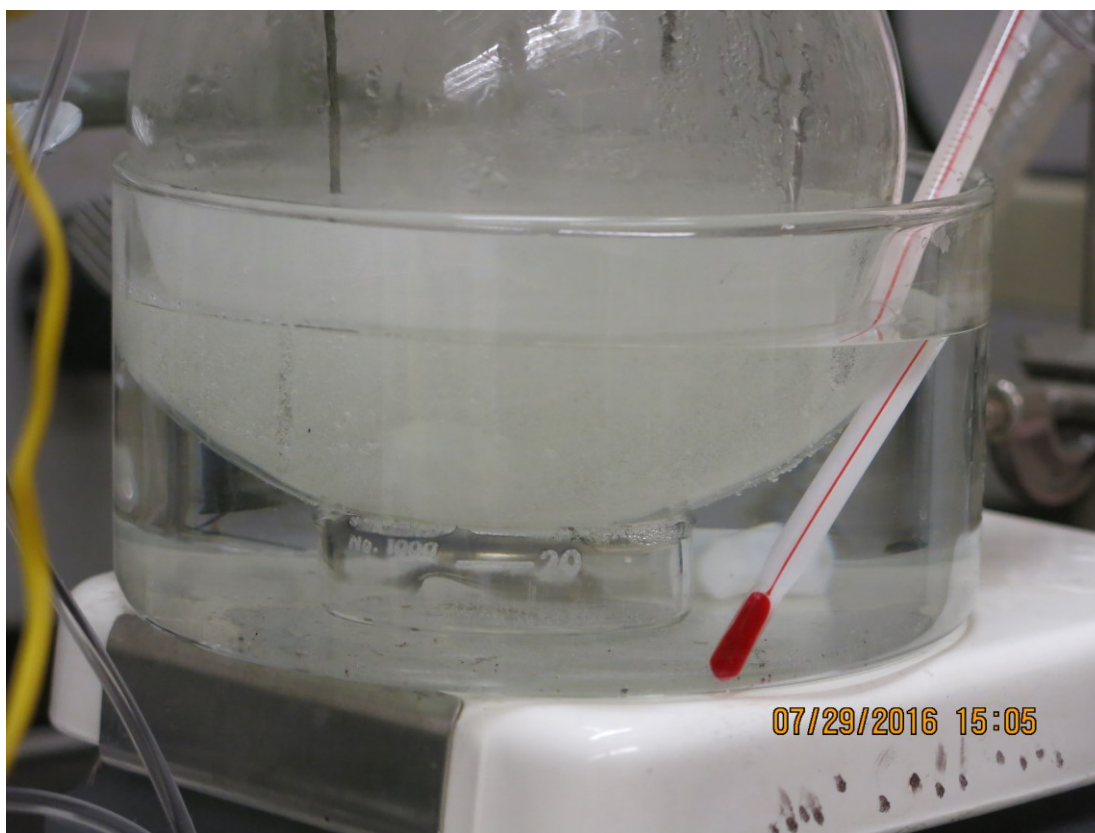


Table 7 provides an overall efficiency estimate for Rx2. Moles of  $\text{NH}_4^+$  and  $\text{NO}_2^-$  put into the campaign are shown, and calculations of moles left at the end are then shown. The efficiency is the ratio of differences, (moles  $\text{NH}_4^+$  consumed/moles  $\text{NO}_2^-$  - consumed).

**Table 7. Overall Moles In and at the End of Rx1 Testing**

	Ammonium Moles	Nitrite Moles
Input	0.931	0.9675
End of test	0.163	0.156
Difference	0.768	0.8115

Overall Efficiency of Reagent use was 94.6%

Figure 6 below shows how occasional pH adjustment with a few drops of 3 M sulfuric acid leads to increased heat release. Temperature increases are seen at each addition as indicated. No external heat was added for most of the test. Heat from the reactor was diffusing to the water bath that it was sitting in, and then was being lost to the chemical hood air flow. The water bath had no active cooling outside of natural heat loss.

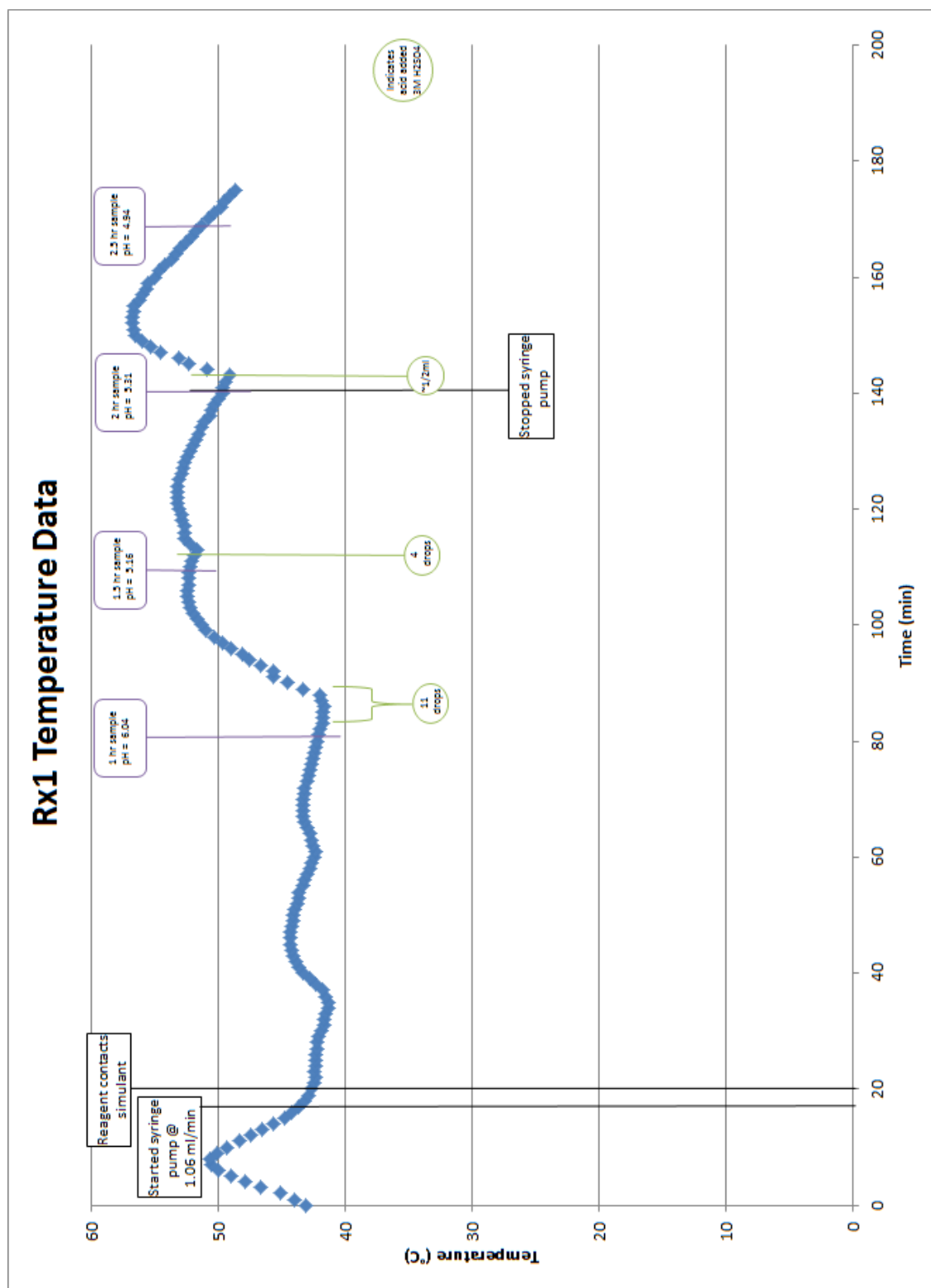


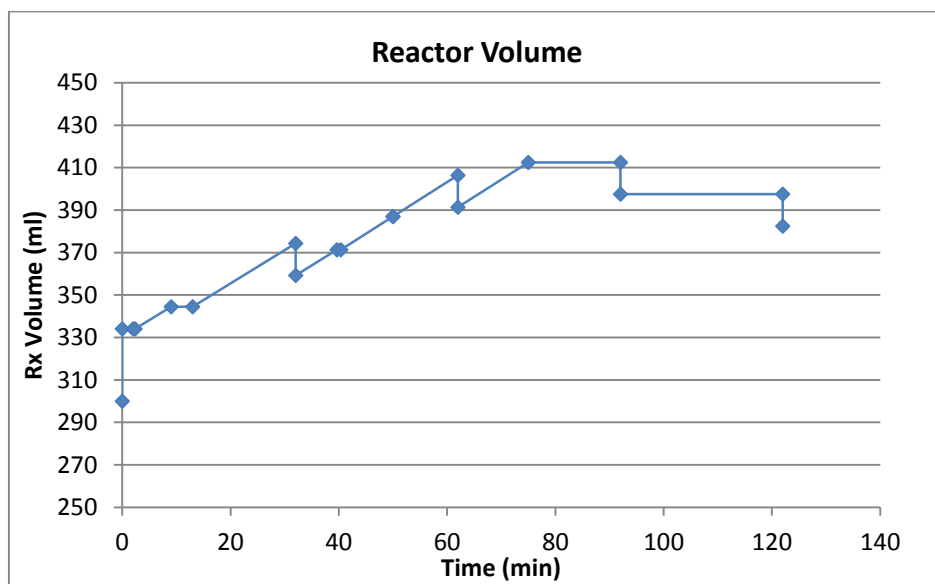
Figure 6. Temperature and pH History for Rx1



Reactor Test 2 was run with the more aggressive nitrite addition program described above, and slightly more total nitrite was added. pH was held lower than for Rx1 as well. Despite the more aggressive strategy, the process was easy to control and its temperature did not rise above the maximum seen in Rx1. The test ran smoothly with no surprises. Figures 7 and 8 show basic data histories for Rx2. The data on the right side of Figure 8 represent a sampling after the reactor sat at room temperature overnight.

An advantage made available for Rx2 was the use of the Raman gas probe. The probe is blind to the argon purge, and only sees polyatomic gases like nitrogen, oxygen, NO<sub>x</sub>, ammonia, and nitrous oxide. Since the argon rate was constant at 100 mL/minute, the nitrogen evolution rate can be estimated from Figure 9. For example, when nitrogen comprised 66.7% of the reactor headspace vapor, nitrogen was being evolved at 200 mL/minute. This calculation was applied to the Raman data to provide the evolution curve in Figure 9.

**Figure 7. Reaction Liquid Volume for Rx2**



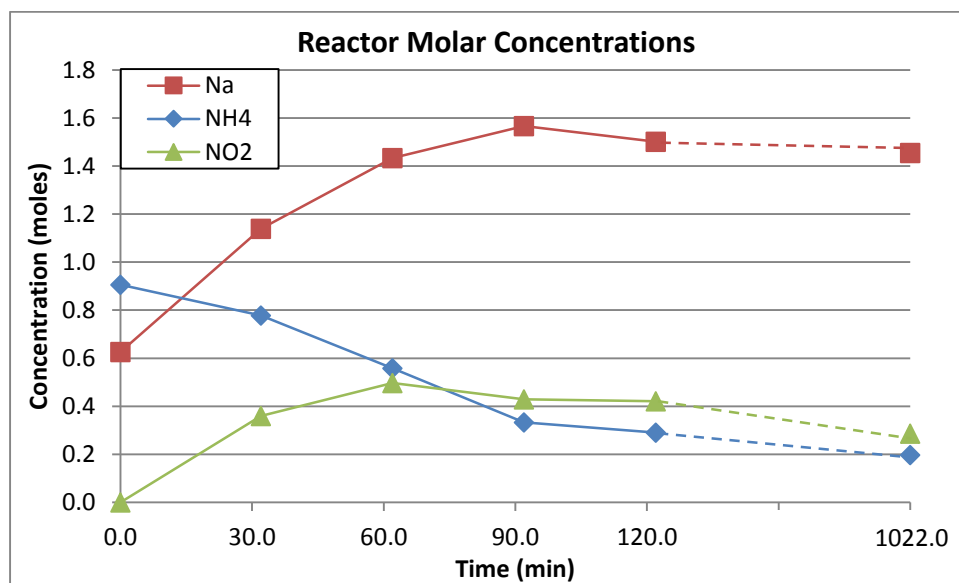
**Figure 8. Chemical Composition History for Rx2**

Table 8 provides an overall efficiency estimate for Rx2. Moles of  $\text{NH}_4^+$  and  $\text{NO}_2^-$  added in the campaign are shown, and a calculation of moles left at the end are also shown. The efficiency is the ratio of differences, (moles  $\text{NH}_4^+$  consumed/moles  $\text{NO}_2^-$  - consumed).

**Table 8. Overall Moles In and at the End of Rx2 Testing**

	Ammonium Moles	Nitrite Moles
Input	0.906	1.073
End of test	0.198	0.286
Difference	0.708	0.787

Overall Efficiency of Reagent use was 90.0%

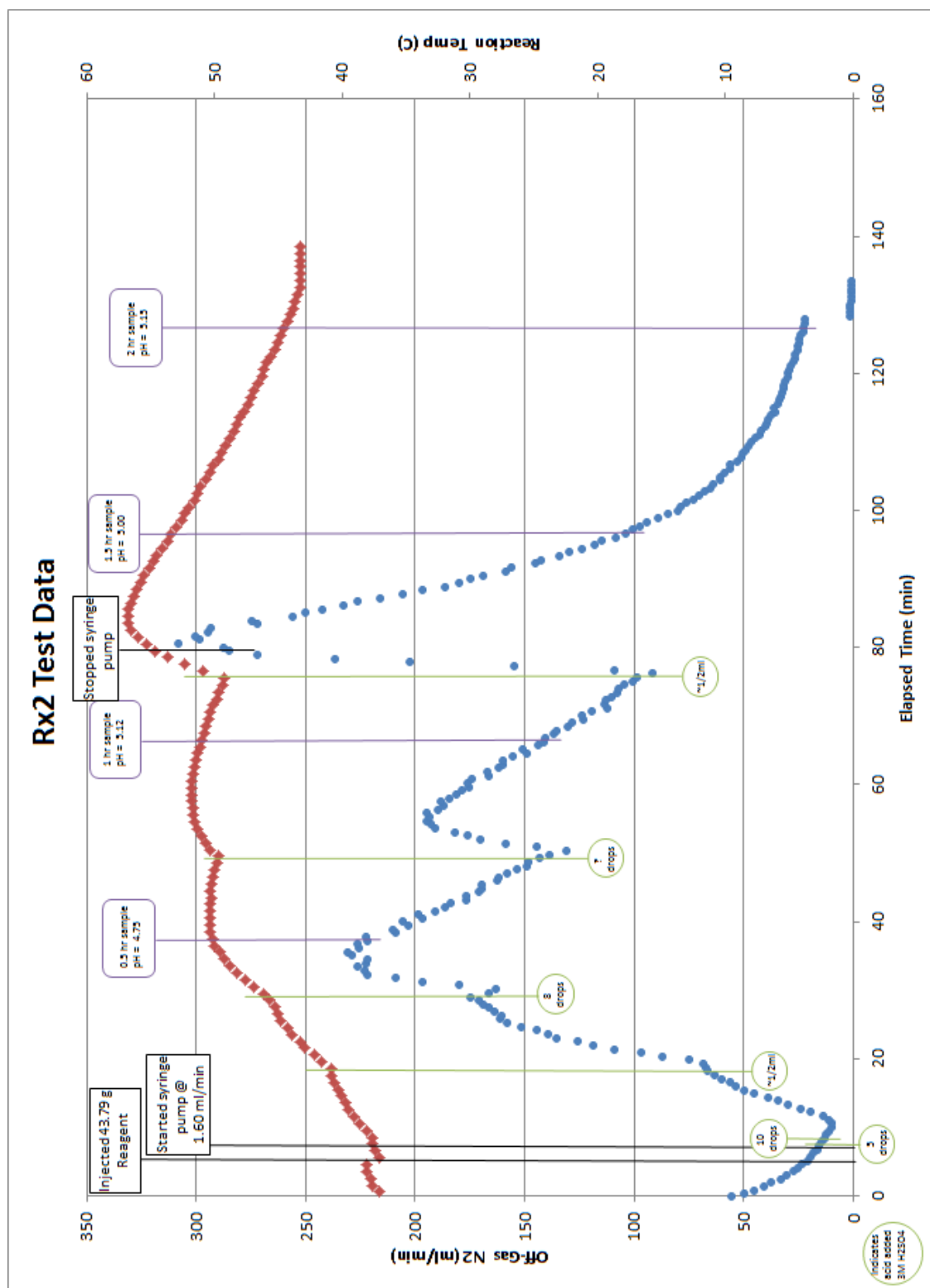


Figure 9. Temperature (blue), Nitrogen Evolution (red), and pH History for Rx2

## CONCLUSIONS

The ammonium / nitrite process demonstrated here is recommended for further consideration as a practical process for ammonia remediation from liquids. Use of this ammonia removal process in the existing Hanford ETF evaporator is likely practical. Key advantages of the process include:

- The oxidant used, sodium nitrite, is relatively non-corrosive compared to other common oxidants like halide oxides or oxygen bearing solutions. Sodium nitrite is a familiar constituent of nuclear waste processing and is also commercially available.
- The process was shown to run at practical rates at moderate temperature and pH of around 5. Tests performed in this study worked well without including catalysts. Higher temperature would increase the reaction kinetics.
- The process was easy to control with very small additions of pH-adjusting reagent (sulfuric acid in this case). The key reaction would not affect pH very much as sodium sulfate, a neutral salt, is produced.
- The process ran at high (90-95%) efficiency of nitrite usage with almost no byproducts.
- Kinetic data from literature is available.

Peroxide processes were found to show some initial promise on the alkaline side. Copper, nickel, or cobalt were held in alkaline solution by ammonia. These ammonia-complexing metals appear to be catalytic when peroxide is used in an alkaline solution. If alkaline solution is required, it is recommended that further examination of such a process with a copper catalyst be pursued. Acid-side hydrogen peroxide testing did not show any promising chemistries in this work.

Sodium peroxydisulfate was very effective in ammonia removal. It is not recommended, though, because of major practical problems. First of all, the mass of sodium peroxydisulfate needed to oxidize a mole of ammonia is excessive. For example, one mole of ammonia weighs 17 grams, and ideally 1.5 moles of sodium persulfate (357 grams) would be needed to oxidize it to nitrogen gas and water. The amount of added sodium sulfate would be excessive per this example. It was also observed that while the reaction is best suited for high pH, the pH frequently dropped, indicating the need for automatic pH control with frequent caustic addition.

## REFERENCES

- <sup>i</sup> Adamson, D.J., Nash, C.A., McCabe, D.J., Crawford, C.L., Wilmarth, W.R., "Laboratory Evaporation Testing of Hanford Waste Treatment Plant Low Activity Waste Off-Gas Condensate Simulant," SRNL-STI-2013-00713, r. 0, January, 2014.
- <sup>ii</sup> Abramowitz, H., Brandys, M., Cecil, D'Angelo, N., Matlack, K.S., Muller, I.S., Pegg, I.L., Callow, R.A., Joseph, I., "Technetium Retention in WTP LAW Glass with Recycle Flow-Sheet: DM10 Melter Testing," VSL-12R2640-1, r. 0, RPP-54130, September, 2012.
- <sup>iii</sup> Halgren, D.L., "200 Area Effluent Treatment Facility Basin 42 Campaign 2013 Process Control Plan", CHPRC-02039 r.0, CH2M Hill Plateau Remediation Company, April 2013
- <sup>iv</sup> Russell, R.L., Westsik, J.H. Jr., Rinehart, D.E., Swanberg, D.J., and Mahoney, J., "Secondary Waste Simulant Development for Cast Stone Formulation Testing", PNNL-24195, Pacific Northwest National Laboratory, April 2015.
- <sup>v</sup> Nash, C. A., "Review of Options for Ammonia/Ammonium Management", SRNL-STI-2016-00104 r. 0, May 2016.
- <sup>vi</sup> McCabe, D.J., "Task Technical and Quality Assurance Plan for (ICP) Secondary Liquid Waste Stream Technology Maturation", SRNL-RP-2015-01038, r. 0, December 2015.

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vii Halgren, D.L., “Effluent Treatment Facility Mass Balance Calculation for DFLAW Mission.” HNF-58821, Revision 0, July 2015, pages 538 to 541. The mass balance calculation used input from RPP-17152, Revision 10, “Hanford Tank Waste Operations Simulator Model (HTWOS) Model Design Description.”

viii Cozzi, A.D., “Preparation and Characterization of a Simulant for the FY16 Liquid Secondary Waste Form Development and Waste Form Quantification Testing”, SRNL-L3300-2016-00017, r.0, June 2016.

ix International Critical Tables of Numerical Data, Physics, Chemistry, and Technology, first edition, E. W. Washburn, editor-in-chief, McGraw-Hill, New York, NY (1929).