Contract No:

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-08SR22470 with the U.S. Department of Energy (DOE) Office of Environmental Management (EM).

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Review of Options for Ammonia/Ammonium Management

C. A. Nash

May 6, 2016

SRNL-STI-2016-00104, Revision 0

SRNL.DOE.GOV

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Prepared for
U.S. Department of Energy

Keywords: *Ammonia*
Hanford

Retention: *Permanent*

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EXECUTIVE SUMMARY

This report is a review of literature supporting practical ammonia/ammonium destruction processes. Melter research supporting Hanford Low Activity Waste (LAW) glass production has shown that significant amounts of ammonia will be in the melter offgas condensate. Further work with secondary waste forms indicates the potential need to remove the ammonia, perhaps by an oxidative process.

This review finds likely practical chemical methods to oxidize ammonia in aqueous solution at moderate temperatures and atmospheric pressure, using easily obtained reagents. Leading candidates include nitrite oxidation to produce nitrogen gas, various peroxide oxidative processes, and air stripping. This work reviews many other processes and provides reasoning to not consider those processes further for this application.

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LIST OF ABBREVIATIONS

DFLAW	Direct Feed Low Activity Waste
ERDF	Environmental Restoration Disposal Facility
ETF	Effluent Treatment Facility
IDF	Interim Disposal Facility
LAW	Low Activity Waste
LAWPS	Low Activity Waste Pretreatment System
ORP	Oxidation Reduction Potential
SBS	Submerged Bed Scrubber
SRNL	Savannah River National Laboratory
WTP	Waste Treatment Plant
WESP	Wet Electrostatic Precipitator

1.0 Introduction

This report reviews methods for the chemical destruction of ammonia that is initially contained in aqueous solution. Ammonia, mainly from Hanford Low Activity Waste (LAW) vitrification, is estimated to be a significant secondary waste component. SRNL scope includes work to address the issue, because ammonia has been found to be evolved when some secondary waste forms are made.[i] Such waste forms are to immobilize evaporator bottoms concentrates mainly from the Hanford 200 Area Effluent Treatment Facility (ETF).

The Hanford ETF currently concentrates chemical species, mainly salts, which are then dried and sent to the Environmental Restoration Disposal Facility (ERDF). Unit operations of reverse osmosis and evaporation are key in the liquid solution concentration. Current alternatives to the drying operation are struvite precipitation (magnesium ammonium phosphate), wet air oxidation, Ceramicrete™ (a pH neutral waste form that contains magnesium phosphate), and steam stripping with controlled release of the ammonia.

This literature survey has found practical processes that can destroy ammonia in aqueous solution. The main byproducts are nitrogen gas and some nitrate or nitrite ions, which are typical of what is already in Hanford waste streams. The study of dissolved ammonia oxidation does not preclude other disposal options, but has been identified as potentially helpful in coordination with grouting options.

2.0 Ammonia Management Strategies

This literature survey considers a wide range of options for the destruction of ammonia/ammonium ion in aqueous solution. Option practicality is addressed, given that some of the options can treat the incoming feed with liquid phase chemistry near room temperature and pressure. In contrast, other processes require high temperature and pressure and the vaporization of the feed to be treated.

2.1 Feeds to Process

Aqueous ammonia-bearing solutions may be found throughout the future LAW system, EMF, and streams to the Hanford 200 Area ETF. In related work, Adamson et al. evaporated a simulant that started at 0.09 M ammonium ion, concentrating it as much as 30 times.[ii] That simulant represented the combined liquid streams from the Waste Treatment Plant (WTP) Submerged Bed Scrubber and also the Wet Electrostatic Precipitator (SBS/WESP), and is more similar to the feed to the EMF. However, most of the ammonia in this stream will partition to the EMF evaporator offgas condensate, and end up in the ETF, where it will be concentrated in that evaporator, increasing the concentration by an order of magnitude. In addition, ammonium levels above 1 M are found in ETF evaporator bottoms (see below).

A benchmark for an ETF evaporator bottoms composition is found in work by Russell and co-workers.[iii] Products for immobilization testing, copied from the Russell et al. work, are shown in Table 2-1 below. It is clear that ammonia is relatively high. Ratios of components shown in Table 2-1 are given as mole/mole sodium, but the actual concentration of sodium in current simulant formulations is about 0.2 M. For practicality it can be said that the feed stream contains mainly inorganic salts that are not that reactive, along with molar quantities of ammonium ion.

Table 2-1. Stream Compositions Found in Russel, ref. iii

Waste Constituent	242-A Evaporator	ERDF Leachate	WTP Off-gas
	Concentration (moles/mole Na)(a)		
Na	1.000	1.000	1.000
K	0.044	--	--
Ca	0.305	0.773	--
Mg	0.120	0.417	--
Si	0.140	--	--
NH_4	7.213	--	1.119
Cl	0.173	0.729	0.020
F	--	--	0.003
SO_4	4.320	1.061	0.847
NO_3	--	0.529	0.397
NO_2	--	--	0.003

(a) After charge balancing.

Another simulant to consider would be the latest SBS/WESP simulant related to Adamson's work mentioned above. A simulant of that stream is being revised based on testing and updated feed compositions, but still contains ammonium ion, chromate, and various inorganic salts. Testing of that simulant would allow observation of any effects that chromate might have on processing. This would be relevant for chromium bearing feeds such as SBS/WESP effluents. Chromium would not be present in evaporator overheads or ETF streams. Some of the literature discussed below mentions chromium salts as possible catalysts for ammonia destruction during peroxide processing.

2.2 Ammonia Destruction Processes that are Likely Practical

2.2.1 Reaction with Nitrite Ion in Solution

Aqueous feeds containing ammonia will easily react with dissolved nitrite ion to produce nitrogen gas.[iv] The reaction as shown in (A) here is a common way to produce nitrogen gas in the chemical laboratory.

$$NH_4^+ + NO_2^- \Rightarrow 2H_2O + N_2 \qquad \text{(A)}$$

The reaction is ideally performed in mildly acid solution (pH 3 to 6). Temperature leads to an increase in reaction rate as expected. The reaction would be slow at high pH where ammonia is deprotonated, in which case dissolved ammonia and ammonia vapor would be present. A problem at excessively low pH is that the nitrite (protonated as nitrous acid, which is weak and unstable) would also cause toxic and reactive nitrogen oxide gases to be released.

The rate of this aqueous phase reaction has been studied extensively, and key works are cited here. Dusenbury and Powell found rate constants above 1E-06 liter per second per mole at 30 °C if the pH is below 4.[v] The rate constant k_f they give is defined in the rate expression equation (B) below. The rate is 1000 times slower at pH 7. Their study of kinetics found the rate to be first order in dissolved NH_4^+ ion and also first order in nitrous acid, HNO_2. From a different perspective, they found that ionic strength of the solution had a retarding effect on the reaction. The reason they give is that the chemical activity of reacting species is higher at low ionic strength. Their temperature dependent rate data showed an about 1.7 times increase in rate constant for every 5 °C in the range of 20 to 35 °C.

$$d(N_2)/dt = k_r * [NH_4^+] * [HNO_2] \qquad (B)$$

Nguyen, Iwaniw, and Fogler also studied the kinetics of the aqueous reaction (A) above and provided both data plots and kinetics equations.[vi] Their equations follow their conclusion that while the rate is first order in ammonium ion, it is second order in nitrite ion. One figure from their work is shown below, showing the effect of pH and temperature. The figure assumes concentrations of 0.5 M both of ammonium and nitrite ion. A temperature of 30 °C corresponds to the middle of the figure (1/T = 0.0033 K). At pH 4 the rate of decline of each species is about 5E-05 mole/L/s or 0.18 M/hr. That rate is approximately doubled if the temperature is increased from 30 to 50 °C. Such rates are significant given the initial reagent concentrations of 0.5 M. The practical limitation of producing gas bubbles without foaming over would be important in controlling the process rate, along with providing sufficient cooling. Limiting of available nitrite by controlled addition is a practical way to control the process rate.

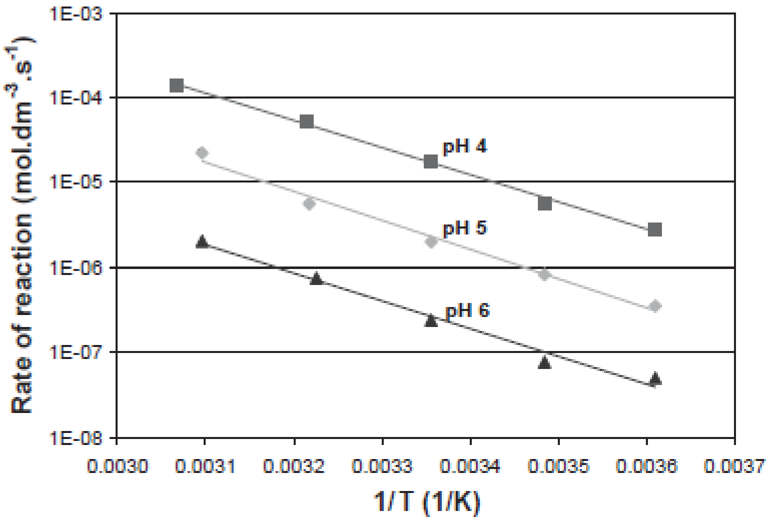


Figure 2-1. Effect of Temperature and pH on Reaction Rate, from ref. vi

Kyser performed small reactor tests with sodium nitrite addition to destroy ammonium ion in various acid strengths.[vii] Nitric or sulfuric acid strengths in the tests solution were 2 to 8 M, and the initial ammonium concentration was 0.25 M. Temperature was 95 °C, since the high solution temperature was found to increase efficiency of nitrite usage to produce nitrogen in this extremely high acid condition. Efficiencies were in the range of 20 to 60%. The work used high acid because of the type of solutions needing remediation in H-Canyon.

Several works indicate various catalysts for this reaction. While much work was done with the gas phase and high temperatures, the current review focuses on aqueous chemistry. Russian work found that dichromate will decompose concentrated (~3 M) ammonium nitrite in a self-heating reaction, even starting at 20 °C.[viii] They found that ammonium nitrite is highly unstable, both in a dry state and in concentrated aqueous solutions. The work mentions the practice that when such solutions are used industrially they are normally stored at a pH of 8 - 9 and a temperature of 5 °C or less. The work is cautionary about decomposition (undesired in that case) because the dichromate concentrations used were very low, on the order of 6 to 15 millimolar. Such results are significant to the current case because Hanford waste contains chromate and some of this carries over from the melter to the SBS.[ix]

There are other works examining the use of transition metal catalysts for the nitrite-ammonium reaction.

Penzeli et al. measured the kinetics of the reaction between aqueous ammonia and nitric oxide when a copper catalyst is present.[x] While they introduced nitric oxide (NO) gas into solution at pH 9, nitrite on the mild acid side will probably also produce NO at some rate. The paper explained that the nitric oxide reacts with ammonia that is complexed with copper. Copper was at micromolar concentrations and reactions were studied at 25 °C.

2.2.2 Fenton Chemistry

Fenton chemistry for the oxidation of dissolved chemicals has been studied for over a century. Fenton reported, for example, that ferrous sulfate acts as a catalyst rather than as a reactant when mixed in small amounts with tartaric acid and hydrogen peroxide.[xi] Since then hydrogen peroxide with an iron catalyst has been used widely for destruction of unwanted organic compounds. There are many reviews of the chemistry of this process, and two are cited here as examples.[xii],[xiii]

A caution needs to be given here about the use of classic Fenton chemistry. While it has been studied and used for a wide selection of waste water chemicals, ammonia destruction appears to be difficult. Relevance to the ammonia issue is given in the review of papers below when available. Some work measured reductions in ammonia nitrogen when other target species were being oxidized. It is likely that peroxide chemistry would have to be modified to best address ammonia in the absence of organic species and nitrogen-containing organics.

Bigda wrote a summary article for the practical engineering scale use of Fenton chemistry to treat wastewater.[xiv] The article lists many organic chemicals that can be oxidized by the Fenton process, though the work does not say why ammonia is not listed (it does list organic amines). It gives the typical conditions for this process, as are also found in other papers on the topic, as cited in this report. Process pH is 3 to 4, and temperature is just over 25 °C (the reaction generates heat – see Section 3.1 below). pH above 6 will begin to precipitate the iron catalyst, inhibiting further processing. The optimum iron to peroxide weight ratio is 1:5 during operation. Hydrogen peroxide is added steadily rather than all at once so that a thermal runaway is avoided. The article points out that the process solution is corrosive when the hydrogen peroxide is reactive, because the hydroxyl radicals in solution are aggressive. Industry typically uses 35 to 50 weight percent hydrogen peroxide. For a wide range of wastewaters, the reaction lowers the pH, so it must be controlled with the continuous and controlled addition of caustic.

Bidga pointed out that the worst safety issue for the Fenton process is thermal runaway on startup. The chemistry has an initiation phase, and patience is required so that the operator does not add excess hydrogen peroxide before the reaction gets underway. Changes in gas evolution, temperature, and pH changes would provide evidence that the chemical reactions are underway.

Shetty and Verma studied Fenton remediation of pharmaceutical waste water.[xv] Their process was run at 30 °C and removed 35 to 65% of ammonia nitrogen in one hour batch runs. They did not use any feed that only contained ammonia. The ammonia nitrogen level started at 65 mg/L, accompanied by chemical oxygen demand (COD) of up to 10,000 mg/L. Their optimal hydrogen peroxide concentration was 900 mg/L (0.026 M), and ferrous sulfate dosages were in the range of 1000 to 4000 mg/L. Note that they appear to use more iron than peroxide, in contrast to Bigda's recommendation. Shetty and Verma did not extend the iron:peroxide ratio beyond the range of 1:1 to 1:3 in molar (not weight) units.

Kulik and co-workers demonstrated Fenton chemistry to destroy organic dyes at pH 3 and 20 °C.[xvi] They cited other work to support their use of 1:6 weight ratio ferrous iron to hydrogen peroxide. The hydrogen peroxide was added to batches all at once. Dye color indicated about 95% destruction for 24 hour treatment tests. The work was in support of industrial waste water treatment.

Li, Comfort, and Shea studied Fenton Chemistry for the treatment of soil and ground water contaminated with military waste chemicals like TNT.[xvii] Their process conditions included: pH 3, temperature held to 23 +/- 2 °C, 0.08 g/L ferrous ion added using ferrous sulfate 7-hydrate, and an initial addition of a measured amount of 30 wt% hydrogen peroxide. pH declined with time but was not controlled. TNT being treated started at 70 mg/L. Under these conditions (using 0.08 g/L iron) they found that the reaction was mostly complete in 5 hours. They reported that reaction rate was mainly controlled by the iron catalyst concentration, since it produces the active hydroxyl radicals from the hydrogen peroxide. They concluded that Fenton chemistry is a successful and useful process for the application.

Padoley et al. tested many conditions for treatment of waste water with Fenton chemistry.[xviii] Chemical oxygen demand (COD) of the feed was very high, being in the tens of thousands of mg/L. Their study of pH found that pH of 1-3 was optimal. They did not report temperature or its control. Ferrous sulfate 7-hydrate was used in the range of 0.4 to 4 g/L. They recommended Fenton chemistry for their application.

Neyens and Baeyens published a review of the use of Fenton's chemistry in wastewater treatment, and presented the effects of different iron:peroxide concentration ratios.[xix] If iron was relatively high or equal to the hydrogen peroxide concentration, ferrous ion can quench the hydroxyl radicals in an undesired side reaction. A low iron:peroxide ratio is more efficient, and pH 3 is optimum.

2.2.3 Fenton-like processing with Copper or other Catalysts

Several works indicate that copper may work as a catalyst for solution oxidation with hydrogen peroxide. While this use to oxidize ammonia per se is not clear, the complexation of ammonia with copper ion likely would assist reactions while keeping the copper soluble in a higher (more alkaline) range of pH. Schweizer's reagent solution is an example of copper-ammonia solution that is stable at high pH.[xx]

Masarwa et al. identified both soluble copper(I) and chromium(II) as catalysts in acid-side Fenton chemistry.[xxi] This is significant because chromium may be present in Hanford waste treatment systems, although most likely as Cr(VI). Copper and chromium concentrations were at order of magnitude 0.01 M in Masarwa's work. Alcohols were being oxidized and the work did not test the effect on ammonia. The work suggested that a copper (III) species may be involved in promoting the oxidation of target chemicals.

Bokare and Choi reviewed Fenton-like processes that use catalysts other than iron. Despite its extensive list of processes using copper, manganese, cobalt, cerium, chromium, and other metals, the paper does not address ammonia oxidation. Some of the metals like copper and cobalt are complexed by ammonia, and that helps keep those catalysts soluble at a wide range of pH.

Shah et al. used transition metals at order of magnitude 0.01 M, pH 3, and hydrogen peroxide addition to measure decolorization of dyes in 24 hours at 22 +/- 1 °C.[xxii] Copper and cobalt were the best catalysts, and succinic acid was the best chelator for these. The work did not use ammonia, though some of the dyes contained organic nitrogen. Copper and cobalt decolorizations exceeded 75% in 24 hours.

Pham et al. studied basic interactions between copper ions and hydrogen peroxide.[xxiii] One series of reactions in the paper indicated that both Cu(I) and Cu(II) ions could cause hydrogen peroxide to release free hydroxyl radicals, similar to the action of iron in standard Fenton chemistry. It is also indicated that Cu(III) may be produced, and that it would be an aggressive oxidizer. Superoxide (O_2^-), another aggressive oxidant, was also identified. Experiments used micromolar concentrations of copper, showing how active it is in directing various reactions.

Peters et al. at SRNL studied alkaline copper/hydrogen peroxide chemistry for the oxidation of the tetraphenylborate and related organic chemicals in SRS Tank 48H.[xxiv] Copper was found to be an essential catalyst, though its effects were limited by its very low solubility at high pH. pH 9 appeared to be optimal for oxidation of the organics in the aqueous high sodium solutions. However, pH on the acid side was not explored because such a process would not be practical in a carbon steel tank on the large scale. Each 15 °C increase in reaction temperature provided a 2-3× decrease in the residual organics in the temperature range of 35 to 75 °C. No ammonia was in the system. Ammonia would be expected to boost the solubility of copper-containing chemicals at high pH.

Wong and Zhang studied the effect of iodide on the reduction of hydrogen peroxide in artificial sea water. Iodide is readily oxidized to elemental iodine by the peroxide.[xxv] The work provided rate constants for the reaction kinetics. Catalytic effects of molybdate were also discussed. pH range tested was 7 to 9. Examination of the effects of these catalysts on an ammonia process would be of interest, since halide oxidation of ammonia would likely occur rapidly in a catalytic cycle.

Yang and co-workers also explored the co-reacting effects of a halide, bromide in their case.[xxvi] Their goal was to reduce nitrate formation when ammonia was oxidized with ozone in solution. The paper lists reactions showing how oxidized bromine would be expected to assist in converting ammonia to nitrogen gas.

2.2.4 Air Oxidation with Catalysis

Muller reported the oxidation of ammonia at high pH (often using molar levels of NaOH) in the presence of oxygen gas, along with copper metal or oxides.[xxvii] The work showed both the catalytic effects of copper oxides and of ammonia conversion when copper metal corroded. Pressure was atmospheric and test temperatures were 25 to 75 °C. The high pH appeared to oxidize the ammonia mainly to soluble nitrite. One problem with gas contact and high pH solution is that significant ammonia can leave solution (above pH 11 or so). This is a complication with this alkaline air-sparged process.

Qin and Aika performed a survey of catalytic metal oxides supported on porous alumina.[xxviii] Their reaction conditions for stirred aqueous solutions of ammonium chloride and sodium hydroxide (initial pH 12) was air exposure at 1.5 MPa (218 psi) and a temperature of 503 K (230 °C). Ruthenium and palladium promoted the oxidation of more than 99% of ammonia in the batches in under 3 hours. A supported molybdenum catalyst reacted 81% of the ammonia in that time. A chromium oxide catalyst processed 15% of the ammonia. No catalyst (control) processed 11% of the ammonia. While a relatively high temperature and pressure was used, the speed and simplicity of the process, especially at high pH, is attractive. The fastest catalysts produced nitrogen gas, while the slower catalysts, including the chromium oxide, produced mostly nitrate.

2.2.5 Alkaline Persulfate/Peroxide with no Apparent Catalysts

Persulfate anion ($S_2O_8{}^{-2}$) is commercially available as the sodium, ammonium, or potassium salt.[xxix] It is a powerful oxidizer and details of its use to oxidize ammonia are given below. Persulfate is a stronger oxidizer on the electrochemical scale than hydrogen peroxide. It is a source of the oxidizing sulfate radical SO_4^-.

This review found work where ammonia can be destroyed by persulfate, peroxide, or a combination of the two. Simplicity is an advantage here if no catalyst is needed. Hilles et al. report kinetics of alkaline peroxide with persulfate in the destruction of organics and ammonia nitrogen in solution.[xxx] While the paper emphasizes the use of persulfate and its combination with hydrogen peroxide, it has some data showing that peroxide alone will destroy ammonia at practical rates at 28 °C and pH 11. 28% of the ammonia was destroyed in 2 hours, while dissolved organics were also destroyed. The initial ammonia concentration was about 0.1 M. While the paper says nothing about catalysts, the waste liquid (actual landfill leachate) did contain low concentrations of copper (0.44 mg/L), nickel (4.63 mg/L), cadmium (0.259 mg/L), and zinc (5.84 mg/L). The catalytic effect of such trace metals on the process was not recognized or investigated in the work.

A straightforward study of ammonia oxidation in aqueous solution at moderate conditions, with no other target species to oxidize, was published by Nakamura et al.[xxxi] They were able to oxidize more than 90% of ammonia in solution in 2 hours at 70 °C using persulfate. In addition, they made comparison tests with hydrogen peroxide to show the better performance of persulfate. Initial ammonia concentrations were in the range of 0.06 to 0.12 M. Both this work and that of Ghauch and Tuqan show that the process liquid temperature should be above 50 °C for practical rates of reaction when using persulfate.[xxxii] Nitrogen gas is the main product. The process is most effective on the alkaline side, pH 8 to 13. The works cited here do not call for a catalyst other than heat at the temperatures mentioned here. Nakamura tested solutions with and without copper ion, and reported some catalytic enhancement with copper, though it also produced more nitrate vs. nitrogen gas. They ran copper tests at pH around 10 while tests without copper were started at pH 13.5.

Another reagent with strong oxidizing powers is peroxymonosulfate, SO_5^-. One industrial source is the DuPont product OXONE™. Anipsitakis and Dionysiou compared OXONE with the classic Fenton chemistry and found that Fenton sometimes worked better to oxidze 2,4 dichlorophenol and atrazine, at pH around 3.[xxxiii] The benefit of OXONE was that it operated better than Fenton at higher pH, up to 9, and that cobalt was a better catalyst than iron or nickel.

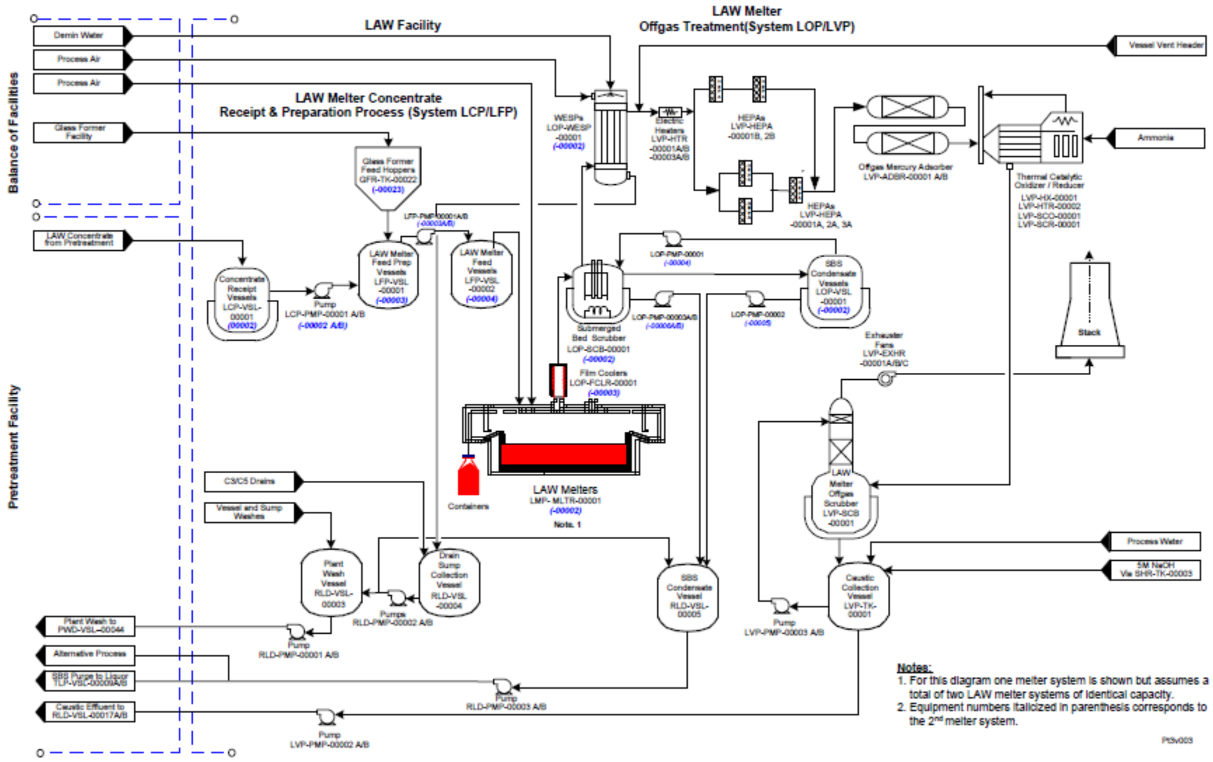
Kuo et al. studied ammonia oxidation at pH 8 to 11 with no known catalysts mentioned.[xxxiv] That process used ozone with and without hydrogen peroxide, but not with peroxide alone. It found that the presence of hydrogen peroxide with the ozone causes a more than one order of magnitude increase in the ammonia oxidation rate. This is a great benefit. Despite the magnitude of the efficiency boost from peroxide, the reaction mechanisms given in the paper require ozone as a co-oxidant.

2.2.6 Air Stripping

This is a simple process that uses air/liquid contact equipment such as a stripper tower. Its practicality depends on adequate disposal of the effluent air that contains the ammonia. If the ammonia concentration and emission rate is below environmental limits, then the air could be vented up a stack. If not, catalytic oxidation of ammonia in the gas phase, similar to a unit operation in the current flowsheet, could be implemented. Engineering of the stripping process is straightforward. pH of the feed must be adjusted upward to assist in driving ammonium ion to the molecular ammonia state. Liao et al. recommended a pH of 10.5, with a pH above 11.5 giving no substantial increase in benefit.[xxxv] They found that stripping towers were more effective than sparged tanks because the ability of the packed tower to handle a high volume of stripping air is much better than that of the tank. In about 10 hours they could remove about 90% of the ammonia in a feed batch recirculated through a stripper tower at 20 °C. The feed had up to 2200 mg/L ammonia initially.

2.3 Ammonia Management using an Operational Change

Figure 2.2 below is of the LAW melter (source of ammonia) and offgas processing equipment.[xxxvi] The SBS is the first operation to collect ammonia. It may be possible to destroy the ammonia there using solution chemistry. Solution chemistry here would include nitrite addition or one of the peroxide processes that should be practical. The SBS would need pH control and the ability to add liquid reagents at steady and controlled rates. Another option may be to operate the SBS on the caustic side (pH 12) so that ammonia passes through and goes to the thermal catalytic oxidizer where ammonia is currently to be added and oxidized. However, this would change the dynamics of mercury processing because of the chemistry between mercury and ammonia, which together form Millon's base. Such changes would require engineering studies beyond the demonstration that ammonia can be oxidized in SBS solution. The ETF is probably the best location to deal with ammonia because the ETF receives ammonia from sources other than the SBS and WESP for the LAW melters as well, particularly the caustic scrubber. That scrubber strips some ammonia from the gas stream that is present as unreacted ammonia from the catalytic oxidizer/reducer. The caustic scrubber liquid stream is sent directly to the LERF/ETF.



Notes:
1. For this diagram one melter system is shown but assumes a total of two LAW melter systems of identical capacity.
2. Equipment numbers italicized in parenthesis corresponds to the 2nd melter system.

Figure 2-2. LAW Melter and Offgas Unit Operations

2.4 Ammonia Management Options that are Not Likely for DFLAW

The field of options for ammonia destruction processing is very wide. Options below were considered and ruled out as unlikely for practice at Hanford for LAW waste water.

2.4.1 Ion Exchange

Ion exchange is practical for removing minor components from solutions, and minor amounts of ammonia would be no exception. However, the problem in the current application is that ammonia is a major and concentrated species, and column loading breakthough would be unacceptably rapid.

As an example, Zheng and co-workers reported on a high capacity 13X zeolite for ammonia removal from liquid.[xxxvii] The adsorbent had a capacity of 2.14 g-mole equivalents per kilogram and a bed density of 0.826 kg/L. If a column was filled with 1 kg of this material, the bed would have an initial volume of 1.2 L. If the feed solution had a typical ammonium concentration of 1.2 M, the bed would be fully loaded when only 1.8 L of feed passed through the 1.2 L bed. In addition to the less than 2-bed volume breakthrough, this process does not destroy the ammonia, so it is far from practical in this application.

2.4.2 Halogen and Oxyhalide processing

Ammonia and ammonium ion readily react with chlorine, hypochlorite (bleach), and similar bromine compounds. Such reactions have been studied extensively, and references are provided here as examples.[xxxviii], [xxxix]

Careful control of the process, keeping ammonia in excess versus added halogen oxidant, can direct the ammonia decomposition towards production of nitrogen gas versus nitrogen halides. However, the nitrogen halide byproducts are very noxious, and in addition it would take a lot of chlorine or its reactive oxides to treat molar levels of ammonia. If hypochlorite (effective Cl^{+1} oxidation state) was reduced to chloride with its action on ammonia at 100% efficiency, 3 moles of hypochlorite would treat 2 moles of ammonia. The product stream from that process would be very high in chloride.

2.4.3 Ozone Treatment

Ozone is widely used in wastewater treatment, and there are many studies including that that look at ammonia nitrogen in the feed. The main problem with applying this to the current case would be the high ammonia content compared with typical levels addressed in wastewater treatment. For example, three works studied ammonia and ozone when the ammonia content in the feed was 8 to 1200 mg/L.[xl,xli] In contrast, an evaporator bottoms liquid of 1.2 M ammonia would be over 20,000 mg/L. The second reference cited here shows how high pH is most favorable for ammonia removal by ozone (optimal pH was 10 in a tested range of 4 to 10). Apparently ozone attacks ammonia more readily than it does ammonium ion.

2.4.4 Biological Remediation

There is a large body of literature covering the use of bacteria to treat ammonia containing waste, especially waste water. This type of process is popular because of the great worldwide need to treat sewage, which has a high content of reduced nitrogen, and the prevalence of natural aerobic bacteria that oxidize ammonia. However, its use is with lower levels of ammonium content, and a biological process would be hard to control with concentrated waste solutions. Variability of feed rate and composition, particularly dissolved metals, would challenge a biological strategy. Bacterial action has been seen as a problem in the Liquid Effluent Retention Facility.[xlii] Process fouling led to the consideration of biocide. Slime and gelatinous material was found in filtration equipment. A biological process would probably need spent biomass removal and disposal, with the organic material being mildly radioactive. Biological remediation was not judged to be practical in this review.

2.4.5 Selective Catalytic Reduction and Gas Phase Processes

Ammonia is used in gas phase processes to reduce nitrogen oxides in stack gases. The process is highly commercialized. This operation is already present in the Hanford LAW and High Level Waste vitrification flowsheet. Ammonia is introduced to NOx-bearing exhaust so that all chemical nitrogen is reacted to form N_2 in a catalytic bed. Gas phase reaction beds are operated at several hundred degrees Celsius. A review of many catalysts that have been studied for this type of process is found in a paper by Jablonska and Palkovits.[xliii]

This process would require methods to vaporize ammonia in the liquid feed. It might be useful if Air Stripping (Section 2.2.7) were considered to treat airborne ammonia, but much engineering work would have to be done.

2.4.6 Oxidation with Ferrate Ion

Ferrate (FeO_4^{-2}) salts are strong oxidizers, though they are relatively unstable, especially if the solution pH is not alkaline. Svanks assessed the process for the secondary treatment of wastewaters that contain ammonia and concluded that the process is not practical.[xliv] While potassium ferrate will oxidize ammonia in solution (Svanks found pH 10 to 11 to be optimal), the process was not efficient and ferrate evolved oxygen by competing decomposition reactions. In addition to the inefficiency, the end products of potassium ferrate use are potassium hydroxide and iron hydroxide. If this were applied to the current application, a lot of chemical solids would have to be handled and disposed.

2.4.7 Organic Reactions

Ammonia and amines react, often rapidly, with aldehydes and ketones.[xlv] Products would be organic and may be water soluble. A good example is the reaction of ammonia with formaldehyde or paraformaldehyde to produce hexamethylenetetramine. This reaction, for example, was proposed for the mitigation of formaldehyde in treated wood for consumer products.[xlvi] It is doubtful that the high resulting organic content of treated solution would be acceptable in the flowsheet. Much analysis of the effects of soluble organic materials on the waste forms would have to follow.

2.5 Quality Assurance

Requirements for performing reviews of technical reports and the extent of review are established in manual E7 2.60. SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2.

3.0 Discussion of Options

3.1 Heat Generation

Ammonia destruction reactions generate heat. Overall heat generation rate is important and can be calculated for several types of proposed chemistry. The International Critical Tables provide heat of formations for chemicals dissolved in water.[xlvii] See Table 3-1. The heat of formation of pure elements like nitrogen and oxygen in their standard state are zero on this thermodynamic scale by convention. Where the enthalpy dependence on aqueous chemical concentration was available, values near 1 M were used.

The most relevant reactions for the oxidation of ammonia are given below, along with their enthalpy per mole as shown in the Table 3-1 data. Reaction C below is the nitrite reaction with ammonium ion. Reaction D is the main overall reaction for Fenton's chemistry. Reaction E occurs any time NaOH is needed to control pH so that it is controlled in a way to not drop too low, such as for Fenton's chemistry. Reaction F assumes that molecular ammonia is the primary reactant as in a caustic environment. There would be some need to add NaOH in practice, since conversion of soluble ammonium ion to the molecular ammonia will consume caustic.

Table 3-1. Enthalpy of Formation of Aqueous Chemicals

Chemical	Enthalpy of Formation, kJ/g-mole
Sodium Nitrite, $NaNO_2$	-348
Ammonium Sulfate, $(NH_4)_2SO_4$	-1154
Ammonia, NH_3	-81
Sodium Sulfate, Na_2SO_4	-1374
Sulfuric Acid, H_2SO_4	-867
Liquid Water, H_2O	-286
Hydrogen Peroxide, H_2O_2	-188
Sodium Hydroxide, NaOH	-469

$$2NaNO_2 + (NH_4)_2SO_4 \Rightarrow Na_2SO_4 + N_2 + 4H_2O \tag{C}$$

$$4H_2O_2 + (NH_4)_2SO_4 \Rightarrow H_2SO_4 + N_2 + 8H_2O \tag{D}$$

$$2NaOH + H_2SO_4 \Rightarrow Na_2SO_4 + 2H_2O \tag{E}$$

$$(3/2)O_2 + 2NH_3 \Rightarrow N_2 + 3H_2O \tag{F}$$

Calculated results in Table 3-2 show that the Fenton process generates significantly more heat than the nitrite or alkaline oxygen processes per amount of ammonium/ammonia processed. The nitrite/ammonium reaction would be most desirable from this standpoint given that it generates the least heat per mole of ammonium/ammonia processed. In addition, the added sodium would help moderate pH, perhaps enough that NaOH would not have to be added. Inefficiencies in using nitrite, such as loss of nitrite as NOx, may even cause pH to climb during processing.

In practice the heat released from the reaction of equation E would be added to that of equations D and F, since those processes consume caustic.

Table 3-2. Enthalpy (Heat) released in the Reactions

Reaction Equation	kJ of Heat Released, for Equations as Shown
(C)	668
(D)	1249
(E)	141
(F)	696

For some perspective on heat generation, it takes 418 kJ of heat to raise one liter of water from 0 to 100 °C. The numbers in Table 3-2 are all applied to the processing of 2 moles of ammonia/ammonium ion. If the feed being treated had 1 M ammonia/ammonium ion then reactions C and F give insufficient heat to bring the 1 liter to boiling if the startup solution is cold. Not so with reaction D, the Fenton process. Addition of all the required peroxide in the beginning would theoretically cause self-heating and would accelerate the reaction to the point that the batch is boiling. The concomitant generation of steam and nitrogen gas would result in vigorous bubbling. The Fenton oxidation process must be operated with continuous peroxide addition for safety's sake. It is also a good idea for the other processes.

3.2 Basic Needs for Ammonia Destruction Operations

The most likely options from this literature survey require a single-pot chemical reaction tank. Nitrogen gas would be the primary product of ammonia destruction, though smaller amounts of ammonia, oxygen, and some NOx might be present in the offgas. Means of cooling, steady and metered reagent addition, temperature and liquid level measurement, and some solids management (from catalysts) would be needed. Fenton chemistry often uses monitoring of oxidation/reduction potential (ORP).

3.3 Peroxide Removal

Many of the practical processes in this review use hydrogen peroxide. At the end of processing of a waste solution, residual peroxide may be present and it is likely that it should be removed before any next step, such as when a secondary waste form is made. Residual peroxide is likely to decompose and release oxygen, which may affect downstream processes. The well-known catalysis of peroxide decomposition by manganese dioxide is likely practical, since manganese dioxide is benign and probably compatible with waste forms. Manganese dioxide is currently used in the ETF for this purpose. Iodide is a water-soluble catalyst as well.[xlviii] If iodide is selected for peroxide removal, it would have to be added as it cannot be assumed to be present in sufficient quantity in the process solution.

4.0 Recommendations, Path Forward and Future Work

This review recommends testing of aqueous feeds containing ammonia. The most likely and practical processes for the secondary waste application include reaction with sodium nitrite, solution oxidation using hydrogen peroxide at a variety of pH and catalyst conditions, oxidation with persulfate, and air/oxygen sparging. Practical temperatures for such operations are not expected to exceed 70 °C. The review found both alkaline and acid side processes, many of which are well known and documented. The Hanford 200 Area ETF already handles NaOH and sulfuric acid for pH adjustment. The ETF also handles 50 wt% hydrogen peroxide for an existing unit operation in that plant. It has an established peroxide destruction process as well, demonstrating the maturity of that process.

Initial testing of solution oxidation of ammonia should have a screening where a feed solution is heated to a desired temperature. Injections of appropriate reagents are then made. Temperature rise, pH changes, and gas evolution should indicate easily measurable changes for the practical processes. The most desirable processes would then be selected for longer term steady state testing and more detailed kinetics measurements.

Air stripping would be practical if the environmental restrictions on ammonia disposal can be addressed. This process by itself does not destroy ammonia.

Operational changes upstream, such as at the LAW melter, SBS, or EMF could also be used to avoid generation of significant ammonia or lower its concentration, circumventing the need for remediation of ammonia at ETF. It is possible that use of pH control along with chemical addition may greatly reduce the ammonia content in the SBS or EMF, so that further downstream processing is not needed.

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