Title: HYDROTHERMAL OXIDATION OF AMMONIA/ORGANIC WASTE MIXTURES

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Hydrothermal Oxidation of Ammonia/Organic Waste Mixtures

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Hydrothermal oxidation is a promising new technology for the treatment of radioactive contaminated hazardous organic wastes. Los Alamos National Laboratory is currently evaluating this technology for the U. S. Department of Energy. In this paper, we present experimental results from the study of the hydrothermal oxidation of an ammonia/alcohol/uranium waste mixture. The use of a co-oxidant system consisting of hydrogen peroxide combined with nitrate is discussed. Experiments demonstrate near complete destruction of ammonia and organic compounds at 500 °C, 38 MPa, and 50 seconds reaction time. The ammonia and total organic carbon (TOC) concentrations in a waste simulant is reduced from 8,500 mg/L of ammonia and 12,500 mg/L TOC to 30 mg/L ammonia and less than 10 mg/L TOC. The major reaction products are CO2, N2, and a small amount of N2O. Comparison experiments with nitrate and hydrogen peroxide used individually show the advantage of the co-oxidant system.

Introduction

Hydrothermal oxidation has many desirable attributes for the treatment of radioactive aqueous and organic wastes. It is highly effective - high destruction and removal efficiencies of organic using hydrothermal oxidation have been reported at mild conditions (< 600 °C) for a broad range of chemical and metabolic wastes, including some difficult to treat wastes such as chlorinated and aromatic hydrocarbons[1]. The low temperature at which the reactions occur generally produce low levels of NOx products in the effluent. The rapid rates of reaction allow for compact process units that can fit into existing nuclear facilities without extensive or expensive facility modifications. Additionally, the effluents from the process can be contained and sampled before they are released to the environment. This combination of features has produced a positive response from the general public to the implementation of the technology for the treatment of radioactive wastes.

Currently, Los Alamos National Laboratory is evaluating hydrothermal oxidation technology for the treatment of several U. S. Department of Energy wastes. These include high level radioactive wastes stored in underground tanks at Hanford, Washington [2]; explosive wastes produced by the dismantlement of nuclear weapons [3]; and combustible wastes [4]. Both laboratory and pilot scale tests have been performed using simulants of each of these waste types.

Although hydrothermal oxidation has been demonstrated to be effective for the destruction of most organic compounds, little success has been achieved in the complete destruction of ammonia which is present in many organic waste streams. In this paper we discuss the use of co-oxidants, nitric acid and hydrogen peroxide, to effectively destroy both organic and ammonia components in a mixed waste. The research focuses on a mixed waste containing uranium, ammonia, and organic alcohols (isopropanol and hydrofurfuryl alcohol). The experimental results presented, describe the efficiency of the hydrothermal oxidation of the ammonia/organic mixture and the effectiveness of the co-oxidant strategy. The treatment process described was designed to remove ammonia at practical rates as well as at temperatures much lower than tested by previous researchers. The quality of the reaction effluent was emphasized. The oxidants were selected in order to reduce the production of problematic reaction by-products, such as NOX.

Literature examples on the destruction of ammonia with/without organic indicate that very high temperatures (> 690 °C) and long reaction times are required for complete destruction of ammonia using oxygen as the oxidizer. Only a few studies have been conducted on the destruction of ammonia wastes in the presence or absence of organic compounds. Webley and co-workers [5] investigated the oxidation of ammonia and ammonia/methanol mixtures by oxygen in a packed and unpacked tubular flow reactor. Only 10% conversion of ammonia was achieved in the unpacked tubular reactor at 700 °C, 25 MPa, and a residence time at the order of 10 seconds. Higher conversion (up to 40%) was reached in the packed reactor under the same conditions, indicating that the reactor material catalyzed the reaction. The presence of methanol did not noticeably affect the oxidation of ammonia.

Takahashi et al. [6] also concluded that ammonia is very stable in the presence of oxygen. Their research of the oxidation of ammonia with acetic acid showed that little oxidation occurs at residence times of 1 hour and temperatures below 500 °C. Killilea et al. [7] achieved a 41% removal of ammonia (from urea feed) at 690 °C and 25 MPa, and at a residence time of 2 seconds. When ethanol was added to the urea feed stream, complete
destruction was achieved at this temperature. At high temperatures, both with and without ethanol, ammonia was mainly converted to N₂. At lower temperatures with ethanol, however, more N₂O was produced than N₂. This was explained by a kinetically limited N₂O reduction.

In a series of nitrate reduction experiments, Cox et al. [8] showed that ammonia is a good reducing agent for nitrate in acidic conditions, even at subcritical temperatures near 350°C and pressures around 18 MPa. The molar ratio of the reactants was 0.42 NO₃⁻:NH₃ (at pH=4) and the reaction time was 2 hours. Experiments at higher pH (7 to 10) by Dell’Orco [10] and Proesmans et al. [12], demonstrated that ammonia and nitrate react rapidly (<10 sec) at temperatures and pressures near 500°C and 35 MPa. These experiments observed a stoichiometric ratio near 0.66 (NO₃⁻:NH₃). In all three studies, the reaction products observed were primarily N₂, with some N₂O, and nitrite. At higher temperatures and lower water density, radical reaction mechanisms dominate. Nitrate is believed to be activated to the primary reactive species NO₂. Nitrate/ammonia reactions can proceed through the following global pathways, leading to three principal gaseous products N₂, N₂O, and NO:

\[
\begin{align*}
5 \text{NH}_3 + 3 \text{HNO}_3 &= 4 \text{N}_2 + 9 \text{H}_2\text{O} \\
\text{NH}_3 + \text{HNO}_3 &= \text{N}_2\text{O} + 2 \text{H}_2\text{O} \\
3 \text{NH}_3 + 5 \text{HNO}_3 &= 8 \text{NO} + 7 \text{H}_2\text{O}
\end{align*}
\]

Reaction conditions such as temperature and pressure, as well as the presence of other reactants, influence which pathway will be dominant. In addition, catalysts can accelerate one pathway over another. For example, thermal decomposition of ammonium nitrate with/without a small amount of water at about 290°C produces primarily N₂O [9], while reaction of excess aqueous ammonia (0.5 M) with nitrate (0.205 M) (pH = 4) at subcritical condition gives N₂ as the major product [8]. At supercritical conditions (T > 374°C, P > 22 MPa) with low concentration reactants, the addition of H₂O₂ increases the N₂/N₂O selection ratio [10].

Nitrite is likely formed by nitrate decomposition, catalyzed by metals in the reactor wall. Higher nitrite concentrations were observed to correlate with higher concentrations of corrosion metals in the effluent of the experiments. The nitrite itself can react with ammonia to form mostly N₂ [10].

This brief summary of the important research on ammonia destruction shows, that for the reaction of ammonia with oxygen, the rapid conversion of ammonia to benign gaseous products has only been achieved at high temperatures (>600°C), and is not yet fully understood. However with nitrate, ammonia reacts rapidly at moderate temperatures producing primarily N₂. A more detailed discussion of the NO₃⁻/NH₃ reaction mechanism is presented elsewhere [12].

In this paper we discuss the use of nitrate and hydrogen peroxide, separately and together, as oxidizers for the hydrothermal treatment of an aqueous mixed waste. The waste contains ammonia (10 \%v/v), isopropanol (15 \%v/v), and tetrahydrofurfuryl alcohol (5 \%v/v) with uranium contamination. The uranium is present in the waste primarily as UO₃ powder. The UO₃ is believed to have settled, forming a relatively insoluble second phase, leaving the remaining fluid at low uranium concentration. When treated, the uranium will be separated from the liquid phase by filtration. Our research focused on developing a hydrothermal treatment of the liquid phase and examined a filtrate containing about 1 M of ammonia, 0.5 M of isopropanol, and 0.1 M of tetrahydrofurfuryl alcohol. Experiments were performed on three different systems: reaction of NH₃ and alcohols with HNO₃, NH₃ and alcohols with H₂O₂, and NH₃ and alcohols with HNO₃ and H₂O₂. Results of the experiments are presented below.

**Experimental**

A bench-scale flow reactor (Fig. 1) was used for the experiments. The reactor consisted of a coiled high pressure tube (Alloy 625 containing Fe, Cr, Mo and Ni, 0.65 cm od, 0.21 cm id, 318 cm long) submerged in a fluidized sandbath. The alcohols, ammonia, and nitric acid reagents were mixed and pumped by a single high performance liquid chromatography (HPLC) pump. Hydrogen peroxide was pumped separately. The two flows were combined prior to reaching the heated section of the reactor. The total volume of the heated portion of the reactor was 10.0 mL. A counter flow heat exchanger, placed at the end of the reactor, rapidly cooled the reaction mixture and quenched the reactions. After cooling, the reactor effluent was filtered. A backpressure regulator controlled the pressure in the system. Nine thermocouples monitored the surface temperature of the reactor and the fluid temperature. Transducers, placed before the reactor and after the filter, measured the pressure. A more detailed description of this reactor is given elsewhere [10].

Feed solutions were prepared using analytical grade isopropyl alcohol, tetrahydrofurfuryl alcohol, H₂O₂ (50 wt.%); reagent grade concentrated ammonium hydroxide (30 wt.%), nitric acid (69-72 wt.%), ammonium nitrate; and de-ionized water. The waste simulants used in this work contained isopropanol and tetrahydrofurfuryl alcohol in a 5-to-1 ratio and ammonia. The concentration and ratio of the organic, ammonia, and oxidizer varied for each set of experiments. The initial concentrations of the components were determined by analytical analysis samples taken from the feed solutions at the start of each experiment. Flow rates ranged from 1 to 20 mL/min for each feed stream. Liquid samples were collected directly into 40 mL vials and kept sealed in the refrigerator until they were analyzed. Gas sampling was accomplished by diverting the effluent to a gas-liquid separator and collecting the effluent gases in an evacuated gas sample cylinder.
The mass flowrate of the feed and effluent was determined by measuring the mass change of the feed and effluent reservoirs with time. The residence time of the reactants in the reactor tubing was calculated from the measured mass flow rates, reactor volume, and the density of the fluid at reaction temperature and pressure. The density of the fluid was assumed to be the same as water at similar temperatures and pressure [11]. For the experiments reported, the temperatures ranged from 401° to 503 °C, the pressure from 35 to 40 MPa, and the density from 0.1 to 0.5 grams/cm³. These conditions produced residence times between 10 to 140 seconds.

Most gaseous products were analyzed using a gas chromatograph (GC). The detectable gases included O₂, N₂, N₂O, CH₄, C₂H₆, CO, and CO₂. Larger hydrocarbon gases (C₃ or greater) could not be analyzed on this system. Infrared spectroscopy was used to analyze gas samples for NOₓ, volatile organics, HCN, etc. The combination of sampling method and detectivity resulted in a minimum detectable concentration of 1 mmol/l H₂; 0.1 mmol/l NO; and 0.4 to 0.6 mmol/l of O₂, N₂, CO, CH₄, C₂H₅ in the reactor effluent.

Concentrations at ambient conditions were used for the analytic determinations of species removal and mass balance calculations. NH₃, NO₃⁻, and carbon removals were calculated based on the liquid phase contents of NH₃, NO₃⁻, and TOC. Mass balances of nitrogen and carbon were calculated considering both gas and liquid phases.

A pH electrode was used to measure feed and effluent pH levels. Hydrogen peroxide concentrations were measured by titration with KMnO₄. Nitrite, nitrate, formate, acetate ions were analyzed by ion chromatography (IC). Ammonium/ammonia was analyzed with an ion selective electrode or IC. Total inorganic carbon (TIC) and TOC were measured using a carbon analyzer. An inductively coupled plasma (ICP) spectrometer was used to determine the concentration of corrosion produced metals (Fe, Cr, Mo, Ni, Pd, Ti) contained in the effluent. The minimum detectable concentration was 0.5 ppm for nitrate, nitrite, formate, acetate; 1 ppm for TOC; and 0.01 ppm for Cr, Mo, Fe, Ni, Pd, and Ti.

**Results and Discussion**

**Oxidation with Nitric Acid.** Six experiments on the oxidation of ammonia / isopropanol / tetrahydrofuranyl alcohol with nitric acid are reported in Table 1. Reaction temperatures were near 500 °C, while reaction pressures ranged between 35 and 40 MPa. The initial TOC, ammonia and nitrate concentrations are given along with the percent removal of each species. If the reaction goes to completion producing CO₂, H₂O, and N₂, each mole of TOC and ammonia will consume 2.93 and 1.5 moles of oxygen atoms respectively, while each mole of nitrate will supply 2.5 moles of oxygen atoms. Experiment A1, with an excess of oxidizer, shows that high removal of the waste constituents can be achieved. Both ammonia and organic destruction efficiencies were higher than 99% at a residence time of about 49 seconds.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Pressure (MPa)</th>
<th>Residence Time (sec)</th>
<th>[TOC]₀</th>
<th>[NH₃]₀</th>
<th>[NO₃]⁻₀</th>
<th>% NO₃⁻ removal</th>
<th>% NH₃ removal</th>
<th>% TOC removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>499</td>
<td>38</td>
<td>48</td>
<td>0.24</td>
<td>0.24</td>
<td>0.50</td>
<td>84.4</td>
<td>99.8</td>
</tr>
<tr>
<td>A2</td>
<td>502</td>
<td>38</td>
<td>48</td>
<td>0.27</td>
<td>0.25</td>
<td>0.50</td>
<td>98.0</td>
<td>91.9</td>
</tr>
<tr>
<td>A3</td>
<td>500</td>
<td>37</td>
<td>47</td>
<td>0.66</td>
<td>0.23</td>
<td>0.50</td>
<td>99.99</td>
<td>80.5</td>
</tr>
<tr>
<td>A4</td>
<td>499</td>
<td>40</td>
<td>40</td>
<td>0.36</td>
<td>0.15</td>
<td>0.50</td>
<td>99.1</td>
<td>88</td>
</tr>
<tr>
<td>A5</td>
<td>500</td>
<td>35</td>
<td>30</td>
<td>0.36</td>
<td>0.15</td>
<td>0.50</td>
<td>97</td>
<td>89.5</td>
</tr>
<tr>
<td>A6</td>
<td>502</td>
<td>38</td>
<td>124</td>
<td>2.04</td>
<td>0.81</td>
<td>0.50</td>
<td>99.99</td>
<td>70</td>
</tr>
</tbody>
</table>

Table 1. Summary of experimental conditions and conversions for the oxidation of the organic/ammonia waste with HNO₃. The uncertainties of the percent removal values are less than 80% of the least significant figure given.

In experiment A2, the amount of oxidizer was nearly stoichiometric. This ratio resulted in lower nitrate concentrations in the effluent, but also produced less removal of ammonia and TOC. In order to achieve complete removal of both the ammonia and alcohols, excess nitrate was required.
This set of experiments demonstrates that nitrate oxidizes both the organic alcohols and the ammonia and that they react at similar rates. Previously, it has been observed that for the reactions of methanol, acetic acid, and phenol with ammonium nitrate, ammonium reacts much faster with nitrate than does methanol or acetic acid, and that the ammonium reacts slightly faster than phenol [12]. Hydrolysis of the organic compound was not investigated, but was assumed to be negligible [12].

For experiments A1 through A5, products in the gas phase were CO2, N2, N2O, NO, NO2 and small amounts of N2O4 and O2. FTIR analysis was only qualitative, and so NOx concentrations were not determined. Comparison of experiment A1 and A3 (same experimental conditions, except for initial carbon concentration) indicates that with higher initial carbon concentration, the NO2/NO ratio increased. N2 to N2O selectivity varied between 5.3 and 129.

Propylene and acetone were also detected by FTIR analysis in experiment A6, as well as NO2. No NO was found. The unknown quantities of NO, NO2, and partially oxidized carbon products (like propylene and acetone) do not fully explain the poor nitrogen and carbon balances (as low as 50%) in this series of experiments. Only experiments with nitrogen and carbon mass balances between 80% and 105% have been presented here.

These results agree qualitatively with those from previous studies, separately examining the reactions of methanol, acetic acid, [10] and EDTA [2] with sodium nitrate. In these experiments, the organic carbon was converted to CO2 and/or carbonate, while the nitrate was converted primarily to N2, NO3-, NH3, and trace N2O.

**Oxidation with H2O2.** The hydrothermal oxidation of the waste simulant using hydrogen peroxide was examined at 455 °C and 500 °C, at pressures between 38 and 42 MPa. Experimental conditions and ammonia and TOC removal percentages are summarized in Table 2.

Nitrogen and carbon mass balances were between 80% and 120%. Good organic destruction was achieved even at temperatures of 455 °C. Ammonia removals were very small, except at 500 °C with a 50% excess of H2O2 (experiment B5). The N2/N2O selectivity ranged from 1.4 to 9.0. No NOx was detected by FTIR. The degree of ammonia destruction in experiment B5 was much higher than ammonia destruction reported in comparable studies [5, 7], but was still not complete. This enhanced reactivity may result from the highly reactive OH radicals generated through homolysis of H2O2. Both Webley [5] and Killilea [7] used O2 (from air or pure O2) as oxidant.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Pressure (MPa)</th>
<th>Residence Time (sec)</th>
<th>% NH3 removal</th>
<th>% TOC removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1</td>
<td>455</td>
<td>38</td>
<td>24</td>
<td>1.07</td>
</tr>
<tr>
<td>B2</td>
<td>455</td>
<td>40</td>
<td>140</td>
<td>0.99</td>
</tr>
<tr>
<td>B3</td>
<td>455</td>
<td>39</td>
<td>41</td>
<td>1.05</td>
</tr>
<tr>
<td>B4</td>
<td>500</td>
<td>42</td>
<td>20</td>
<td>1.01</td>
</tr>
<tr>
<td>B5</td>
<td>500</td>
<td>38</td>
<td>25</td>
<td>0.81</td>
</tr>
</tbody>
</table>

Table 2. Summary of experimental conditions and conversions for the oxidation of the organic/ammonia waste with H2O2. The uncertainties of the percent removal values are less than 70% of the least significant figure given.

Oxidation of Organic/Ammonia Waste with Peroxide and Nitric Acid. Oxidation of NH3 / isopropanol / tetrahydrofurfuryl using hydrogen peroxide and nitric acid was investigated in more detail than the previous systems. The organic/ammonia waste simulant was oxidized at temperatures between 400 °C and 500 °C, at pressures of circa 38 MPa, and residence times of 13 to 98 seconds. A summary of the experimental conditions and ammonia and nitrate removal is given in Table 3. The complete destruction of both ammonia and organic was easily achieved. Nitrate to ammonia ratios were varied to minimize the nitrate and ammonia concentration in the effluent. Hydrogen peroxide was added in excess to the total carbon/ammonia in the feed (up to 50% excess).

Reported experiments all yielded carbon and nitrogen balances between 80% and 120%.

At 500 °C, a TOC removal of 99.7% was achieved for all but one experiment, even for residence times as short as 13 seconds (C11). Comparison of experiments C1, C6, and C13, which were conducted at the same residence times and NO3-/NH4+ ratios, shows that increasing temperatures facilitates organic destruction. Experiments C1 and C2 indicate that longer residence times are needed to obtain complete organic removal at temperatures of 400 °C. The organic alcohols were 92% oxidized at a residence time of 73 seconds. At shorter residence times, the destruction of organic compounds was as low as 68% at 400 °C (C13).
Table 3. Summary of experimental conditions and conversions for the oxidation of the organic/ammonia waste with H₂O₂ and HNO₃. The uncertainties of the percent removal values is less than 90% of the least significant figure given.

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>Pressure (MPa)</th>
<th>Residence Time (sec)</th>
<th>[NO₃]₀</th>
<th>[H₂O₂]₀</th>
<th>[TOC]₀</th>
<th>[NH₃]₀</th>
<th>% NO₃ removal</th>
<th>%NH₃ removal</th>
<th>%TOC removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>401</td>
<td>37</td>
<td>33</td>
<td>0.52</td>
<td>4.99</td>
<td>1.02</td>
<td>0.76</td>
<td>99.8</td>
<td>86</td>
</tr>
<tr>
<td>C2</td>
<td>401</td>
<td>38</td>
<td>74</td>
<td>0.54</td>
<td>4.80</td>
<td>1.06</td>
<td>0.79</td>
<td>99.99</td>
<td>89</td>
</tr>
<tr>
<td>C3</td>
<td>450</td>
<td>38</td>
<td>44</td>
<td>0.47</td>
<td>4.59</td>
<td>1.02</td>
<td>0.59</td>
<td>99.98</td>
<td>98</td>
</tr>
<tr>
<td>C4</td>
<td>451</td>
<td>37</td>
<td>40</td>
<td>0.45</td>
<td>4.68</td>
<td>1.04</td>
<td>0.51</td>
<td>79</td>
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<tr>
<td>C5</td>
<td>455</td>
<td>38</td>
<td>89</td>
<td>0.37</td>
<td>5.01</td>
<td>0.89</td>
<td>0.46</td>
<td>99.99</td>
<td>94.8</td>
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<tr>
<td>C6</td>
<td>470</td>
<td>38</td>
<td>29</td>
<td>0.59</td>
<td>4.37</td>
<td>1.15</td>
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<td>99.99</td>
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<tr>
<td>C7</td>
<td>499</td>
<td>37</td>
<td>46</td>
<td>0.49</td>
<td>5.21</td>
<td>1.06</td>
<td>0.85</td>
<td>99.95</td>
<td>82</td>
</tr>
<tr>
<td>C8</td>
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<td>38</td>
<td>45</td>
<td>0.49</td>
<td>5.21</td>
<td>1.18</td>
<td>0.82</td>
<td>99.99</td>
<td>86</td>
</tr>
<tr>
<td>C9</td>
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<td>38</td>
<td>98</td>
<td>0.35</td>
<td>5.32</td>
<td>0.84</td>
<td>0.49</td>
<td>99.97</td>
<td>99.2</td>
</tr>
<tr>
<td>C10</td>
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<td>38</td>
<td>30</td>
<td>0.46</td>
<td>4.54</td>
<td>1.06</td>
<td>0.52</td>
<td>80</td>
<td>99.97</td>
</tr>
<tr>
<td>C11</td>
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<td>13</td>
<td>0.51</td>
<td>4.86</td>
<td>1.02</td>
<td>0.56</td>
<td>84</td>
<td>99.9</td>
</tr>
<tr>
<td>C12</td>
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<td>27</td>
<td>0.45</td>
<td>4.91</td>
<td>1.05</td>
<td>0.47</td>
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<tr>
<td>C13</td>
<td>501</td>
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<td>0.82</td>
<td>0.43</td>
<td>99.94</td>
<td>99.7</td>
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</table>

Figure 2. Ammonia and Nitrate Removal at 500 °C versus Nitrate to Ammonia Ratio in the Feed Solution (C6 through C14).

Fig. 2 shows the ammonia and nitrate removal at 500 °C as a function of the molar ratio of nitrate to ammonia in the feed stream. To obtain high ammonia removal combined with low effluent nitrate concentrations, this ratio should be between 0.7 and 0.8. The best destruction result (NO₃⁻, 99.94%; NH₃, 99.7%; TOC, 99.9%) was obtained in experiment C14, in which the reactant NO₃⁻/NH₃ ratio was 0.79 and influent and effluent pH were 8.9 and 5.6, respectively. At molar ratios between 0.7 and 0.8, the N as NO₃⁻ concentrations in the effluent were < 5 ppm and the N as NH₃ concentrations less than 120 ppm.

The nitrogen products formed were N₂, N₂O, and small amounts of nitrite. NO₂ or NO were not detected in the effluent. N₂ to N₂O ratios ranged from 8 to 25, with the higher N₂ selectivities occurring at the lower temperatures. The main carbon product was carbon dioxide (or HCO₃⁻, CO₃²⁻). Trace amounts of carbon monoxide were detected in some of the experiments at reaction temperatures below 500 °C. No methane or hydrogen gas was detected in the gas samples. Acetate accounted only for 10% to 20%, on average, of the remaining TOC in the effluent. Formate was only a few percent of the TOC.

Similarly shaped curves to those in Fig. 2 were measured for the reaction of ammonia with nitrate in the absence of organic compounds and are reported elsewhere [12]. The similarity of these curves for the two different systems suggests that the primary reaction pathways are similar, regardless of the presence of hydrogen peroxide and organic material. The optimum nitrate/ammonia ratio, 0.75, in Fig. 2 is larger than the stoichiometric ratio for the ammonia/nitrate system (0.65). Most likely, ammonia is competing with the organic species for the nitrate. Several researchers have suggested that nitrate may react faster than oxygen in the oxidation of organic [2, 10]. The oxidation products of nitrate with organic are ammonia, nitrite, nitrous oxide, and N₂. Nitrite, in turn, is an oxidizer for the organic compounds, or can react with the ammonia.

The overlap of the two destruction curves in Fig. 2, covers a wider range of ratios than for the ammonia/nitrate curves without organic material [12]. This suggests that several reaction pathways are competing. The wider overlap between the two
curves may be due to the competition between the major reaction systems of H₂O₂/alcohol and nitrate/ammonia and the competing nitrate/alcohol and H₂O₂/ammonia reactions. The presence of organic compounds and H₂O₂ appears to facilitate the complete destruction process: excess ammonia can be removed by H₂O₂ while organic compounds react with the nitrate residue.

**Corrosion.** Corrosion products concentrations found in the effluent are shown in Figure 3. Corrosion was low for the experiments with good ammonia, nitrate, and organic removal (experiments C9, C13, C14). Corrosion was high for the experiments with a high NO₃⁻/NH₃ ratio. The excess nitric acid used in these experiments produces a very acidic effluent.

![Figure 3. Corrosion Products in the Effluent versus Effluent pH for the Organic/Ammonia Waste Treated with H₂O₂ and NH₃ (Experiments C7-C14).](image)

**Conclusions**

The experiments presented in this report demonstrate, that for hydrothermal processing of an organic/ammonia waste stream, a co-oxidant system using a mixture of nitrate and hydrogen peroxide is effective and superior to either hydrogen peroxide or nitrate alone. The co-oxidant allows complete destruction of the ammonia and organic compounds and an effluent that is free of nitrate and NOₓ.

**References**


2. Foy, B. R.; Dell’Orco, P. C.; Wilmanns, E.; McInroy, R.; Ely, J.; Robinson, J. M.; Buelow, S.


