Nitric-Phosphoric Acid Oxidation of Organic Waste Materials(U)

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Nitric-Phosphoric Acid Oxidation of Organic Waste Materials

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ABSTRACT

A wet chemical oxidation technology has been developed to address issues facing defense-related facilities, private industry, and small-volume generators such as university and medical laboratories. Initially tested to destroy and decontaminate a heterogenous mixture of radioactive-contaminated solid waste, the technology can also remediate other hazardous waste forms. The process, unique to Savannah River, offers a valuable alternative to incineration and other high-temperature or high-pressure oxidation processes.

The process uses nitric acid in phosphoric acid; phosphoric acid allows nitric acid to be retained in solution well above its normal boiling point. The reaction converts organics to carbon dioxide and water, and generates NOx vapors which can be recycled using air and water. Oxidation is complete in one to three hours.

In previous studies, many organic compounds were completely oxidized, within experimental error, at atmospheric pressure below 180°C; more stable compounds were decomposed at 200°C and 170 kPa. Recent studies have evaluated processing parameters and potential throughputs for three primary compounds: EDTA, polyethylene, and cellulose. The study of polyvinylchloride oxidation is incomplete at this time.

## INTRODUCTION

Nitric-phosphoric acid oxidation has been developed specifically to address solid waste management issues at the Savannah River Site and other defense-related facilities. The system has been tested to destroy and decontaminate SRS solid, Pu-contaminated job-control waste (a heterogeneous mixture of plastics, cellulose, rubber, resins, metals, etc.); the technology has also exhibited
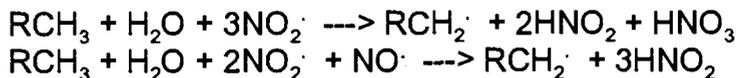
potential for remediating hazardous and mixed waste forms. The process, developed and advanced by the authors, offers a valuable alternative to other oxidation processes that require extreme temperatures and/or elevated pressures. The process envisioned will be configured to handle a wide range of solid Pu-contaminated waste, and is being developed to operate below 205°C at moderate pressures (0-205 kPa).

To address a wide range of waste types, many different organic compounds, have been oxidized. These compounds represented a cross-section of the waste that must be treated. Materials that have been completely oxidized, within experimental error, at atmospheric pressure below 180°C include neoprene, cellulose, nitromethane, tributylphosphate, and EDTA.[1] More stable compounds such as benzoic acid, polyethylene, oils, and resins have been completely decomposed below 200°C and 170 kPa. Oxidation is complete in one to three hours.[2]

The basis for the process stems from extensive studies conducted by Seminov[3] and Dickerson.[4] They found that direct oxidation of most organic compounds by HNO_3, nitric acid, is possible but very slow due to the stability of the carbon-hydrogen bond. The oxidation of organic compounds is usually initiated by the production of organic radicals. These are generated by reactions with nitric acid equilibrium products, NO_2 and NO radicals. For many types of oxygenated organic compounds the attack by $NO_2\cdot$ can be first order.

$$CH_3(OH)CH_2 + NO_2\cdot \longrightarrow CH_3(OH)CH\cdot + HNO_2$$
$$CH_3CHO + NO_2\cdot \longrightarrow CH_3(O)C\cdot + HNO_2$$
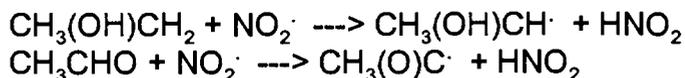
For aliphatic compounds, higher concentrations of $NO_2\cdot$ and $NO\cdot$ are needed to obtain comparable oxidation rates.

$$RCH_3 + H_2O + 3NO_2\cdot \longrightarrow RCH_2\cdot + 2HNO_2 + HNO_3$$
$$RCH_3 + H_2O + 2NO_2\cdot + NO\cdot \longrightarrow RCH_2\cdot + 3HNO_2$$

Seminov demonstrated that above 130-150°C, most organic compounds will decompose to release water and carbon dioxide.[3] Below 130°C, the formation of stable intermediate compounds is common.

Work by the authors conducted with other oxidation systems, such as Ag^{2+}, yielded results that agreed with Seminov, namely that incomplete oxidation was observed at lower temperatures. The nitric-phosphoric acid approach employs small amounts of concentrated nitric acid as the main oxidant in a concentrated phosphoric acid media. In doing this, phosphoric acid allows nitric acid to be retained in solution at atmospheric pressure well above its normal boiling point of 121°C.[5] Temperatures of 185°C at atmospheric pressure have been successfully used in the oxidation of benzoic acid and polyethylene.[2] The

reaction forms NOx vapors which can be readily oxidized and recycled using air and water. The addition of 0.001M Pd(II) reduces CO generation (explosive above 5%) to near 1% of the released carbon gases.[1]

Prior studies focused on the reaction in detail, making sure that the oxidation reaction was complete and did not form any stable nitrated organic compounds.[1] Earlier work also investigated the direct impact of nitric acid concentration and temperature on oxidation rates of several organic compounds, and the indirect effect of pressure as it relates to nitric acid concentration and temperature.[2] That work found that short-chained, non-aliphatic compounds oxidized quickly at low and high temperatures. Long-chain aliphatic materials benefitted more from increased temperatures and lower acid concentrations than from high nitric acid levels at low temperatures.

Related experiments investigated the conditions which cause "red oil" explosion reactions between concentrated nitric acid and organics.[6] The tests showed that conditions for forming "red oil" occurred when a solution of organics and nitric acid becomes dehydrated, which occurs in nitric acid at 125-130°C. At lower temperatures, water quickly reacts with nitrated compounds to form alcohol groups which are further oxidized. When dehydration occurs, the mechanism for hyrolysis of nitrated organics is removed and nitrated organic compounds build up in solution. Phosphoric acid helps retain water within its structure well above operating temperatures, thereby maintaining the ability to hydrolyze any nitrated organics that might form during oxidation.

This paper addresses characteristics of this process on a larger scale. It focuses on the limitations of the oxidation reaction and the process throughput. Specifically, the paper discusses the oxidation of EDTA, cellulose, and polyethylene. Oxidation rates of these three compounds are reviewed as a function of temperature. Limitations to throughput due to high organic concentrations are also discussed.

EXPERIMENTAL DETAILS

All oxidation experiments were conducted using some variation of the unit shown in Figure 1. A glass reaction vessel was set up with a mixture of nitric and phosphoric acids; palladium catalyst was also added to convert CO to CO_2. The custom-made glassware used Teflon® fittings and Viton® o-rings to create gas seals. Pressure was measured using a Marshalltown Manufacturing compound gauge which measures from 30"Hg - 30 psig. The system temperature was monitored using a Luxtron Model 750 Fluoroptic temperature probe. Weights were taken using a calibrated Mettler AE200 balance which is accurate to 0.0001g. Polyethylene samples were taken from Nalgene® bottles. J.T. Baker Chemical Company was the supplier of EDTA (disodium ethylenediamine-tetracetic acid dihydrate, 99.8% purity).

When a test was run, the sample was added to a mixture of nitric-phosphoric acid with a palladium concentration of 0.003M. The starting concentration of nitric acid depended on the experimental temperature because of nitric acid solubility in phosphoric acid as a function of temperature. Once the sample was added, the acids were rapidly heated to the desired reaction temperature. The "start" of the experiment was viewed as that time when NOx generation began. For EDTA and cellulose the starting temperature was near 100°C; for polyethylene, it was about 170°C. The final temperature, determined before the experiment began, was obtained within five to ten minutes of the "start" of the test. The final temperature was varied in some tests to measure the effect of temperature on oxidation rates.

As the reaction progressed CO_2, NO_2, and water vapor were the primary gases generated. Carbon monoxide generation was small and NO gas, although formed, was rapidly oxidized to NO_2 by air in the vessel. These gases were flushed with an air or nitrogen purge through 1M sulfamic acid. For atmospheric pressure experiments, a continuous purge was supplied; an intermittent purge was used in pressurized experiments because the present system had to be de-pressurized to be flushed.

Sulfamic acid (supplied by EM Science) removed NO_2 gases from the reaction vessel off-gas stream so they did not interfere with downstream carbon dioxide measurements. Downstream of the sulfamic acid was drierite (W. A. Hammond Drierite Co.) which absorbed moisture from the gas stream. Ascarite-II® (Thomas Scientific) absorbed CO_2 and was weighed as a function of time to determine how much carbon dioxide had been released by the reaction. Ascarite provides a quantitative measurement for carbon dioxide.

An occasional "standard" was run for the oxidation system. This was done by putting a known amount of dry sodium oxalate in the system and monitoring the carbon dioxide generated at 150°C. The test has shown the system to accurately measure total CO_2 generation to ±2%.

RESULTS

The objective of identifying optimum operating conditions and maximum throughput dictates finding the least severe conditions where high oxidation rates occur. The data is listed in table form because most of the data overlaps. The effects of raising the temperature for each of the compounds differed considerably. For EDTA, the oxidation rate at 125°C was higher than expected, but still lower than can be achieved at higher temperatures (Table 1). The reaction rate at 175°C was extremely rapid, but apparently controllable. However, such a high reaction rate may cause problems on a large scale.

Cellulose oxidation as a function of temperature reflects what happened with EDTA in the temperature range from 140-160°C. Once again, at higher temperatures the reaction rate accelerates significantly (Table 2). The oxidation characteristics for polyethylene are very dependent upon both increased temperatures and higher nitric acid concentrations achieved using higher pressures (Table 3).

Using even higher temperatures and pressures for plastics should be beneficial, but has not yet been studied because one of the primary program objectives is to keep operating pressures low. Limits to process throughputs also vary between compounds. The oxidation of EDTA is limited because conditions are achieved which suggest a runaway reaction is possible. As shown in Table 4, the reaction rate using 2.15 grams of EDTA far exceeded those at lower EDTA concentrations. When the oxidation rate accelerated, the temperature rose uncontrollably to 170°C, well past the 140°C set point.

The processing rate of cellulose is limited by physical considerations instead of chemical ones. As can be seen from the data in Table 5, the total amount of paper oxidized remains relatively high as a function of time even at elevated concentrations of cellulose. However, because of the actual density of paper, higher levels of paper than those listed in Table 5 begin soaking up most of the acid in the reaction vessel.

Oxidation throughput studies for polyethylene are incomplete at this time due to limitations in experimental equipment. As can be seen from the data in Table 6, the results are both promising and consistent. However, since elevated temperatures and pressures are used, starting acid concentrations in the reaction vessel are lower. As a result, the nitric acid is depleted quickly during the reaction thereby reducing the rate of reaction. Thus far, attempts to add nitric acid during the reaction without reducing the system pressure have caused the liquid temperature to drop 30-40°C, leading to a substantial decrease in the reaction rate. Future experiments will be set up to overcome this minor setback.

DISCUSSION

Although this study is more of a qualitative one, conducted from an engineering viewpoint, some valuable information has been collected regarding the capabilities of nitric-phosphoric acid oxidation. Foremost, this work, though incomplete, shows that the process will likely be suitable for heterogeneous solid waste streams containing both cellulose and plastics. Liquid waste streams containing high concentrations of EDTA can also be remediated. As shown in Tables 4 and 5, there are no significant concerns about oxidizing oxygenated compounds such as cellulose or EDTA. The impact of easily-oxidized compounds on the process are even less important in light of the more severe conditions that will be required to oxidize the plastics which are also present.

However, the extremely rapid oxidation rates of cellulose and EDTA at the conditions needed to oxidize plastics probably dictate that processing heterogeneous streams should be done in a semi-batch configuration.

It is clear that even higher temperatures and pressures will yield improved oxidation rates for polyethylene, particularly because this will protect against the process becoming acid-deficient. This is important from a processing viewpoint because the oxidation rate of plastics will likely be the rate-limiting step for the entire system. Although elevating process conditions offsets some of the process advantages from a safety standpoint, nitric-phosphoric process condition are still low compared to many other available oxidation techniques. Experience over the course of this and previous work has shown that there are very few organic materials that cannot be oxidized (i.e. Teflon). Additional experiments must be done with polyvinylchloride because it has been found to oxidize slower than polyethylene because of its greater resistance to dissolution. Dissolved compounds have a greater surface area for reaction than solid materials which produces higher oxidation rates.

Using the maximum oxidation rates observed over the first five to ten minutes of reaction, some approximate throughputs can be estimated for each of the three compounds tested. Assuming one liter of nitric-phosphoric acid solution, the process rates for EDTA, cellulose, and polyethylene are 140 g/hr, 90 g/hr, and 15-40 g/hr, respectively. Polyethylene is stated as a range because this work is incomplete; 15 g/hr represents what has been shown experimentally while 40 g/hr reflects trends experienced with other compounds.

All things considered, the results are promising, especially for low-volume generators. An in-situ treatment could be easily installed in a laboratory hood, and very little development needs to be done for a lab-scale system. The most significant area of development remaining for treating wastes with hazardous or radioactive metal involves metal removal from the acid. There are several techniques used by the phosphoric acid industry which are probably suitable, but none have been investigated in detail. Additional work should also be conducted in the area of volatile organics.

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TABLES AND FIGURES

Figure 1. Experimental Set-Up
Table 1. Oxidation of EDTA
Table 2. Oxidation of Cellulose
Table 3. Oxidation of Polyethylene
Table 4. Oxidation of EDTA at 140°C
Table 5. Oxidation of Cellulose at 155°C
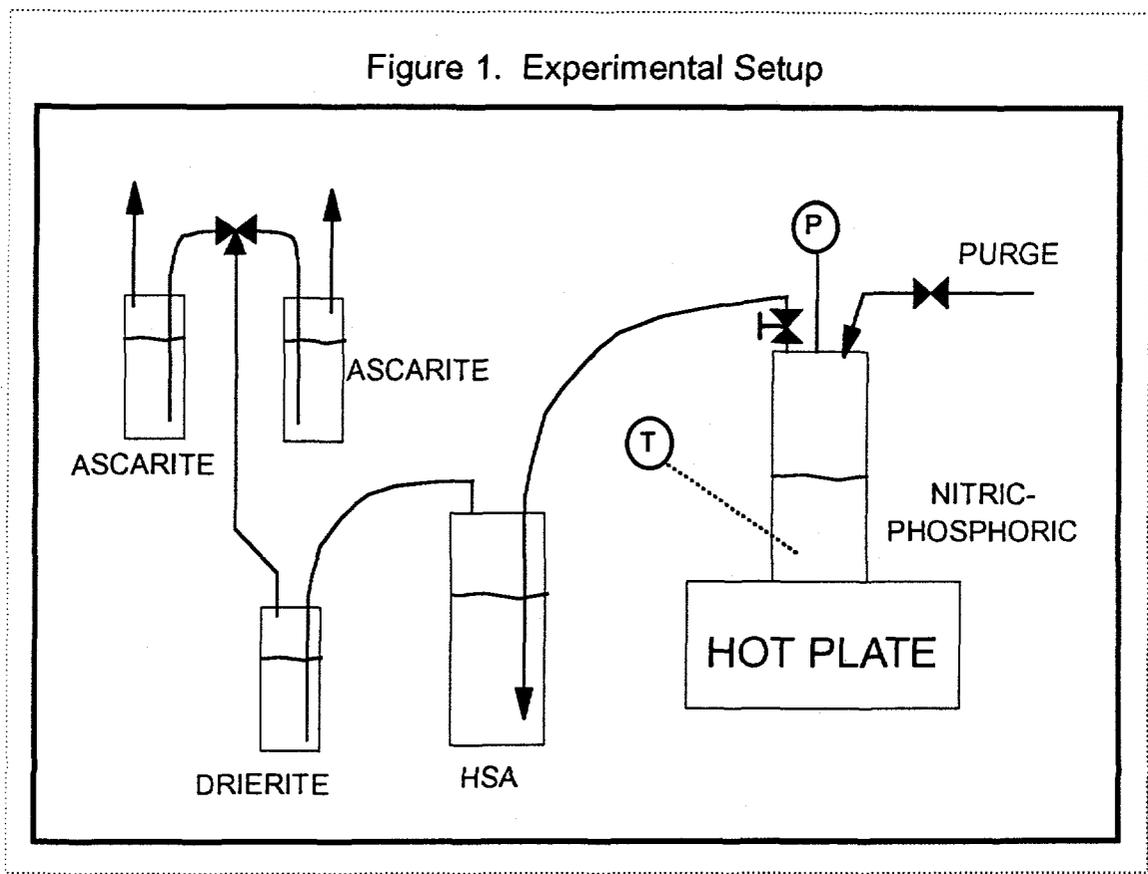Table 6. Oxidation of Polyethylene at 200°C

Figure 1. Experimental Setup

Table 1. Oxidation of EDTA
% Carbon Released as Carbon Dioxide

Time (min)	125°C	140°C	160°C	175°C
15	35.5	46.3	43.3	90.1
30	56.9	74.1	76.3	96.3
45	70.7	87	87.4	99.3
60	79.5	92.2	93.1	100.5
75	85.3	93.9	96.3	101.4
90	90.3	95.1	98.2	

Table 2. Oxidation of Cellulose
% Carbon Released as Carbon Dioxide

Time (min)	140°C	155°C	165°C
5	---	---	74.9
10	62.5	64.8	81.7
20	76.7	78.6	
30	82.4	87.5	
45	85.1	90.9	
60	87.5	94.3	
75	88.5	95.6	

Table 3. Oxidation of Polyethylene
% Carbon Released as Carbon Dioxide

Time (min)	170-175°C 101-115 kPa	185-190°C 101-115 kPa	200-205°C 170-205 kPa
20	28.4	30.5	74.2
40	52.5	60.5	87.5
60	64.5	74.1	92.9
80	69.9	77.9	97.1
100	73.9	83.5	100.3

Table 4. Oxidation of EDTA at 140°C
% Carbon Released at Carbon Dioxide

Time (min)	0.33g EDTA in 28 mL	0.68g EDTA in 30 mL	1.30g EDTA in 32 mL	2.15g EDTA in 34 mL
5	---	---	---	50.4
10	50.3	62.5	57.7	72.6
15	69.1	72.2	70.2	82.7
20	78.9	80.5	77.3	90.4
30	87.4	86.3	85.3	94.7
40	91.1	91.6	89.8	95.8
50	93.9	93.5	92.6	96.5
60	95.4	95.1	95.6	97

Table 5. Oxidation of Cellulose at 155°C
% Carbon Released as Carbon Dioxide

Time (min)	0.12g paper in 28 mL	0.25g paper in 28 mL	0.49g paper in 30 mL	1.01g paper in 32 mL
5	---	48	38.9	39.2
10	64.8	75.7	68	69.5
15	---	83.4	---	73.4
20	78.8	---	81.5	---
30	90.9	90.3	87.5	83.8
45	94.3	93.8	89.6	85.4
60	95.6	96.4	90.9	86.1

Table 6. Oxidation of Polyethylene at 200-205°C, 170-205 kPa
% Carbon Released as Carbon Dioxide

Time (min)	0.06g PE in 25 mL	0.12g PE in 25 mL	0.24g PE in 25 mL
20	74.2	75.7	29
40	87.5	86.5	58.1
60	92.9	89.5	68.2
80	97.1	92.6	
100	100.3	93.4	