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ABSTRACT

Nitric-phosphoric acid oxidation has been developed specifically to address issues that face the Savannah River Site, other defense-related facilities, private industry, and small-volume generators such as university and medical laboratories. Initially 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-hazardous waste forms. The process is unique to Savannah River and offers a valuable alternative to other oxidation processes that require extreme temperatures and/or elevated pressures.

To address the broad categories of waste, many different organic compounds which represent a cross-section of the waste that must be treated have been successfully oxidized. Materials that have been quantitatively oxidized at atmospheric pressure below 180°C include neoprene, cellulose, EDTA, tributylphosphate, and nitromethane. More stable compounds such as benzoic acid, polyethylene, oils, and resins have been completely decomposed below 200°C and 10 psig.

The process uses dilute nitric acid in a concentrated phosphoric acid media as the main oxidant for the organic compounds. Phosphoric acid allow nitric acid to be retained in solution well above its normal boiling point. The reaction forms NOx vapors which can be reoxidized and recycled using air and water. The addition of 0.001M Pd(II) reduces CO generation to near 1% of the released carbon gases.

The advantages of this process are that it is straightforward, uses relatively inexpensive reagents, operates at relatively low temperature and pressure, and produces final solutions which are compatible with stainless steel equipment. For organic wastes, all carbon, hydrogen, and nitrogen are converted to gaseous products. The process catalysts are either not consumed or can be regenerated. If interfaced with an acid recovery system which converts NOx back to nitric acid, the net oxidizer would be oxygen from air.

INTRODUCTION

The purpose of this program has been to demonstrate a nitric-phosphoric acid destruction technology which can treat a heterogeneous waste stream. This technology is being developed to convert hazardous liquid and solid organics to inorganic gases and salts while simultaneously performing a surface decontamination of the noncombustible items (the decontamination effects of this process are not discussed here). Plutonium-contaminated waste is an issue because of its stringent storage, shipping and disposal requirements.

The process envisioned will be configured to handle a wide range of solid Pu-contaminated waste of which 60% is combustible. The process will oxidize the combustibles (a mixture of 14% cellulose, 3% rubber, 64% plastics, 9% absorbed oil, 4% resins and sludges, and 6% miscellaneous organics) without requiring separation from the noncombustible portion. The system is being developed to operate below 200°C at moderate pressures (0-15 psig).
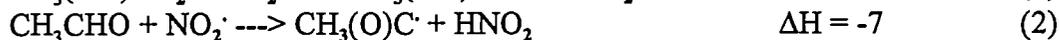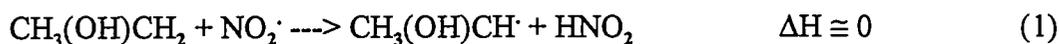
OXIDATION CHEMISTRY

The technology being developed is unique to SRTC and is the subject of WSRC invention disclosures. The process identified by SRTC is a wet-chemical process for completely oxidizing organic materials at moderate temperatures and pressures using common inorganic acids, nitric and phosphoric. It differs from other comparable technologies in that it does not require the use of extreme processing conditions or RCRA-listed hazardous metals to decompose the waste.
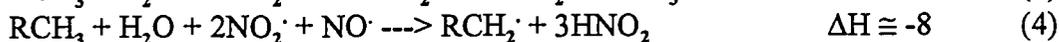
The process uses dilute nitric acid in a concentrated phosphoric acid media as the main oxidant for the organic compounds. Phosphoric acid allows oxidation at temperatures up to 200°C and is relatively non-corrosive on 304-L stainless steel near room temperature. A simple process that uses oxygen from air or another readily available cheap oxidant as the net oxidizer would be relatively inexpensive per unit of waste consumed.

Many organic materials have been completely oxidized to CO_2, CO, and inorganic acids in a 0.1M HNO_3/14.8M H_3PO_4 system; others have been decomposed in 1.0M HNO_3/13.9M H_3PO_4. Compounds quantitatively oxidized include nitromethane, cellulose, tartaric acid, tributylphosphate, EDTA, neoprene, benzoic acid, polyvinylchloride, and polyethylene. Addition of 0.001M Pd^{+2} converts most of the CO in the released carbon gases to CO_2.[1] The oxidation is usually complete in one or two hours for most organic materials with the oxidation rate for non-aliphatic organic solids being moderately fast and surface area dependent. Aliphatic compounds, because of their relative stability, oxidize slower than non-aliphatic materials.

Direct oxidation of most organic compounds by nitric acid, is energetically favorable but very slow due to its inability to break the carbon-hydrogen bond[2,3]. The oxidation of organic compounds is usually initiated by the production of organic radicals generated by dissolved $NO_2\cdot$ and $NO\cdot$ in solution. For many types of oxygenated organic compounds the attack by $NO_2\cdot$ can be first order.

$$CH_3(OH)CH_2 + NO_2\cdot \longrightarrow CH_3(OH)CH\cdot + HNO_2 \qquad \Delta H \cong 0 \qquad (1)$$
$$CH_3CHO + NO_2\cdot \longrightarrow CH_3(O)C\cdot + HNO_2 \qquad \Delta H = -7 \qquad (2)$$

For aliphatic compounds, higher concentrations of $NO_2\cdot$ and $NO\cdot$ are needed to obtain comparable oxidation rates.

$$RCH_3 + H_2O + 3NO_2\cdot \longrightarrow RCH_2\cdot + 2HNO_2 + HNO_3 \qquad \Delta H \cong -15 \qquad (3)$$
$$RCH_3 + H_2O + 2NO_2\cdot + NO\cdot \longrightarrow RCH_2\cdot + 3HNO_2 \qquad \Delta H \cong -8 \qquad (4)$$

The organic radicals may then readily react with nitric and nitrous acids or $NO_2\cdot$.

$$RCH_2{\cdot} + HNO_3 \longrightarrow RCH_2OH + NO_2{\cdot} \qquad \Delta H \cong -35 \qquad (5)$$
$$RCH_2{\cdot} + HNO_2 \longrightarrow RCH_2OH + NO{\cdot} \qquad \Delta H \cong -42 \qquad (6)$$
$$RCH_2{\cdot} + NO_2{\cdot} \longrightarrow RCH_2NO_2 \qquad \Delta H \cong -52 \qquad (7)$$
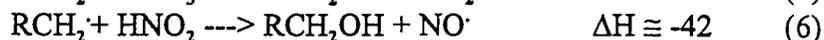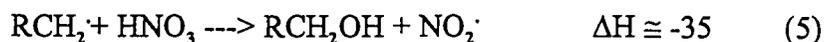
Hydrogen-carbon bonds on carbon atoms which are also bonded to oxygen are weakened, allowing much quicker hydrogen abstraction and further oxidation. As the organic molecules gain more oxygen atoms the organic molecules become increasingly soluble in the nitric-phosphoric acid solution. Once in solution, the molecules are quickly oxidized to CO_2, CO, and water. If the original organic compound contains chlorine, hydrochloric acid will also be formed.

Acid recycle will be a key part of the process. As the reaction progresses, NO and NO_2 are released from solution and nitric acid is depleted. As a result, the NO and NO_2 need to be recovered as nitric acid in order to maintain the initiation of reactions. At the same time, HCl gas from the oxidation of chlorinated compounds must be allowed to pass through to be recovered in a subsequent step. Acid recovery units for converting NOx to nitric acid are a commercially available technology.

EXPERIMENTAL SETUP

All oxidation experiments were conducted using some variation of the following. A glass reaction vessel is set up with a mixture of nitric and phosphoric acids; palladium catalyst is also added to help convert CO to CO_2. The custom-made glassware uses 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 is monitored using a laboratory thermometer in some cases and a Luxtron Model 750 Fluoroptic temperature probe in others. Sulfamic acid (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 is drierite (W. A. Hammond Drierite Co.) which absorbs moisture from the gas stream. Ascarite-II® (Thomas Scientific) absorbs CO_2 and then is weighed to determine how much carbon dioxide has been released from the reaction. Weights are taken using a calibrated Mettler AE200 balance which is accurate to 0.0001g. Polyethylene samples were taken from Nalgene® bottles. Trimsol® is a product of Master Chemical Company.

OXIDATION OF DIFFERENT COMPOUNDS

Early experiments demonstrated the application of nitric-phophoric oxidation for various organic materials, and the importance of adding trace Pd catalyst to reduce CO generation.[1] These tests show that in 0.05-0.1M HNO_3 in H_3PO_4 at 120-160°C and atmospheric pressure that many types of compounds can be quantitatively destroyed. Compounds completely oxidized, within experimental error, include cellulose, EDTA, tributylphosphate (TBP), nitromethane, and neoprene. Addition of 0.001M Pd(II) reduced the percent CO of the total CO and CO_2 released by a factor of 15-25. For example, cellulose released 20% CO in the absence of Pd(II) and only 0.9% when Pd(II) was present; for TBP, 43% CO evolved without palladium compared to 1.3% with Pd(II), and the percentage of CO released during nitromethane oxidation was reduced from

60% down to 2.3%. Using similar oxidation conditions, it was found that the destruction of polyethylene was slow and incomplete.

In separate tests, high density polyethylene has been quantitatively oxidized to CO_2 and CO using typical microwave sample digestion conditions (150-160°C, elevated pressures) in 1M HNO_3/13.9M H_3PO_4 (Table I).[4] Addition of 0.001M Pd(II) to solution reduces CO production by a factor of three; higher concentrations will probably reduce the CO fraction even further. Recent work has shown that the primary advantage to sealed-vessel microwave dissolutions is the ability to obtain both high temperatures and acid concentrations at the same time. The rapid oxidation of aliphatic plastics such as polyethylene and PVC depends on obtaining higher temperatures and acid concentrations. Experimental work in this area is discussed later.

TABLE I. Oxidation of HDPE Using Microwave Digestion at 100 Watts

Oxidizing Solution	Digestion Time (min)	%C Released to Gas Phase	Carbon Gas Composition %CO	%CO$_2$
15.9M HNO_3	30	50.0±2	21	79
15.9M HNO_3	40	81.5±2	21	79
1.05M HNO_3/ 13.8M H_3PO_4	40	74±2	18	82
0.55M HNO_3/ 14.3M H_3PO_4	55	84±2	14	86
0.001M Pd(II)/ 1.00M HNO_3/ 13.9M H_3PO_4	50	98±2	6	94

As discussed earlier, oxygenated compounds are more easily decomposed than aliphatic compounds, requiring one NO_2^- to cleave a bond instead of three. This is clearly depicted in Figure 1 which shows the oxidation, under different conditions, of the primary compounds in the target feed stream. Each sample of PVC, polyethylene, cellulose, and benzoic acid contained comparable levels of carbon. Cellulose oxidizes fastest because it is already partially oxygenated. The differences between PVC and polyethylene stem from different dissolution characteristics. Polyethylene dissolves faster than PVC and, therefore, experiences faster reaction rates due to the increased surface areas of
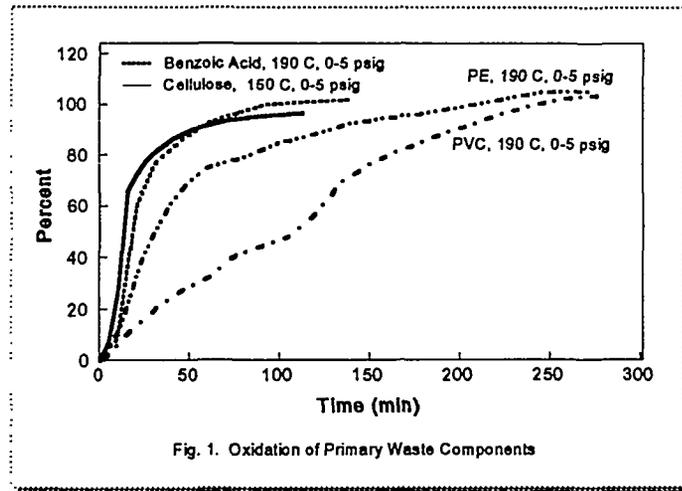

Fig. 1. Oxidation of Primary Waste Components

its dissolved state. The nearly constant oxidation rate of PVC may be attributed to its slow dissolution.

The oxidation of benzoic acid, an aromatic compound, is relatively fast at atmospheric pressure; the high oxidation rate is not surprising because benzoic acid readily dissolves in the process liquid. Oxidation rates of ion exchange resins, a component of the target waste stream which contains styrene, are expected to be comparable to plastics and not benzoic acid. However, the benzoic acid oxidation does demonstrate that aromatic compounds will be completely oxidized once they dissolve.

PARAMETRIC STUDIES

As is evident from Figure 1 and the fact that plastics account for about 40% of SRS solid transuranic (TRU) waste, the rate-limiting step in the process is oxidation of plastics. Because of this, a parametric study was run with a water-soluble oil (Trimsol®) to better understand the effects of temperature and acid concentration on soluble aliphatic compounds. Trimsol® simulates plastics once they dissolve; it is also the same oil used in machining operations throughout the DOE Complex, particularly Rocky Flats.

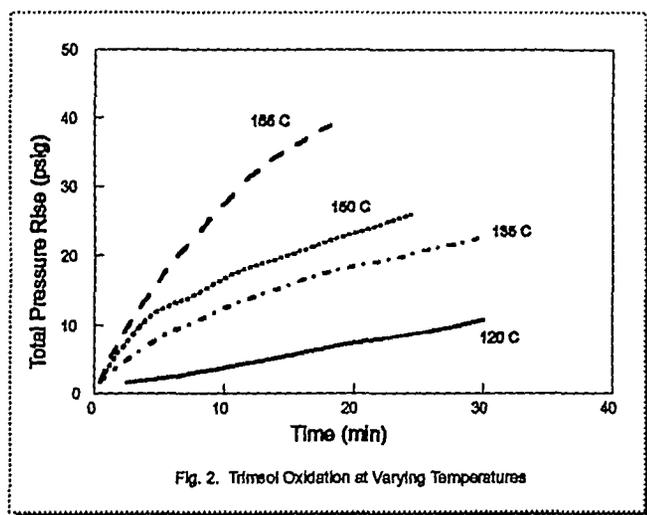Although it is known that reaction rate increases with both temperature and acid concentration, our experiments quantify those effects. Figure 2 shows the importance of temperature. Calculated oxidation rates for runs at 120, 135, 150, and 165°C, respectively, are 0.7, 1.8, 3.3, and 5.5 mL/(hr·liter of solution). It is interesting that the data suggests that the reactions at 120, 135, and 150°C probably do not go to completion, which is in general agreement with what was reported by Seminov.[2] Follow-up studies revealed the role of nitric acid concentration at 165°C. The corresponding oxidation rates for 0.1, 0.5, and 1.0M nitric acid in concentrated phosphoric acid are 1.4, 5.0, and 5.7 mL/(hr·liter of solution).

Fig. 2. Trimsol Oxidation at Varying Temperatures

A subsequent test was run to determine which parameter plays a greater role, temperature or acid concentration. In this experiment, starting solutions were made at 155, 170, and 185°C which had the maximum soluble nitric acid concentration; solubility is a function of temperature. The respective nitric acid concentrations in concentrated phosphoric acid (determined by ion chromatography measuring the nitrate ion) were 0.148, 0.0645, and 0.0195 g/mL. The data has been plotted in Figure 3.

The initial oxidation rate for each experiment is approximately 35 mL/(hr·liter of solution). The results were unexpected as each reaction exhibits essentially the same initial reaction rate

independent of the acid concentration-temperature combination. However, the oxidation characteristics of more stable compounds is apparent as the reaction at 155°C stops before completion and the reaction at 170°C achieves complete oxidation at a much slower rate than 185°C. The slowing of the reaction at 185°C may be a function of acid depletion, but this has not been determined experimentally.

Fig. 3. Trimsol Oxidation at Maximum Nitric Acid Conditions

OXIDATION OF PLASTICS

The earliest experiments in the oxidation of plastics used sealed vessels and microwave heating. This approach was taken because microwave vessels offered high-pressure capabilities, and it was originally thought that microwaves might play a role in the oxidation. Making precise statements based on the early tests is difficult due to the inability to monitor temperature or pressure. Nonetheless, experiments run using microwaves and the same digestion conditions provided insight into the effects of nitric acid concentration on polyethylene dissolution (Table II). This set of data reflects quite well what was observed in comparable experiments using Trimsol. A later microwave test during a vendor demonstration suggests that the temperature for the tests represented in Table II was approximately 150-160°C and 15 psig (205.1 kPa).

Table II. Parametric Microwave Digestion of HDPE

HNO$_3$ Molarity in Conc. H$_3$PO$_4$	Time (min)	Liquid (mL)	% Digested
1.0	45	7.5	87.5
0.5	45	7.5	50.7
0.2	45	7.5	17.4
0.1	45	7.5	0
1.0	45	15	100
0.5	45	15	82.3
1.0	55	15	100
0.5	55	15	88.7

The results observed with microwaves fostered tests using conventional heating to oxidize polyethylene. Runs at 175 and 190°C, 0-5 psig (101.5-136.0 kPa), and the maximum soluble concentration of nitric acid yielded the results of the bottom two curves in Figure 4. Once again,
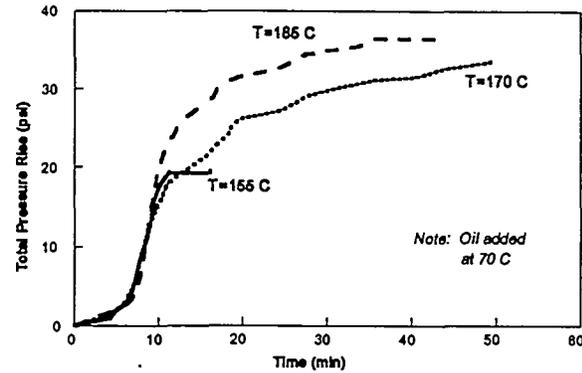
as was observed with Trimsol® in Figure 3, the initial reaction rates are almost identical. It was also observed, consistent with Figure 3, that the test at the higher temperature showed better oxidation of the more-stable, long-chain intermediates. The temperature effect for plastics is not as pronounced as that for the oil because the plastic is a solid and has a more limited surface area in contact with solution. Tests using the same reaction temperature and acid concentration while varying the system pressure seemed to have little effect on oxidation rates.

Because the parameter of pressure by itself had no observable impact on plastic oxidation, it was determined that the primary value of pressurized systems (as in the microwave) is that they permit both higher reaction temperatures and acid concentrations instead of forcing the selection of one or the other. The effect o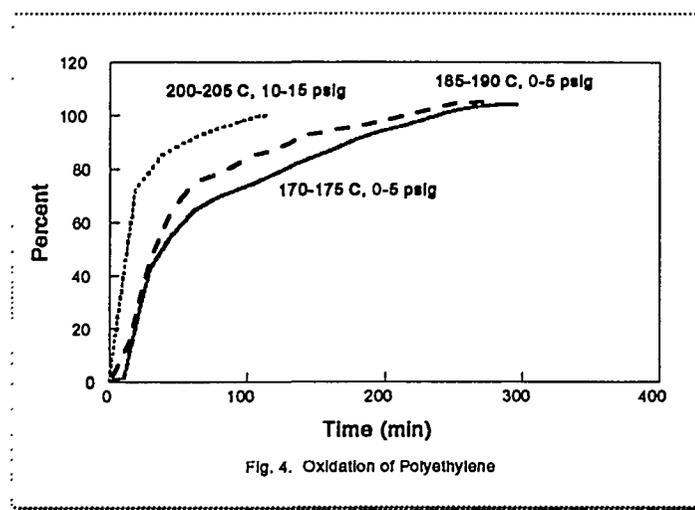f having both higher temperatures and acid concentrations is clearly shown in the top curve for polyethylene in Figure 4. Calculations using the graph yield oxidation rates at 175, 190, and 205°C of 0.036, 0.034, and 0.107 $g/cm^2 \cdot hr$, respectively.

Fig. 4. Oxidation of Polyethylene

Based on this experiment, it is believed that optimum conditions for easily-oxidized or short- chain compounds such as cellulose involve lower temperatures and higher acid concentrations due to rapid reactions and corresponding rapid acid depletion. Conversely, the optimum system for plastics, where the oxidation of long-chain intermediates is more important, will seek a safe way to maximize temperature and nitric acid concentration using elevated pressures. However, moderate oxidation rates can still be achieved using slightly lower temperatures and atmospheric pressure.

MATERIALS OF CONSTRUCTION

The fact that nitric-phosphoric acid attacks stable organic materials at elevated temperatures makes it likely that it will also aggressively corrode many metals. Prior corrosion data and information in the literature on the corrosivity of phosphoric acid and nitric acid provided hope that high-alloy metals would be satisfactory for construction of main processing equipment.[5] This, however, is not as substantial an issue as it first appears. Since the system will operate near atmospheric pressure, glass-lined and Teflon®-lined vessels are suitable materials for the oxidation vessels. The use of glass-lined and Teflon®-lined vessels helps keeps the capital cost of equipment and replacements low. All other equipment which handles lower-temperature processing can be constructed from less expensive materials such as 304L or 316L stainless steel or Hastelloy C-276.

SUMMARY

Nitric-phosphoric acid-air oxidation has been developed to address the treatment of heterogeneous solid waste. This technology aims to destroy or decontaminate Pu-contaminated job control waste, a heterogeneous mixture of plastics, cellulosics, rubber materials, and noncombustibles. Since the issue of contaminated organics is not unique to SRS Solid Waste Management, the goals of this program are also consistent with other issues at Savannah River, DOE facilities, DoD installations, commercial nuclear operations, hazardous waste generators in private industry, and small-volume generators such as university and medical laboratories. Based on current data, the technology has also exhibited potential for remediating hazardous liquids and solids.

To address this broad category of waste, many organic compounds have been quantitatively oxidized in nitric-phosphoric acid. These compounds represent a cross-section of waste that must be treated, and contain most types of chemical bonds to be encountered. Elevating the temperature to 200°C and the pressure to 15 psig significantly enhances oxidation rates, particularly for plastics, resins, and solid aromatic compounds. The use of even higher temperatures and pressures could eliminate the need to use a phosphoric acid medium, but is currently perceived as undesirable because of the impact on scale-up and safety.

The process is nearly ready for testing with larger-scale equipment (5-10 gallons) using organic feeds with little or no metals. Additional developments in the areas of volatile organic compounds and mixed aqueous-organic streams, although not applicable to Solid Waste Management, could prove to be beneficial to SRS as well as other generators of hazardous or contaminated organic materials.

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