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MIXED ACID OXIDATION

Robert A. Pierce
Westinghouse Savannah River Company
Aiken, SC 29808

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Introduction

Several ***non-thermal*** processes have been developed to destroy organic waste compounds using chemicals with high oxidation potentials. These efforts have focused on developing technologies that work at low temperatures, relative to incineration, to overcome many of the regulatory issues associated with obtaining permits for waste incinerators. One such technique with great flexibility is mixed acid ***oxidation***. Mixed acid oxidation, developed at the Savannah River Site, uses a mixture of an ***oxidant*** (nitric acid) and a carrier acid (phosphoric acid). The carrier acid acts as a non-volatile holding medium for the somewhat volatile oxidant. The combination of acids allows appreciable amounts of the concentrated oxidant to remain in the carrier acid well above the oxidant's normal boiling point.

In the process, 70 wt.% nitric acid (boiling point = 121°C) remains in solution at 150-200°C even when the system is at or near atmospheric pressure. The nitric acid converts hazardous organic molecules to the associated oxidation products, CO_2, CO, water, and inorganic acids. Hazardous metals in the incoming waste stream dissolve into the mixed acid matrix. Nitric acid in the range of 150-200°C can effectively oxidize a wide range of stable organic materials, including paper, oils, polyvinylchloride (PVC), polyethylene, neoprene rubber, and polystyrene [Pierce, et.al., 1995].

Nitric acid is reduced primarily to NO, NO_2, and water; the NOx can be recycled. Phosphoric acid, contaminated with hazardous metals, is not consumed in the oxidation process and is disposed. The mixed acid oxidation concept has been combined with simple nitric acid recycle techniques and phosphoric acid immobilization techniques to produce a closed-loop process for treating both hazardous and radioactive organic wastes.

The mixed-acid technology was originally developed to address the specific needs of the Savannah River Site, other DOE facilities, and commercial nuclear operations. Of particular interest was the treatment of solid contaminated ***job-control waste***, a heterogeneous mixture of plastics, cellulose, lead, rubber, resins, absorbed solvents and oils, oils, steel, ceramics, HEPA filters, etc., contaminated with transuranic (TRU) elements. As a result of its process capabilities, the technology may also be applied to other hazardous and radioactive waste streams.

Fundamentals of Mixed-Acid Oxidation

Oxidation: Mixed-acid oxidation is a simple process that uses oxygen from air or another readily available oxidant as the net oxidizer. Nitric acid is (HNO_3) used as the oxidant since it can be regenerated in an acid recovery system and, to some extent, in the reaction solution. Because the oxidation occurs in the liquid phase and converts organic molecules to gaseous compounds, the process does not produce organic ash byproducts.

Liquid phase oxidation of organic molecules should be easier than gas phase oxidation at a given temperature. This is due to the ability to produce high concentrations of the reactants and to reduce termination reactions since radicals have a harder time diffusing to the walls [Seminov, 1958]. Direct oxidation of most organic compounds by HNO_3 can be energetically favorable (Eq. 1), but very slow due to the inability to break the carbon-hydrogen bond. Other oxidation pathways are not energetically favorable, as shown in Equations 2 and 3. The following heats of reaction, ΔH, values are in kcal/mole. [Seminov, 1958; Dickerson, 1969]

$$RCH_3 + HNO_3 \text{--->} RCH_2OH + HNO_2 \qquad \Delta H \cong -25 \qquad (1)$$

$$RCH_3 + HNO_3 \text{--->} RCH_2\cdot + H_2O + NO_2\cdot \qquad \Delta H \cong 35 \qquad (2)$$

$$RCH_3 + HNO_2 \text{--->} RCH_2\cdot + H_2O + NO\cdot \qquad \Delta H \cong 28 \qquad (3)$$

R denotes an organic group that does not affect the ΔH for the shown reaction. 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 organic compounds, the attack by $NO_2\cdot$ can be first order. [Smith, 1993]

$$CH_3(OH)CH_2 + NO_2\cdot \text{--->} CH_3(OH)CH\cdot + HNO_2 \qquad \Delta H \cong 0 \qquad (4)$$

$$CH_3CHO + NO_2\cdot \text{--->} CH_3(O)C\cdot + HNO_2 \qquad \Delta H = -7 \qquad (5)$$

For aliphatic compounds, higher concentrations of $NO_2\cdot$ and $NO\cdot$ are needed to initiate the reaction. At the same time, because of the apparent reaction order of three (Eq. 6 and 7), these reactions ought to be significantly accelerated under conditions of elevated pressure.

$$RCH_3 + H_2O + 3NO_2\cdot \text{--->} RCH_2\cdot + 2HNO_2 + HNO_3 \qquad \Delta H \cong -15 \qquad (6)$$

$$RCH_3 + H_2O + 2NO_2\cdot + NO\cdot \text{--->} RCH_2\cdot + 3HNO_2 \qquad \Delta H \cong -8 \qquad (7)$$

A typical aliphatic carbon-hydrogen bond strength of 99 kcal/mole was used in the calculations [Smith, 1993]. The organic radicals are then either oxidized by nitric and nitrous acids or nitrated by $NO_2\cdot$. When this happens, hydrogen-carbon bonds on carbon atoms that are also bonded to oxygen are weakened, thereby allowing much quicker hydrogen abstraction and further oxidation. As the organic molecules gain more oxygen atoms the organic molecules become increasingly soluble in the oxidation solution. Once in solution the molecules are quickly oxidized to CO_2, CO, water. If the original organic compound contains chlorine then HCl (hydrochloric acid) and NOCl can be formed; chlorine gas has not been observed.

Along with oxidation, there is likely a dehydration reaction aiding in the decomposition of the organic oxidation products. This occurs due to the presence of 14.8M (or higher) H_3PO_4, which is a strong dehydrating agent. For example, due to the strong dehydrating ability of the reaction solution, cellulose can be carbonized in concentrated H_3PO_4 near 140°C through a series of intermediate compounds to form carbon and water. The carbon is readily attacked by nitric acid with CO being one of its reaction products. The fraction of CO released can be as high as 60%. It is possible that the relative production of CO and CO_2 is determined to some extent by competing mechanisms; the CO by way of a dehydration mechanism and the CO_2 from oxidation with HNO_3 and $NO_2\cdot$ [Smith, 1993]. The presence of large amounts of CO in the offgas led to the addition 0.0010-0.0015M of dissolved palladium in the phosphoric acid to reduce the CO levels to below 2.5%

Implementation of the technology is made possible by the limited, but sufficient, solubility of nitric acid in concentrated phosphoric acid. Concentrated nitric acid (70 wt. %) boils at 121^{o}C, which is well below the temperature range (150-200^{o}C) needed for vigorous reaction rates. At atmospheric pressure, phosphoric acid can retain up to 148 g/L HNO_3 at 155^{o}C and 20 g/L HNO_3 at 185^{o}C. The solubility of HNO_3 in H_3PO_4 increases with increasing pressure (Table 1). While pressurization of nitric acid to raise its boiling point has been used in the oxidation of small organic sample, safety concerns about elevated pressures and runaway nitric acid reactions inhibit further development.

An important process-related issue exists with regard to safety when considering the reaction of organic molecules with nitric acid. The common concern is that stable nitrated organics can form explosive mixtures. While ***nitration*** of organic molecules is a common industrial method, the conditions existing in the mixed acid oxidation system do not provide the appropriate matrix for stable nitrated organic molecule formation [Olah, et.al., 1989]. Two conditions work together and rapidly hydrolyze any potential nitrated compounds. First, the presence of water readily strips nitro groups to form the corresponding alcohol. If moisture is not removed from the reaction, explosive compounds are difficult to form. A second reaction involves the reaction of hot, concentrated mineral acids with nitroparaffins to produce a hydroxylamine and organic acid. [Fuson, 1950] As a result, nitrated organics do not build up during mixed-acid oxidation and the process can be safely operated.

Off-gas Handling: Several approaches exist for handling the offgas, but the most attractive involve the recycle of nitric acid. Some options employ proprietary technology of which little is known aside from vendor claims. The best-known approach is the one used in nitric acid manufacturing. Nitrous oxide (NO) is combined with air (to form NO_2 gas) and then contacted with water in a distillation column. The downsides of this approach, high operating pressures (6-12 atm) and large reaction columns, make this approach impractical for small-scale operations.

The most attractive alternative for most situations is hydrogen peroxide absorption. Hydrogen peroxide readily absorbs both NO and NO_2 to produce nitric acid. Calculations of the maximum theoretical nitric acid concentration expected for absorption of NO_2 using hydrogen peroxide indicates nitric acid concentrations in excess of 60 wt.% could be obtained using 30% hydrogen peroxide. Using the equation

$$2\ NO_2 + H_2O_2 \text{ - - - - - > } 2\ HNO_3 \qquad (8)$$

it was determined that a maximum concentration of 61.3 wt% could be obtained with 30% H_2O_2 and 78.7 wt% with 50% H_2O_2. These calculations do not account for any acid formation that may occur due to NO_2 absorption by the balance of water in the hydrogen peroxide solution.

It is important to note that the presence of NO gas in the stream reduces the maximum theoretical concentration. The reaction of NO with H_2O_2 is as follows:

$$2\ NO + 3\ H_2O_2 \text{ - - - - - > } 2\ HNO_3 + 2\ H_2O \qquad (9)$$

Not only is peroxide efficiency reduced, but there is also dilution from water in the reaction products. The stoichiometry yields theoretical maximum acid concentrations of 47.0 wt% for 30% H_2O_2 and 60.8 wt% for 50% H_2O_2. [Pierce, et.al., 1998]

Hazardous Metal Immobilization: The ideal process would remove metals from the acid stream and recycle the phosphoric acid. Several techniques were evaluated including ion exchange, solvent extraction, and precipitation. In each case, the difficulty of having many metals together in a viscous acid solution limits the metal recovery while making the overall process more complex. As a result, techniques were sought to immobilize the hazardous constituents within the acid matrix. Two approaches were identified that simplify the process while providing a chemically stable final waste form.

The first approach uses an iron phosphate (FeP) glass to immobilize the phosphoric acid along with residual metal contaminants. The Fe_2O_3-P_2O_5 system offers many benefits over traditional borosilicate glasses that make it well suited for this need [Ramsey, et.al., 1995]. First, FeP has a low melting point for a waste glass (1050-1100^{o}C) and low viscosity. These characteristics permit short process cycle times at relatively low temperatures. Second, the FeP system can incorporate high concentrations of metal ions, especially iron. This is important because it is expected that metal corrosion products will be a primary source of metals in the acid (carbon and stainless steels are major components of job control waste, and both exhibit high corrosion rates in the HNO_3-H_3PO_4 solution). Third, a glass waste form reduces the volume of the waste stream by approximately 40% when compared to phosphoric acid. Last, the FeP glass is extremely resistant to leaching of metals from the matrix thereby providing a waste form that is at least as stable as the current borosilicate high-level waste glasses.

Another immobilization alternative uses the chemically bonded ceramic waste forms advanced at Argonne National Laboratory (ANL) [Singh, et.al., 1994]. Two variations of the waste form were developed, magnesium phosphate (MgP) and potassium magnesium phosphate (KMgP). Of the two, the KMgP shows the most promise for incorporation into the acid oxidation process. The ceramic forms have the advantages of being made at room-temperature using low-tech equipment. ANL has demonstrated the immobilization process at the 55-gallon scale. Furthermore, KMgP waste forms are chemically stable and have been shown to pass the Toxicity Characteristic Leach Procedure (TCLP), ASTM C1220-92, for hazardous metals.

The ceramic is valuable for immobilizing RCRA metals and short-lived radioisotopes such as Cs-137 and Sr-90. The iron phosphate glass, which has the stability of a high-level waste glass, is preferable for immobilizing actinide metals. In comparison, the ceramic is easier to make while the glass provides a greater volume reduction and a more stable form.

Technology Application

Oxidation: Application of the technology is strongly dependent upon the waste matrix. For example, oxygenated hydrocarbons are more susceptible to attack than long-chain aliphatics, and acid-soluble compounds react faster than insoluble ones. Regardless, in the range of 140-210^{o}C and 0-15 psig most compounds can be quantitatively oxidized to CO_2, CO, water, and inorganic acids. Compounds that have been quantitatively oxidized as measured by CO_2 release, within experimental error (+/-2%), include cellulose, tributylphosphate, nitromethane, neoprene, benzoic acid, polyethylene, polypropylene, PVC, and both aliphatic and naphthenic oils. Any CO released was contacted with palladium metal at 150^{o}C in air to convert it to CO_2.

Experiments show the onset of oxidation for the soluble, oxygenated hydrocarbons at about 120^{o}C (e.g. cellulose, nitromethane). At 140^{o}C the oxidation of these compounds is essentially complete in less than 15 minutes (no NO_2 gas being released from solution). The result for nitromethane is important because it confirms Fuson's observations that nitrated compounds can be quickly hydrolysed in strong mineral acids at this temperature. [Fuson, 1950]. Representative reactions are as follows [Smith, 1993]:

$CH_3NO_2 + H_2O + H_3PO_4 \text{--->} HCO_2H + H_2NOH \cdot H_3PO_4$ $\Delta H \cong -44$ (10)

$H_2NOH \cdot H_3PO_4 + HNO_2 \text{--->} N_2O + 2H_2O + H_3PO_4$ $\Delta H = -66$ (11)

The surface oxidation of neoprene (poly [2-chloro-1,3 butadiene]) was found to be uniform, allowing measurement of the surface area and weight loss during its destruction. The release of chloride formed during the oxidation of neoprene had no observable effect at concentrations up to 0.1M. The effect of concentrations above 0.1M was not evaluated. Oxidation of neoprene is relatively rapid (compared to polyethylene and PVC) due to carbon-carbon double bond weakening of carbon-hydrogen bonds in α positions relative to the double bond.

The oxidation rate of aliphatic compounds such as polyethylene, PVC, and n-dodecane was found to be unmeasureably slow in an air-sparged reaction solution below $180^{o}C$. In an air-sparged system the concentration of $NO\cdot$ and $NO_2\cdot$ are too low for reactions (6) and (7) to have any appreciable effect. Complete oxidation was achieved by increasing the system pressure and eliminating the air sparge to facilitate higher $NO\cdot$ and $NO_2\cdot$ concentrations in solution. Data reflecting the oxidation behavior of polyethylene is shown in Figure 1.

The reaction rate dependence of aliphatic compounds on $NO\cdot$ and $NO_2\cdot$ levels is demonstrated in a more pronounced manner when using microwave-based sample dissolution techniques. These are well-developed methods that use mineral acids and oxidants, such as hydrogen peroxide or nitric acid, at elevated pressure (100-150 psig) and temperature (150-200^{o}C) to digest organic samples. When 0.1 gram samples of aliphatic compounds and 5 mL of 70% nitric acid are placed in a 100 mL digestion vessel, the samples dissolve in 5-10 minutes. Rapid dissolution was demonstrated on PVC, low- and high-density polyethylene, polypropylene, and Tygon®. The role of the microwave energy, other than heating, is expected to be small since it is of insufficient energy to cause bond breakage. Reactions (6) and (7) are very likely the initiating oxidation steps since the pressure vessel makes it possible for $NO\cdot$ and $NO_2\cdot$ to exist at much higher concentrations. Upon completing the digestion, process solutions were blue, indicating the presence of nitrous acid.

During rapid oxidation reactions, the ratio of CO to CO_2 in the offgas tends to increase. Under certain conditions the CO percentage can be quite high. For compounds such as cellulose, ethylenediaminetetraacetic acid (EDTA), tributylphosphate (TBP) and nitromethane, CO percentages were measured as high as 20%, 25%, 43%, and 60%, respectively. Because of the high CO fractions, palladium was added to the phosphoric acid as a catalyst for converting CO to CO_2. Concentrations of 0.0010 to 0.0015 moles per liter palladium were used. The palladium reduced the CO for cellulose, EDTA, TBP, and nitromethane by a factor of 20-25 to 0.9%, 0.9%, 1.3%, and 2.3%, respectively [Smith, 1993].

The selection of reaction conditions is very important when balancing reaction rates with process safety (i.e. limited acid concentrations, pressures, and temperatures). At the same time, conditions must be identified that will produce complete oxidation. Since increases in both temperature and acid concentration increase reaction rates, which is more important? Is it better to reduce acid concentration for higher temperatures or vice versa? Experience indicates that more stable organic compounds, such as aliphatics, will require higher temperatures for complete oxidation than those needed for oxygenated molecules, such as cellulose.

The stability of the oxidation byproducts of aliphatic molecules was demonstrated during the destruction of water-soluble oils. Starting solutions were prepared at 155, 170, and 185^{o}C with the maximum soluble nitric acid concentrations – 0.148, 0.0645, and 0.0195 g/mL, respectively. The data is listed in Figure 2. At each temperature, the initial reaction rate was essentially the same. However, the oxidation characteristics of stable intermediate compounds become apparent as the reaction at 155^{o}C stops abruptly before completion. Seminov also showed this principle. He demonstrated that organic hydroperoxides, a type of compound that has great potential for forming in this system, would decompose to release water and carbon dioxide above 130-150^{o}C. However, below 130^{o}C, the formation of stable intermediates is common [Seminov, 1958].

Conversely, when oxygenated compounds such as cellulose are oxidized above 165^{o}C they produce very rapid reactions and high volumes of gas byproducts. As a result, optimum reaction conditions for easily oxidized compounds (i.e. cellulose) include lower temperatures with higher acid concentrations to offset rapid reactions and a corresponding rapid decrease in acid concentration. Optimum conditions for PVC, polyethylene, and other long-chain aliphatics will use elevated temperatures where the destruction of long-chain intermediates is necessary [Pierce, et.al., 1995].

The application of this principle was demonstrated on a mixture of cellulose, latex rubber, polyethylene, and Tyvek®. When heated slowly, the cellulose dissolves before

90^{o}C, latex at 140-145^{o}C, polyethylene at 160-170^{o}C, and Tyvek® at 180-185^{o}C. When the waste mixture is added to the process at 160^{o}C, all material dissolves within 15 minutes except the Tyvek®. Tyvek® does not dissolve until the temperature is raised to 180-190^{o}C. When the waste mixture is added and processed at 180-190^{o}C, all materials except Tyvek® dissolve within 10 minutes. Under these conditions, the Tyvek® dissolves within 45 minutes.

Batch tests were also conducted with a mixture of cellulose, neoprene, polyethylene, and PVC at 170^{o}C/1.0M HNO_3/8-10 psig and at 185^{o}C/0.5M HNO_3/8-10 psig. The oxidation of cellulose, neoprene, and polyethylene at 170^{o}C and 1.0M HNO_3 occurred at rates similar to those at 185^{o}C and 0.5M HNO_3. In both cases the neoprene and polyethylene were dissolved within of 15 minutes, and at rates somewhat higher than anticipated. The PVC sample was dissolved in 60 minutes at 185^{o}C, and 85 minutes at 170^{o}C. It is expected that the accelerated rate for neoprene and polyethylene is caused by the oxidation of cellulose, which by its reaction produces $NO\cdot$ and $NO_2\cdot$ for an increase in initiation reactions (6) and (7). Based on the experiments conducted over the range of conditions, typical oxidation rates have been identified. These rates are listed in Table 2.

Differences between materials are not the only issue to be considered in applying the technology. Variations in thickness, density, and melting point of similar materials must also be addressed. Tests were run in a semi-continuous mode in which similar samples were added over a three-hour period. Low-density polyethylene (LDPE) from bags (thickness = 0.004”) was added to the reaction vessel at 185^{o}C and 10-12 psig. The samples dissolved within 15 minutes throughout the experiment and were subsequently oxidized. The rate of addition corresponded to a throughput rate of 20 grams per liter of solution per hour. Next, the experiment was repeated using a thicker (nominal thickness = 0.05”), higher density LDPE from bottles. Overall dissolution was 3-5 times slower because of the increase in thickness and density; the material required 50 minutes to dissolve instead of 10-15 minutes. However, the continuous oxidation rate eventually stabilizes and is only about one-half that of the polyethylene bag.

Comparable behavior has not been observed when material properties vary more significantly. For example, PVC bag samples can be oxidized in approximately one hour at 205^oC and 8-10 psig. Dense PVC pipe samples under the same conditions are essentially non-reactive. As a result, scouting studies should be run on representative waste material to assess the suitability of mixed-acid oxidation as a treatment method.

While oxidation rates are important, it is equally important to know how much waste can be processed through a known volume of phosphoric acid before the acid must be immobilized. Since phosphoric acid is not consumed in the process, inorganic material solubility determines its useful life. Based on typical job control waste streams, the inorganic compounds of greatest concern are iron, aluminum, and silicon. Iron is present as carbon and stainless steel, aluminum is present as the metal, and silicon is often a major component in cellulose. Each component has a solubility limit, and its behavior at that limit can be critical.

In practice, the greatest concern is with iron precipitation because 1) it is the most prominent metal in the waste streams, and 2) iron phosphate hydrate precipitates as a continuous gelatinous mass. The precipitate does not dissolve in water; in fact, precipitation is even worse if water is added because it increases the amount of water available to form a network of hydrates. Experimental work dissolving Fe_2O_3 into 85%

phosphoric acid shows the following iron solubility: 187 g/L at 141°C, 165 g/L and 165°C, and 144 g/L at 183°C.

Work with silica coming from paper oxidation shows that the precipitation of dissolved silica does not present immediate processing problems. Silica precipitates as an anhydrous silicon phosphate that is well divided and dispersible. At 165°C, the solubility limit for silicon in 85% H_3PO_4 is approximately 40 g/L. Experiments with aluminum also show that its precipitate could cause a need for additional processing. Additions of aluminum nitrate to 85% phosphoric acid at 190°C show an aluminum solubility limit of 75 g/liter. Furthermore, when the precipitate forms, it forms as a gelatinous mass, similar to that observed for iron. On the other hand, experiments indicate that the precipitate is water-soluble.

Off-gas Handling: In situations where HCl is generated as a byproduct of oxidation, it must be removed prior to nitric acid recovery and recycle. Experiments show that no detectable HCl remains in the oxidation vessel after the oxidation cycle. If not removed separately, the HCl will end up in the acid recycle system and, subsequently, build up throughout the system. The use of water as a scrubber for HCl was tested. While the scrubber was effective at removing HCl quantitatively up to 2000 ppm, the water also absorbs essentially all NO_2 present to form HNO_3. As the acid absorption limit for water was approached, absorption of HCl was proportional to the total acid concentration ($[HCl] + [HNO_3]$) [Pierce, et.al., 1998]. The data clearly shows that a water scrubber does not separate HCl from NO_2.

A secondary approach evaluated a simple condenser for the removal of HCl and water vapor without significant NOx absorption. The first experiments with a low surface area condenser yielded a retention of approximately 50% of the HCl while allowing 99% of the NOx to pass through the system. NOx losses come from water absorption of NO_2 to produce HNO_3. The condenser arrangement was modified for improved condensation of both HCl and water. The modified arrangement yielded somewhat better results at 67% HCl retention with 3% loss of NOx. Improved designs should yield results that will meet most process requirements. It is anticipated that removal of 75% of the HCl with less than 5% NOx loss should be sufficient.

After HCl and excess water vapors are removed, the remaining NOx stream is recovered as nitric acid by contacting it with oxygen and reacting it with hydrogen peroxide. To optimize the process, four key parameters were evaluated: 1) $NO:O_2$ ratio, 2) residence time to convert NO to NO_2 prior to absorption, 3) percent hydrogen peroxide, and 4) the use of oxygen versus air to convert NO to NO_2.

The studies revealed the following: 1) tests with pure NO yield a nitric acid concentration of 23 wt% [4.1M] (well below theoretical of 47 wt%) as compared to 61 wt% [13.2M] (at theoretical yield) when NO is mixed with air prior to absorption; 2) controlled absorption conditions have consistently shown conversion of 30% hydrogen peroxide to 13.0-13.4M HNO_3, which is at the theoretical yield; 3) 50% hydrogen peroxide absorbs to 67 wt% (compared to 79% theoretical, which is above the 70 wt% HNO_3 azeotrope) and does not offer an advantage over 30% peroxide commensurate with the higher cost, concentration, and chemical instability; 4) oxygen does not seem to provide any significant benefit over air; 5) the optimum residence time required for maximum use of the hydrogen peroxide is 60-90 seconds, although times as little as 30 seconds can be effectively used; and 6) the optimum $NO:O_2$ ratio is 1:1, but ratios as low as 1:2 reduce NOx absorption by less than 10% [Pierce, et.al., 1998]. A table of relevant data is shown in Table 3.

In conjunction with optimization testing, analyses were also conducted on the NOx concentration emitted after being passed through three absorption vessels in series. Continuous monitoring of NOx emissions from the third peroxide vessel always showed 30 ppm or less, and was primarily below 5 ppm. This is within the clean air standard limit of 200 ppm. Although absorption efficiency is largely a function of geometry and gas-liquid contacting, the data is indicative of what can be expected from nitric acid recycle operations.

A separate series of tests was devised to identify hazardous and volatile components in the off gas with the ultimate objective being able to evaluate dioxin production potential. On the bench scale, tests were run with surrogate waste streams and dioxin precursors to address the range of temperature, pressure, and nitric acid compositions anticipated. Cellulose, polyethylene, neoprene, and PVC samples were used as the bulk waste. Pentachlorophenol (PCP) and trichlorophenol (TCP) were added as dioxin precursors. Water scrubbers and charcoal filters were placed in series in the off-gas stream to collect organic emissions.

The water scrub for the oxidation of the above surrogate waste was found to contain no chlorinated or aromatic compounds. There were trace quantities (less than 1 mg/L) of mixed ketones – ketones are generally thought of as neutral, mobile volatile liquids that are the second step in the oxidation of a hydrocarbon. Trace quantities of alkyl nitrates and short-chain chlorinated hydrocarbons were also identified in the scrubber. No organic compounds were found in the activated carbon filter downstream of the liquid scrubber. The residual concentrated phosphoric acid was also analyzed following a series of eight tests. It contained trace quantities of both chlorinated pyridine and nitrochlorobenzene, but no other related compounds. The findings demonstrate that nitrated organics, although present in trace quantities, do not build up in solution. Furthermore, there were no phenols or dioxins identified in solution above the detection limit of 1 mg/L.

Off-gas tests were replicated using a 40-liter pilot system. These tests used much larger quantities of surrogate waste stream, but still used the same charcoal tubes for final emissions testing. The water wash for the tests had an organic mix of 2-4 ppm alkyl nitrates and other trace chlorinated hydrocarbons. In is unclear whether the alkyl nitrates were absorbed as alkyl nitrates, or whether they had been absorbed as a different compound and then nitrated by the stream of NOx passing through the water. Throughout pilot testing, there were no dioxins or phenols detected. This combination of bench-scale and pilot-scale tests indicates that no detectable organic emissions should pass through the nitric acid recycle system – an extremely important characteristic for an incineration alternative.

Hazardous Metal Immobilization: Although relevant immobilization techniques are well-represented in the literature, they do not directly address the specific needs as they relate to mixed-acid oxidation. In evaluating the ceramic forms, both MgP and KMgP were tested. MgP is produced by gradually mixing an appropriate mixture of MgO and H_3BO_3 to diluted phosphoric acid (<60 wt%). During the addition of MgO and H_3BO_3, a large heat spike occurs due to the neutralization of the acid, and, if not managed correctly, can lead to premature curing of the ceramic. The KMgP process first neutralizes the H_3PO_4 stream with KOH and the optimum amount of water to produce a solution with KH_2PO_4 crystals present. Next, a mixture of MgO and additional KH_2PO_4 is added and the slurry is stirred until it begins to thicken. With KMgP, because the heat of neutralization occurs with KOH addition, the solid components can be added much more liberally without premature curing.

A primary issue associated with producing the KMgP is optimizing the formulation to minimize the waste volume. Two different compositions were made, one formulation recommended by Argonne National Lab and the other with 15% less water; water dampens the curing reactions. The first sample was stirred for 9 minutes before it began to set up. The reduced-water sample reached a higher temperature than the first sample, and it was stirred for only 4 minutes. The samples were allowed to cure for two weeks before being submitted for leach testing.

The samples were leach tested using a modified TCLP method. The results show that Si^{4+}, PO_4^{3-} and NO_3^- leach from the second sample at 2-3 times the rates observed in the first sample. Furthermore, the first sample showed less that 0.007 mg/L Mg leached versus 309 mg/L Mg for the second sample. The variations in leach rates, particularly with the Mg, are caused by the insufficient curing brought about by rapid solidification. Argonne National Lab has performed a wide range of TCLP tests under varying conditions to characterize the leach rates of both MgP and KMgP waste forms. The ANL studies have shown that both phosphate-bonded ceramics consistently meet the RCRA limits [Singh, et.al., 1994].

Nonradioactive and radioactive work was also conducted on iron phosphate glass to identify the preferred glass composition for immobilizing radioactive solutions.

Testing examined the range of primary components: Fe_2O_3, 15-45 wt.%; Na_2O, 0-6 wt.%; SrO, 0-3 wt.%; balance is P_2O_5. Glasses were consistently produced for formulations containing 20-40% Fe_2O_3, 4-6% Na_2O, 2-3% SrO, and 51-74% P_2O_5. Based on the quality of glasses formed, the preferred formulation is 33% Fe_2O_3, 5.5% Na_2O, 2.5% SrO, and 59% P_2O_5. This composition allows fluctuation in the composition without jeopardizing glass formation.

As a follow-up, glasses were made with the preferred formulation using radioactive and nonradioactive mixed-acid oxidation process solutions with the exception that barium was used instead of strontium. Samples were submitted for leach testing using the Product Consistency Test (PCT), ASTM C-1285. The leachability for the primary components of the nonradioactive glass were as follows: P = 0.022 g/L, Ba = 0.001 g/L, Na = 0.087 g/L, and Fe = 0.001 g/L. Results for the radioactive glass were P = 0.031 g/L, Ba = 0.002 g/L, Na = 0.104 g/L, and Fe = 0.000 g/L. Comparing this to the Environmental Assessment (EA) glass standard for borosilicate glass is difficult because the major components differ. However, both the EA and FeP glasses contain comparable amounts of sodium, 12.1% for the EA glass versus 5.5% for the FeP. The allowable leachability for sodium from the EA glass is 13 g/L and is approximately 100 times greater than the sodium leach rates observed for FeP. In addition, TCLP results indicated that the RCRA metals present did not leach at detectable limits with the exception of barium (present at 2.5 wt%) which leached at 1.05 mg/L (which is below the RCRA limit of 100 mg/L). Strontium eventually replaced barium to avoid the use of a RCRA hazardous metal in the glass formulation.

Both KMgP and FeP prove to be acceptable final waste forms for the mixed-acid oxidation process. Of particular value is their tolerance of wide ranges of impurities. When combined with the acid oxidation and nitric acid recycle, the three components yield a closed-loop process that can treat a wide range of waste types. All unit operations are based on simple technology and can be easily integrated. Integrated systems have been demonstrated in the laboratory and with an engineering-scale system (40-liter oxidation vessel).

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For Further Information

The cited references by Pierce and Smith contain detailed discussions of the technology as it has evolved from its inception to the current state of development. Phosphate bonded ceramics such as MgP and KMgP are discussed extensively in Chapter 8 of this handbook.

Defining Terms

Job-control waste: A heterogeneous mixture of plastics, cellulose, lead, rubber, resins, absorbed solvents and oils, steel, ceramics, etc., generated during process operations.

Nitration: A chemical reaction that introduces the NO_2 group into an organic compound.

Non-thermal**:** A classification established for alternative oxidation technologies that sets maximum operating conditions at 350°C and 200 psig.

Oxidant: The substance that causes the oxidation of another element through the donation of electrons; the electron donation may involve the transfer of oxygen atoms.

Oxidation: The process by which the oxidation number of a substance is increased; the process frequently involves the union of the substance with oxygen.

Table 1. HNO_3 Solubility in Concentrated H_3PO_4

	Temperature		
Pressure	**155°C**	**170°C**	**185°C**
0 psig	148 g/L	64 g/L	20 g/L
10 psig	195 g/L	107 g/L	46 g/L
20 psig	252 g/L	147 g/L	73 g/L
Pressure	**190°C**	**205°C**	**220°C**
15 psig	40 g/L	15 g/L	1.3 g/L

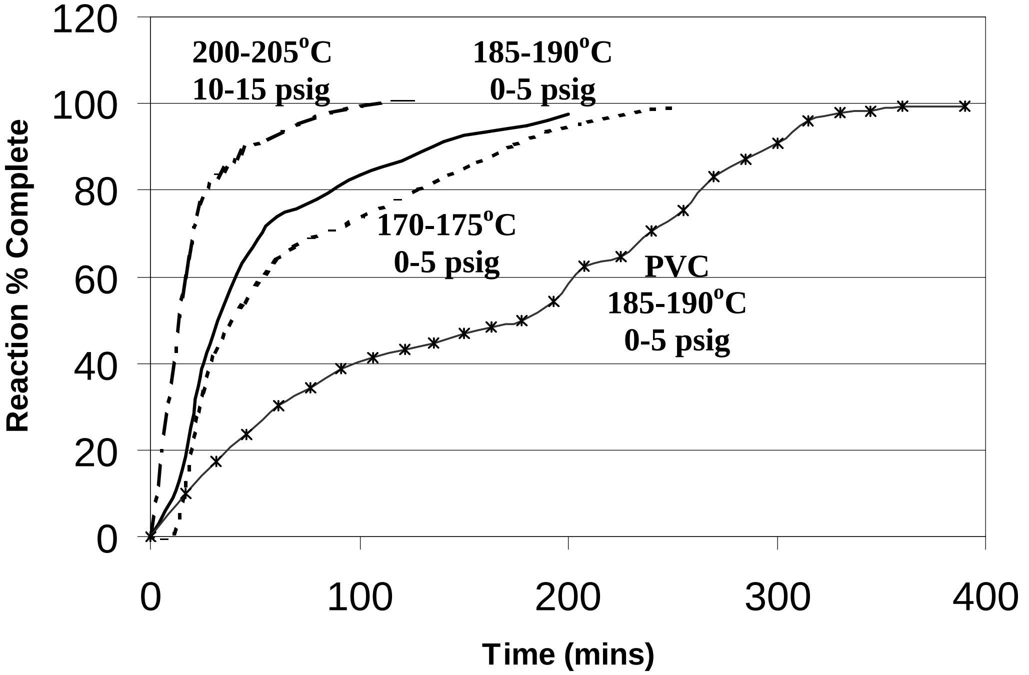
Table 2. Typical Oxidation Rates (g/hr) per Liter of Reaction Solution

Compound	155°C 0-5 psig	170°C 0-5 psig	185°C 0-5 psig	170°C 12-15 psig	185°C 12-15 psig	205°C 12-15 psig
Cellulose	95	150	>150	>150	--	--
Neoprene	--	40	--	70	--	--
LDPE	2	5	13	14	40	90
HDPE	--	--	--	--	--	25
PVC	<1	1	4	4	15	35
Benzoic Acid	--	--	--	--	45	--
Styrene Resin	--	30	--	65	--	--

Table 3. NOx Absorption into 30% Hydrogen Peroxide

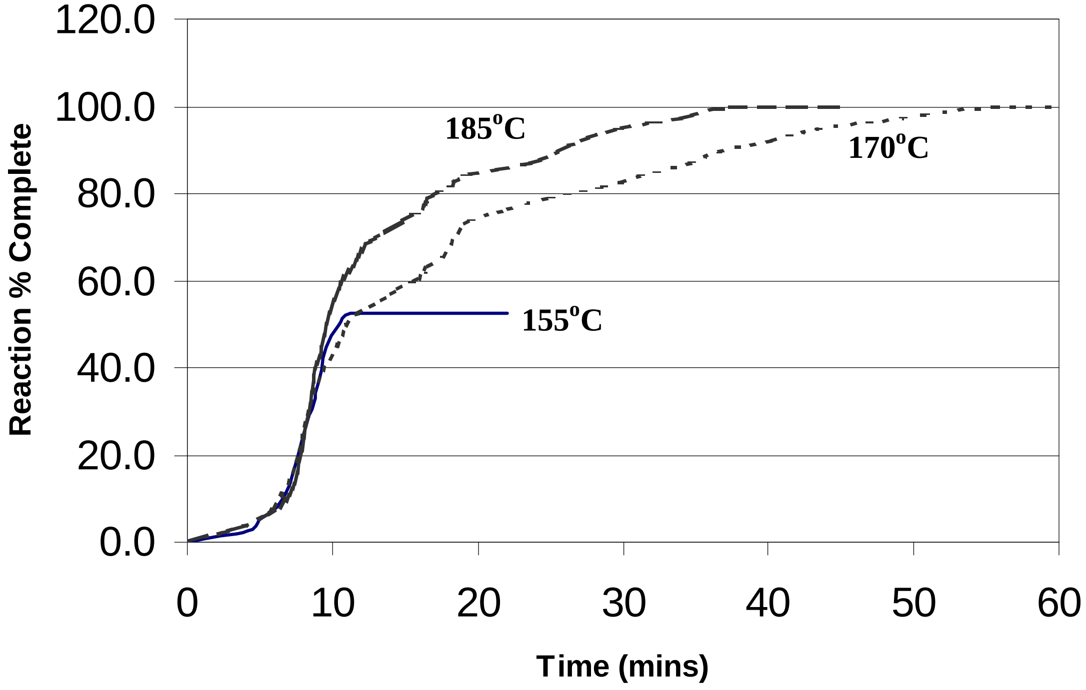
O2:NO	0	1:2	2:2	5:2	1:2	1:2	1:2	1:2
Oxidant	n/a	Air	Air	Air	Oxy	Air	Oxy	Air
Res. Time	60	60	60	60	60	30	30	120
Moles NOx Fed	**Acid Concentrations Measured Using Titration (Moles/liter)**							
0.000	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.016	1.35	2.04	2.11	1.74	1.16	1.02	0.86	0.62
0.032	2.75	4.70	5.63	3.87	2.83	3.33	3.13	2.40
0.065	4.10	8.44	9.20	7.24	6.54	6.54	7.90	6.19
0.098	4.14	10.34	11.64	9.26	9.21	8.59	10.42	9.13
0.114		11.10	12.32	9.79	10.26	9.58	11.33	9.41
0.146		12.25	12.77	10.89	11.67	10.87	12.40	10.77
0.179		12.78	13.31	11.60	12.58	11.26	12.85	12.30
0.211		12.83	13.39	11.67	13.03		12.93	13.26
0.228					13.10			13.34

Figure 1. Oxidation of Polyethylene



Source: Pierce, R.A., Smith, J.R. and Poprik, D.C. *Nitric-Phosphoric Oxidation of Solid and Liquid Organic Materials*, WM95 Proceedings. WM Symposia, Inc., Tucson, AZ. With permission.

Figure 2. Oil Oxidation vs. Temperature



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