Progress Report on Nitric-Phosphoric Acid Oxidation (U)

by

R. A. Pierce

Westinghouse Savannah River Company

Savannah River Site

Aiken, South Carolina 29808

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R. A. Pierce

**Westinghouse Savannah River Company
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CONTENTS

INTRODUCTION	1
TECHNOLOGY DESCRIPTION	1
Oxidation Chemistry	1
Other Process Chemistry	2
RESULTS AND DISCUSSION	3
Previous Results	3
Recent Findings	4
Experimental Setup	4
Oxidation of Different Compounds	4
Parametric Studies with Water-Soluble Oil	5
Oxidation of Plastics	6
Nitric Acid Recovery	8
Decontamination Effects	9
Materials of Construction	10
CONCLUSIONS	10
SUMMARY	12
REFERENCES	13
ATTACHMENT	14

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. Pu-238 waste is an issue because it must be shipped to WIPP. However, the presence of organics and Pu-238 exceeds packaging requirements because of concerns of hydrogen generation. If the TRU can be separated from the organics, the allowable heat load of a container increases a factor of 25. More importantly, since the current shipping package is limited by volume and not heat loading, destroying the organic compounds and decontaminating noncombustible can potentially create a three-order magnitude decrease in the number of shipments that must be made to WIPP.

The process envisioned will be configured to handle 1 million pounds (as of 12/91) of a wide range of solid TRU-contaminated waste of which 600,000 pounds 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 400,000 pounds of noncombustibles. The system is being developed to operate below 200°C at moderate pressures (0-15 psig). This report primarily discusses results obtained over the past 3 1/2 months and their impact on the feasibility of a pilot-scale system.

TECHNOLOGY DESCRIPTION

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 hazardous materials or extreme processing conditions to decompose the waste.

Oxidation Chemistry³

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, especially at room temperature. Liquid phase oxidation process shouldn't produce any ash, making the system more environmentally contained. 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 CO₂, CO, and inorganic acids in a 0.1M HNO₃/14.8M H₃PO₄ solution (see Attachment 1). Addition of 0.001M Pd⁺² reduces the CO to near 1% of the released carbon gases. To accomplish complete oxidation the solution temperature must be maintained above 130-150°C. The oxidation is usually complete in a few hours for soluble organic materials. The oxidation rate for non-aliphatic organic solids is moderately fast and surface area dependent.

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^{1,2}. The following heats of reaction, ΔH , values are in kcal/mole^{1,2,3}.

R denotes an organic group not affecting the ΔH for the shown reaction. The oxidation of organic compounds is usually initiated by the production of organic radicals generated by dissolved $\text{NO}_2^\bullet$ and $\text{NO}^\bullet$ in solution (NO_2 and NO are radicals and will be noted as such). For many types of organic compounds the attack by $\text{NO}_2^\bullet$ can be first order.

For aliphatic compounds higher concentrations of $\text{NO}_2^\bullet$ and $\text{NO}^\bullet$ are needed to obtain comparable oxidation rates.

A typical aliphatic carbon-hydrogen bond strength of 99 kcal/mole was used in the calculations². The organic radicals are then oxidized by nitric and nitrous acids or nitrated by NO_2 :

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 then HCl (hydrochloric acid) will also be formed.

Other Process Chemistry

In addition to dissolution of plastics, hot concentrated phosphoric acid has been shown to dissolve plutonium oxide more efficiently than 0.05M HF in HNO_3 (the solution often used at SRS for dissolution of PuO_2).⁴ This means that the dissolution liquid should be very effective at decontaminating the non-combustible solids fed to it. As a result, the process will be suitable for all of the waste types present in the TRU waste containers.

Acid recycle will also be another key part of the process. As the reaction progresses, NO and NO₂ are released from solution and nitric acid is depleted. As a result, the NO and NO₂ 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 PVC must be allowed to pass through to be recovered in a subsequent step. Several different approaches are being considered with the goal being to simplify the process as much as possible. Acid recovery units for converting NO_x to nitric acid are a commercially available technology.

The presence of TRU components, fission products, stainless steel, and lead will lead to a number of metal ions in the oxidation solution. Of particular concern is the potential for a build-up of materials to form a critical mass. Metals can be recovered by precipitation as either as phosphates or oxalatophosphates. The precipitates can then be separated using a centrifuge.⁵ These solids will be rinsed, dried, and shipped to WIPP.

RESULTS AND DISCUSSION

Previous Results

Early experiments demonstrated the application of nitric-phosphoric oxidation for various organic materials, and the importance of adding trace Pd catalyst to reduce CO generation (Table 1).⁷

Table 1. Carbon Balance for Various Oxidations
in 0.05M-0.1M HNO₃/14.8M H₃PO₄, 120-160 C

Compound	Co-Catalyst Metal (Conc.)	%C Released as CO and CO ₂	Percent CO of CO ₂ & CO
Cellulose	none	98±2a	20±1
Cellulose	Pd (0.0012M)	99±2	0.9±1
Cellulose	Rh (0.003M)	97±3a	6.3±1.5
EDTA	none	99±2	25±1
EDTA	Pd (0.0012M)	>91±2	0.9±1
EDTA	Rh (0.003M)	>84±3a	19±1.5
TBP	none	103±3a	43±1b
TBP	Pd (0.0012M)	—	1.3±1
Nitromethane	none	101±2	60±1
Nitromethane	Pd (0.0012M)	—	2.3±1
Tartaric Acid	none	>96±2	15±1
Neoprene	Pd (0.001M)	101±10	<17

a. GC analysis observed no H₂, methane, or ethane

b. Determined from butanol (a hydrolysis product of TBP)

High density polyethylene has been, within experimental error, quantitatively oxidized to CO₂ and CO under typical microwave digestion conditions in dilute nitric acid (Table 2).⁷ Recent data, to be discussed later, sheds additional light on the likely role of microwaves in organics oxidation. Addition of 0.001M Pd to solution reduces CO production by a factor of three; higher concentrations will probably reduce CO even further.

A separate set of tests were performed to obtain corrosion rates for 304-L stainless steel in solutions expected to be typical following oxidation. The tests were run at

room temperature since solutions will be cooled before further operations. HCl was included as a parameter since much of the TRU organic waste contains chloride (PVC and neoprene). The results of the study are given in Table 3.⁷ Solutions of expected nitric acid concentrations in phosphoric acid produced non-corrosive mixtures. The combination of HCl and HNO₃ is very corrosive. One of these two compounds would have to be eliminated prior to processing. Nitric acid can be destroyed with oxalic acid, and HCl can be boiled off with air sparging at temperatures above 150°C. Up to 1.0M HCl in phosphoric acid is in the good range (<20 mils/yr).

Table 2. Carbon Balance for Oxidation of HDPE Using Microwave Digestion at 100 W

Oxidizing Solution	Digestion Time (min)	% Carbon 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 ₃ PO ₄	40	74±2	18	82
0.55M HNO ₃ / 14.3M H ₃ PO ₄	55	84±2	14	86
0.001M Pd(II)/ 1.00M HNO ₃ / 13.9M H ₃ PO ₄	50	98±2	6	94

Table 3. 304-L Corrosion in HCl/HNO₃/H₃PO₄ at 20 C

HCl (M)	HNO ₃ (M)	H ₃ PO ₄ (M)	Corrosion Rate (mils/yr)
0.12	0	0	3.1
1.0	0	0	10.0±1.2
0	0.1	14.8	<0.36
1.0	0.1	13.5	224
1.0	0	13.6	16

Recent Discoveries

Experimental Setup:

All oxidation experiments were conducted using some variation of the test set-up in Figure 1, with the exception of early microwave tests. Pressure was measured using a Marshalltown Manufacturing compound gauge which measures from 30"Hg - 30 psig. The system temperature was monitored using a laboratory thermometer in some cases and a Luxtron Model 750 Fluoroptic temperature probe in others. Ascarite-II® (Thomas Scientific) absorbs CO₂ 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. Sulfamic acid (EM Science) removes NO₂ gases from the off-gas stream so they do not absorb on the ascarite. Drierite (W. A. Hammond Drierite Co.) absorbs moisture from the gas stream. Polyethylene samples were taken from Nalgene® bottles. Trimsol® was provided by Master Chemical Company.

Experimental Set-Up

Figure 1

Oxidation of Different Compounds:

As discussed earlier, oxygenated compounds are more easily decomposed than aliphatic compounds, requiring one NO₂ to cleave a bond instead of three. This is clearly depicted in Figure 2 which shows the oxidation, under different conditions, of the primary compounds in the target feed stream (each sample contained comparable levels of carbon). The difference between PVC and polyethylene stems from different dissolution characteristics. Polyethylene dissolves faster than PVC and, therefore, experiences faster reaction rates due to the increased surface

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

Parametric Studies with Water-Soluble Oil:

As is evident from Figure 2 and the fact that plastics account for about 400,000 of the 1 million pounds of solid TRU waste, the rate-limiting step in the process is oxidation of plastics. Because of this, a brief parametric study was run with a water-soluble oil

(Trimsol) to better understand the effects of temperature, acid concentration, and organic concentration.

Trimsol simulates the plastics once they dissolve; it is also the same oil used in machining throughout the DOE Complex, particularly Rocky Flats.

Figure 2

Although it is known that reaction rate increases with both temperature and acid concentration, these experiments quantify those effects. Figure 3 shows the importance of temperature.

Figure 3

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.¹ Figure 4 depicts the role of nitric acid concentration at 165°C. The corresponding oxidation rates for 0.1, 0.5, and 1.0M nitric acid are 1.4, 5.0, and 5.7 mL/(hr liter of solution).

Figure 5 shows oxidations at varying oil concentrations.

Based on Figure 5, it has been estimated that

the optimum oil concentration in this system would occur at 12-14 mL, or 2% by volume.

Under these conditions, the corresponding oxidation rate is estimated at 26 mL/(hr liter of solution). It is not yet clear how the data of Figure 5 correlates with other dissolved organic compounds, but is expected to be conservative because the aliphatic nature of the oil tends to be difficult to oxidize.

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

Figure 4

concentration; solubility is a function of temperature. The respective nitric acid concentrations in concentrated phosphoric acid were 0.148, 0.0645, and 0.0195 g/mL. The data has been plotted in Figure 6. The initial oxidation rate for each of these is about 35 mL/(hr liter of solution).

The results were unexpected as each temperature exhibited essentially the same initial reaction rate. 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 also be a function of acid depletion, but this has not been determined experimentally.

Based on this experiment, it is believed that optimum conditions for easily-oxidized compounds (cellulose) involve lower temperatures and higher acid concentrations due to rapid reactions and corresponding rapid acid depletion. Optimum conditions for plastics use elevated temperatures where the oxidation of long-chain intermediates is more important. The value of using elevated

pressures to obtain both higher temperatures and acid concentrations will be discussed in the next section.

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 expected 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 provided insight into the effects of nitric acid concentration on polyethylene dissolution (Table 4). This set of data reflects quite well what was shown in Figure 5 using Trimsol. A later microwave test during a vendor demonstration

Table 4. Microwave Digestion of HDPE

HN03 Molarity in Conc. H3PO4	Time (min)	Liquid Volume (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

suggests that the temperature for the tests represented in Table 4 was approximately 150-160°C and 15 psig.

In later experiments, when equipment was built in which oxidation could be observed, a better understanding of the effects of microwaves was obtained. The first tests ran with only acid in the digestion vessel and with temperature monitoring at the liquid surface and at the center of the liquid. When this was done, it was observed that surface temperatures were sometimes 20-30°C higher; this is because microwaves are absorbed at the liquid surface. A follow-up test observed the response of a plastic sample that was both submerged and sticking out of solution. This test showed reaction to be slow for the submerged portion and much faster at the surface; some sample bubbling was seen just above the liquid surface. Based on this data, it is suspected that microwaves affect oxidation in two ways. First, they provide a higher surface temperature for reaction while the bulk solution temperature is lower. Second, microwave may actually interact with and heat partially-reacted plastics which are not normally susceptible to microwave energy absorption; this increases temperatures and reaction rates at the plastic surface. More work is still needed in this area, and microwaves may still play a valuable role.

The results observed with microwaves fostered tests using conventional heating to oxidize polyethylene. Runs at two different temperatures, 0-5 psig, and the maximum soluble concentration of nitric acid yielded the results of Figure 7. Once again, as was observed with Trimisol in Figure 6, the initial reaction rates are almost identical. It was also observed 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 Trimisol because the plastic is a solid and has a more limited surface area in contact with solution. Tests using the same temperature and acid concentrations while varying the 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 one or the other. The effect of having both higher temperatures and acid concentrations is clearly shown for polyethylene in Figure 8. Calculations using the graph yield oxidation rates at 175, 190, and 205°C of 0.036, 0.034, and 0.107 g/cm²hr, respectively.

Figure 9 shows the comparative data for PVC and benzoic acid. The oxidation of benzoic acid, an aromatic compound, is sufficiently fast to not require elevated pressures; the higher oxidation rate is not surprising because the benzoic acid readily dissolves into the nitric-phosphoric acid. Oxidation rates of ion exchange resins, a component of the target waste stream which contains benzene rings, 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. Based on this data, it is clear

that the optimum system for plastics will seek a safe way to maximize temperature and nitric acid concentration using elevated pressures. However, moderate oxidation rates can still be achieved using lower temperatures and atmospheric pressure.

Nitric Acid Recovery:⁸

Since the oxidation process reduces nitric acid to nitrous acid and then to NO and NO gases, acid recovery will be an essential operation for maximizing chemical recycle and minimizing emissions or secondary waste streams. Some of the prominent reactions (there are many) governing acid recovery are:⁹

Tests were run with four compounds to gain preliminary understanding into NOx generation levels for the broad range of potential feeds: cellulose (oxygenated, solid), starch (oxygenated, water-soluble), TBP (aliphatic, water-soluble), and polyethylene (aliphatic, solid). The results are shown in Table 5.

The main thing obvious from Table 5 is that oxygenated compounds generate more NOx per mole of carbon than aliphatic compounds. This is attributable to acid reabsorption. Oxygenated compounds generate more NOx because their reaction rates are much faster and permit less time for reabsorption to occur. Another observation that is significant is that polyethylene generates minimal NO gas. This can also be attributed to reaction rates because NO, the decomposition product of HNO₂, is given more time to recombine with oxygen to form NO₂. The same is also true for TBP, but not as prevalent because TBP oxidizes much faster than polyethylene. A third noteworthy observation is that the two water-soluble compounds exhibited a NO₂:NO ratio of about 2; however, this may just be coincidence. These conclusion are only preliminary

observations, and the gas generation characteristics require additional study, particularly as a function of temperature and oxidation rate.

The importance of this set of data is it shows that fostering nitric acid recombination in the oxidation vessel can significantly reduce the size of acid recovery unit needed. Design calculations conducted prior to these experiments projected NO_x generation to be 2 moles per mole of carbon for polyethylene, the primary waste component. Revised calculations place the gas generation rate closer to 0.5 moles of NO_x per mole of carbon, a four-fold reduction.

Table 5 Acid Recovery Preliminary Results
(NO_x Generation/Mole C)

	Oxidation		Aliphatic	
	Cellulose		Polyethylene	
Solid	0.95 mol NO 0.17 mol NO ₂		0.00 mol NO 0.36 mol NO ₂	
Water Soluble	Starch		TBP	
	0.80 mol NO 1.68 mol NO ₂		0.15 mol NO 0.27 mol NO ₂	

Decontamination Effects:

The principle behind these tests is that literature states that hot phosphoric acid is excellent at dissolving plutonium oxide. Consequently, it is expected that this chemistry can be extended to the removal of surface contamination from noncombustible solids while the oxidation of combustible materials occurs. Coupons of five different materials were tested; the materials tested include glass, carbon steel, Plexiglas®, hard rubber, and soft rubber. Where applicable, samples contains rough and smooth surfaces where contamination may collect which cannot be removed using mechanical scrubbing.

All samples produced promising results. Each sample was prepared by contacting it with a Pu-bearing solution. The samples were then surveyed to determine the levels of smearable and fixed contamination. Next, they were soaked in 0.1M nitric acid for 3 hours and cleaned by hand with a decontamination chemical; this removed most or all of the smearable

Table 6. Phosphoric Acid Decontamination Effects
(alpha/beta-gamma)

Sample	Initial Contamination	Fixed Contamination	Final Contamination
glass (s)	1E5/-	1E4/5E4	nd/nd
glass (r)	7E5/-	2E4/5E4	nd/nd
Plexiglas (s)	2E5/5E5	5E4/5E4	1000/nd
Plexiglas (r)	6E5/8E5	1E5/5E4	3000/nd
Hd. Rub. (s)	>1E6/>8E5	>1E6/>8E5	3000/1500
Hd. Rub. (r)	>1E6/>8E5	>1E6/>8E5	3000/1500
Soft Rubber	>1E6/>8E5	7E5/8E5	4000/nd
Steel	>1E6/>8E5	>1E6/>8E5	1000/nd

contamination. Last, the samples were placed individually in hot nitric-phosphoric acid for 5 minutes and then an additional 10 minutes; the soft rubber and Plexiglas® were returned to the acid for an additional 45 minutes while the glass sample spent only the original five minutes in solution. Surveying of the samples yielded the results in Table 6 for alpha/beta-gamma contamination (nd=none detected).

The results with the glass and steel are most significant because they are noncombustible and will not be completely oxidized by the solution. Additionally, difficult to oxidize materials (such as plastics) may be decontaminated without

having to oxidize them while materials that oxidize easily (rubber and paper) can be completely

oxidized. This opens new possibilities for treating this waste without having to completely oxidize all of the combustibles.

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 too. Earlier corrosion data, mentioned earlier, and information in the literature on the corrosivity of phosphoric acid provided hope that high-alloy stainless steels would be satisfactory for construction of main processing equipment. In an attempt to identify suitable materials of construction, scoping tests were run with seven candidate metals in nitric-phosphoric acid at 150-160°C: the materials used were 304L, 316L, 317L, and Alloy-20 stainless steels, C-22 and C-276 Hastelloys, and tantalum (Table 7).

Table 7. Scoping Study Corrosion Rates

Material	Seven-day Corrosion Test		
	Liquid Phase	Vapor Phase	Condensate Phase
304L Stainless	0.44	0.25	0.09
316L Stainless	0.24	0.18	0.00
317L Stainless	0.34	0.008	0.00
Alloy 20 Stainless	0.27	ind	0.00
Hastelloy C-22	0.21	0.0013	0.00
Hastelloy C-276	0.44	ind	0.00
Tantalum	0.0001	0.00	0.00

**Note C-22 and Tantalum data from 14-day test

Data on vapor phase corrosion showed that 317L SS and Hastelloy C-22 are good candidates for the acid recovery system. Of the seven materials tested, only tantalum exhibited sufficient corrosion resistance to be used as the oxidation vessel; this raises concerns regarding the cost of a digestion vessel. 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 also candidate materials for the oxidation vessels. The use of glass-lined and Teflon®-lined vessels helps keep the capital cost of equipment and replacements low. All other equipment which handles lower-temperature processing can be constructed from inexpensive materials such as 304L or 316L stainless steel or Hastelloy C-276.

CONCLUSIONS

A process exists which could greatly benefit Solid Waste Management through the complete oxidation and decontamination of their solid Pu-238 waste. Most types of organic compounds can be quantitatively decomposed in nitric-phosphoric acid below 200°C at atmospheric pressure. Of the main waste stream organics, cellulose oxidizes readily while polyethylene and PVC react at moderate rates. Increasing the system pressure to 10-15 psig greatly improves the oxidation rates of polyethylene to that of cellulose; this greatly increases process throughput. Trace amounts of palladium should be used to maintain the production of CO well below flammable levels.

Released HNO₃, NO, and NO₂ can be recovered and recycled in a standard air driven acid recovery system providing a cheap source of oxidant. Acid recovery data shows that much of the NO_x reabsorbs back into the phosphoric acid, thereby reducing the size of acid recovery

system required. The process also has shown a significant capacity for decontaminating noncombustible compounds such as glass and steel, a major component of the Pu-238 waste..

The work conducted over the past few months has brought this technology a long way towards understanding what must be done to run a process on a larger scale. Based on what is known, this system is nearly ready for scale-up to a five- to ten-gallon system. The next twelve months of this program are likely to center on the following:

1. Complete small-scale testing with PVC. Almost all plastics studies have looked at polyethylene. However, what little has been done with PVC indicates that its oxidation characteristics are not analogous to those of polyethylene.
2. Investigate mechanisms for enhancing oxidation rates. We have yet to conduct any studies in this arena and this is the logical step prior to building anything for larger-scale testing.
3. Design and build a 5- or 10-gallon unit for larger-scale testing.
4. Conduct larger-scale testing on the primary components in the target feed stream (cellulose, polyethylene, and PVC). Also, begin tests on simulant feed mixture containing various organic materials to be encountered in the target feed.
5. Complete NO_x generation testing and use the data to build an acid recovery unit for testing with the larger-scale unit.
6. Complete testing on the recovery of dissolved metals in solution.
7. Provide a preliminary full-scale design, flowsheet, and cost estimate.

A related area which shows promise and should be investigated is the use of partial oxidation and partial decontamination. In this approach, less severe processing condition would be used such that the noncombustibles and plastics are decontaminated while easily oxidized materials (paper and rubber) are decomposed. This would result in less-severe processing conditions and reduced system cost because decontamination takes only a few minutes whereas plastics oxidation requires two hours and system capable of maintaining 10-15 psig. The use of a partial decontamination could greatly reduce the demands placed on the system; this could lead to less-severe processing conditions and lower overall costs.

Other developments of this technology outside of the current line of testing could also prove to be very beneficial to SRS and other end users. This first development involves using the technology for destroying volatile organic compounds. This could probably be done in a packed-bed reactor with little change to the existing chemistry; volatile components are expected to oxidize quickly. The second development area entails developing an oxidation system that uses only nitric acid (the subject of a recent SRTC invention disclosure). Early studies of plastics oxidation showed dissolution of many different polymers in only nitric acid. A

nitric-acid-only system would have to be run at elevated pressures, but offers the valuable benefits associated with recovering metals from solution using either evaporation, ion exchange, or precipitation. In addition, materials of construction requirements may be less severe.

SUMMARY

Nitric-phosphoric acid-air oxidation has been developed to address the needs of SRS Solid Waste Management. This technology aims to destroy or decontaminate over 1 million pounds of SRS Pu-238 contaminated job control waste, a heterogeneous mixture of plastics, cellulose, rubber materials, and noncombustibles. The Pu-238 will then be concentrated and shipped to WIPP. This process will provide at least a 99.9% volume reduction and result in an estimated cost savings of \$35-50 million in storage, packaging, and shipping costs. Since the issue of contaminated organic waste is not unique to 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 different 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.

Tests have shown that acid recovery requirements will be lower than expected, as much as 75% lower. Other experiments have shown the technology to have exceptional decontaminating capabilities for noncombustible materials. Preliminary precipitation data indicates that small amounts of metals in the feed (as in mixed-hazardous wastes) should be removable with little impact on operation; cases for larger quantities require more study.

The process is nearly ready for testing with larger-scale equipment (5-10 gallons) using organic feeds with little or no metals. Prior to scale-up, some development should be conducted on methods to enhance oxidation rates. 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 and become a significant source of technology transfer initiatives.

REFERENCES

1. Seminov, N.N., Some Problems in Chemical Kinetics and Reactivity, Princeton Univ. Press, Vol. 1 and 2, 1958.
2. Dickerson, R.E., Molecular Thermodynamics, the Benjamin/Cummings Publ. Co., 1969.
3. Smith, J.R., "Air-Nitric Acid Destructive Oxidation of Organic Wastes," WSRC-MS-93-169, Savannah River Site, Aiken, SC 29808.
4. Katz, J.J., Seaborg, G.T., and Morss, L.R. (editors), The Chemistry of the Actinide Elements, Chapman and Hall, 1986, pp. 700-701.
5. Cleveland, J.M., The Chemistry of Plutonium, American Nuclear Society, 1979, p 438.
6. Schweitzer, P.A. (editor), Corrosion Resistance Tables, 3rd Edition, Marcel Dekker, Inc., 1991.
7. Smith, J. R., Pierce, R. A., and Sturcken, E. F., "Nitric-Phosphoric Acid Treatment of TRU Wastes," WSRC-RP-93-1304.
8. Poprik, D. C., Laboratory Notebook, WSRC-NB-94-0192, Issue 6-27-94.
9. Counce, R. M., et. al., "Performance Models for NO_x Absorbers/Strippers," Environmental Progress, 1990 (Vol. 9, No. 2), pp. 77-92.

Attachment 1: Compounds Oxidized

Tartaric Acid

Benzoic Acid

Cellulose/Starch