Innovative Technology
Summary Report

Acid Digestion of Organic Waste

Mixed Waste Focus Area

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Acid Digestion of Organic Waste

OST Reference #1827

Mixed Waste Focus Area

Demonstrated at
Savannah River Site
Aiken, South Carolina

Purpose of this document

Innovative Technology Summary Reports are designed to provide potential users with the information they need to quickly determine if a technology would apply to a particular environmental management problem. They are also designed for readers who may recommend that a technology be considered by prospective users.

Each report describes a technology, system, or process that has been developed and tested with funding from DOE's Office of Science and Technology (OST). A report presents the full range of problems that a technology, system, or process will address and its advantages to the DOE cleanup in terms of system performance, cost, and cleanup effectiveness. Most reports include comparisons to baseline technologies as well as other competing technologies. Information about commercial availability and technology readiness for implementation is also included. Innovative Technology Summary Reports are intended to provide summary information. References for more detailed information are provided in an appendix.

Efforts have been made to provide key data describing the performance, cost, and regulatory acceptance of the technology. If this information was not available at the time of publication, the omission is noted.

All published Innovative Technology Summary Reports are available on the OST Web site at http://OST.em.doe.gov under "Publications."

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SECTION 1

SUMMARY

Technology Summary

The Best Demonstrated Available Technology (BDAT) for the destruction of organically contaminated solid mixed waste [generated from past Department of Energy (DOE) nuclear operations] is incineration. However, there is interest in treatment alternatives to excess air, open flame combustion. This interest derives from public concern for potential stack emissions and the fact that large volumes of gaseous effluents conceivably could result in significant releases of environmentally harmful contaminants. End users in the DOE complex and stakeholders do not believe that adequate attention has been directed toward development of alternative oxidation techniques involving nonthermal, nonflame processes. Both in response to these concerns and pending Environmental Protection Agency (EPA) regulation changes that will impose additional emission limits and monitoring requirements [i.e., the Maximum Achievable Control Technology (MACT) rule], the DOE's Mixed Waste Focus Area (MWFA), an EM-50 program, sponsored the development of several technologies that are alternatives to incineration. These alternative processes are referred to as Alternative Oxidation Technologies (AOTs).

The subject Acid Digestion Process, an AOT process, is characterized by relatively low operating temperatures and pressures, decreased offgas volumes, and reduced emissions of volatiles (including dioxins and furans). The process can be deployed in locations or instances where incineration may not be suitable due to the presence of actinides and volatile mercury and tritium.

Developed and demonstrated by Principal Investigators at the DOE's Savannah River Site (SRS), Acid Digestion is an oxidative destruction technology for organic constituents of mixed waste. In the Acid Digestion Process waste is fed into a reaction or oxidation vessel containing nitric acid in a phosphoric acid carrier solution. The principal organic portion of the waste is then broken down and mineralized by the acid solution at temperatures below 200^0C and at atmospheric or moderate pressures (<20 psig). The Acid Digestion Process leaves the waste's original inorganic constituents, including Resource Conservation and Recovery Act (RCRA) hazardous metals, in solution and produces gases of CO_2, CO, O_2, and NO_x. The inorganic constituents remain in solution and are subsequently solidified in a glass or ceramic. Larger insoluble undigested inorganics are appreciably decontaminated.   The released gases are treated in the offgas scrubbing system, where the potential to convert NO_x back to reusable nitric acid using hydrogen peroxide is achievable. Advantages of the technology include:

- Low-temperature, low-pressure organic oxidation capability,
- straightforward scale-up due to the relative simplicity of the process,
- simple process operations,
- system design and ease of operation indicate that this process could be designed to be transportable,
- volume of the final waste form can be reduced by a factor of 20X or greater
- final waste form can be either a low-temperature ceramic or glass,
- process oxidant (nitric acid) can be regenerated.

Although treatment of liquid organic wastes such as tributylphosphate is possible, the Acid Digestion technology primarily targets solid DOE mixed waste streams that are categorized as job control waste of an organic matrix. Large inorganic matrices are not oxidized by the process, but are substantially decontaminated. As well as containing hazardous metals and radioactive species, these job control wastes usually consist of cellulose (paper), polyethylene, latex rubber, Tyvek ™, neoprene, polyvinyl chloride, polystyrene ion exchange resins, filters, plastics, and/or chlorinated cutting oils.

Acid Digestion potentially could assist in the cleanup of many DOE sites, including the SRS and the Rocky Flats Environmental Technology Site (RFETS) where transuranic (TRU) job control wastes are ubiquitous and usually significantly contaminated with plutonium isotopes. In addition to substantial volume reduction, onsite Acid Digestive treatment of organic mixed waste classified as TRU will eliminate the undesired potential of the radiolytic gas generation problem caused by interaction of

hydrogenous organics with alpha emitting transuranics. Destruction of the organic constituents will eliminate any potential for hydrogen gas generation and allow treated and stabilized waste to be shipped to the Waste Isolation Pilot Plant (WIPP).

Westinghouse Savannah River Company awarded a license for use of the Acid Digestion wet oxidation technology to a private start-up company in May of 1997. The founders were engineers and scientists from the SRS. A patent disclosure was submitted and is currently pending at the United States Patent Office. As a result of this commercialization step, the spin-off company is in a position to potentially take the technology to deployment scale in order to accommodate any DOE complex end users who may determine that Acid Digestion is suited for their specific organic mixed wastes. If successfully commercialized, the process may find additional application in treating both mixed and hazardous organic wastes generated at commercial research, university, and medical facilities. The process may also find applicability in the nuclear power industry.

Demonstration Summary

Since 1995, the Acid Digestion technology has been developed and demonstrated at both the bench (~2-5 liter) and pilot (40 liter) scales. Testing was performed with both radioactive and nonradioactive surrogates at the SRS. Objectives of these development efforts and tests were multiple, but were primarily directed at determining the oxidation conditions (e.g., acid concentration, temperature, and pressure) and oxidation rates for various specific organic waste matrices, as well as mixtures of these matrices. Additional objectives required development in areas to determine acid depletion rates, acid recovery and recycle methods, offgas chloride removal techniques, and spent acid solution stabilization processes, including final waste form testing. Considerable testing was also undertaken to: (1) determine corrosion rates for material selection, (2) identify the presence of any hazardous and volatile components in the offgas (i.e., dioxins and furans), (3) identify monitoring requirements for safety, process control, and optimization, (4) assess metal and actinide retention and behavior, and (5) evaluate the viability of waste and acid handling methods.   As a result of this testing, material and energy balances, associated flow diagrams, and cost estimates applicable to specific treatment scenarios were prepared. Plans for installing a 400-liter scale pilot facility were also initiated.

In summary, past experimental work has advanced Acid Digestion technology toward demonstrating viability as a production-scale system. Key issues such as acid recycle, materials of construction, dioxin formation, process monitoring, final waste form development, radionuclide entrainment, and operability were successfully addressed. Concerns regarding waste throughput were also addressed on a small scale, but were limited due to waste feeding problems at the 40-liter pilot scale throughput. Increases can be realized through elevated temperatures and pressures, but these conditions are not desired by potential DOE end users, like those at the SRS. Open issues still exist regarding consistent treatment of organic liquids, chloride stripping, nitric acid volatility, process scale-up, waste feeding, and the ceramic waste form. Solutions have been proposed, but have not yet been investigated completely.

Based on the development efforts, the following conclusions can be drawn:

- The process converts most solid organics, including plastics and resins, to CO_2 and water at acceptable rates.
- Organics are converted at process operating conditions of 150 to 200°C, 0 to 20 psig
- Nitric acid used in the process can be recycled at a reasonable cost.
- Hazardous metals within the processed waste can be easily immobilized in a glass or ceramic.
- The process can result in volume reductions of 20 to 100 times.
- The operation of the process has proven to be relatively simple.
- Analysis of the oxidation process indicates no dioxin/furan formation.

Contents

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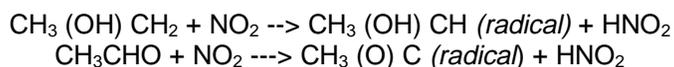FAX: (505) 667-0649
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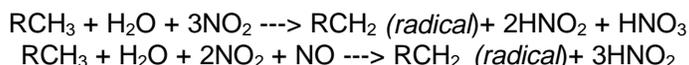
SECTION 2

TECHNOLOGY DESCRIPTION

Overall Process Definition

The Acid Digestion technology uses a mixture of an oxidant (nitric acid) and a carrier acid (phosphoric acid). The carrier acid acts as a holding medium and allows appreciable amounts of the oxidant to be retained in solution above its normal boiling point. As a consequence, the nitric acid stays in solution at atmospheric pressure and at the temperatures needed for oxidation. When an organic material is introduced into the solution, it is oxidized primarily to CO_2, CO and H_2O. Palladium is included as a catalyst at very low concentrations (up to 0.005M) to enhance conversion of CO to CO_2. Experiments indicated that CO generation resulting from oxidation of cellulose in the absence of palladium can exceed 10% by volume of the gaseous effluent and must be oxidized to CO_2. The palladium can also convert any generated N_2O to NOx

To accomplish complete oxidation, the solution temperature must be maintained above 130–150°C. Oxidation is complete in minutes for less stable compounds (paper) and requires up to an hour for some plastics. While the oxidation rate for nonaliphatic (nonstraight chain) organic solids is rapid, it is very surface area dependent. Typically, the organic compound oxidation is usually initiated by the production of organic radicals within the solution. These free radicals contain an unpaired electron and are highly reactive with oxidizers. The dissolved NO_2 and NO from the nitric acid oxidant generate these radicals. For many types of compounds, the attack by NO_2 can be first order as indicated by the following reactions for the simple organic compounds of alcohol and aldehyde:

$$CH_3 (OH) CH_2 + NO_2 \rightarrow CH_3 (OH) CH \text{ (radical)} + HNO_2$$
$$CH_3CHO + NO_2 \rightarrow CH_3 (O) C \text{ (radical)} + HNO_2$$

For aliphatic or straight chain organic compounds, higher concentrations of NO_2 and NO are needed to obtain comparable oxidation rates:

$$RCH_3 + H_2O + 3NO_2 \rightarrow RCH_2 \text{ (radical)} + 2HNO_2 + HNO_3$$
$$RCH_3 + H_2O + 2NO_2 + NO \rightarrow RCH_2 \text{ (radical)} + 3HNO_2$$

The organic radicals are then oxidized by nitric and nitrous acids or nitrated by NO_2. The first two reactions listed below are of the type that puts NOx to the offgas for potential recovery and conversion to acid for reuse:

$$RCH_2 + HNO_3 \rightarrow RCH_2 OH + NO_2$$
$$RCH_2 + HNO_2 \rightarrow RCH_2OH + NO$$
$$RCH_2 + NO_2 \rightarrow RCH_2NO_2$$
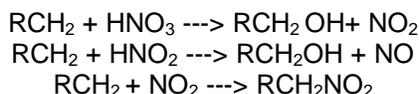
The radical formation process weakens the remaining hydrogen-carbon bonds on carbon atoms, thus allowing much quicker hydrogen abstraction and further oxidation. Nitrated compounds quickly undergo hydrolysis when heated with strong mineral acids:

$$CH_3CH_2CH_2NO_2 + H_2O + HNO_3 \rightarrow CH_3CH_2CO_2H + H_2NOHHNO_3$$

As the organic molecules gain more oxygen atoms, the organic molecules become increasingly soluble within 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.

A readily implemented alternative for acid recovery in radioactive service is hydrogen peroxide absorption of the emitted NOx. Calculations of the maximum theoretical nitric acid concentration

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expected for absorption of NO_2 using hydrogen peroxide indicate that high nitric acid concentrations can be obtained
using a 30% solution. Using the equation

$$2\ NO_2\ +\ H_2O_2\ ----->2\ HNO_3$$
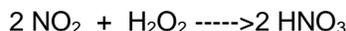
it was determined that a maximum nitric acid concentration of 61.3 wt% could be obtained with 30% H_2O_2 and 78.7 wt% with 50% H_2O_2. These calculations do not account for any acid formation that may occur due to NO_2 absorption by the balance of water in the hydrogen peroxide solution.

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:

$$2\ NO\ +\ 3\ H_2O_2\ ------>\ 2\ HNO_3 + 2\ H_2O$$

Not only is peroxide use efficiency reduced, but there is also a dilution effect from the water in the reaction products. This yields theoretical maximum acid concentrations of 47.0 wt% for 30% H_2O_2 and 60.8 wt% for 50% H_2O_2.

System Operation

The Acid Digestion Process is diagrammed in Figure 1. The process consists of three primary components or systems: (1) reaction or oxidation vessel, (2) acid recycle and offgas treatment system, and (3) acid stabilization and waste immobilization system. Other support equipment will be necessary, including feed tanks, pumps, solid feeders, and heating and cooling equipment.
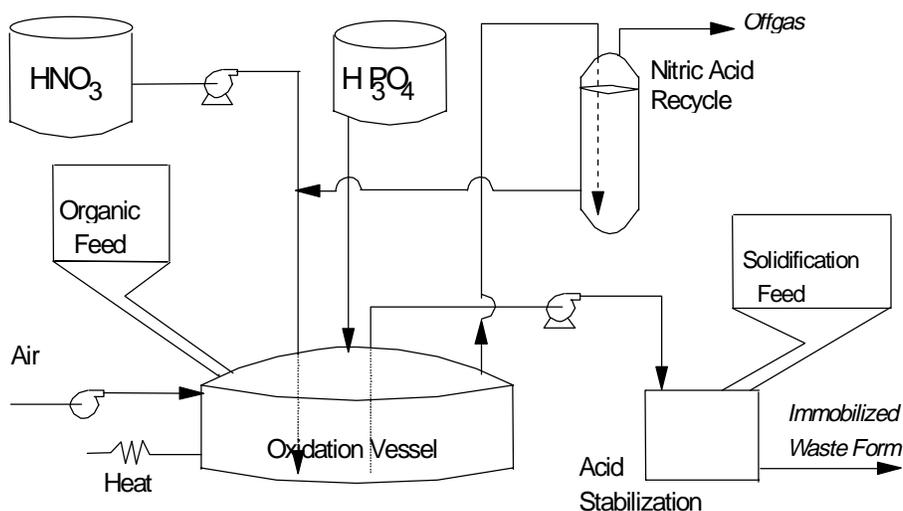

Figure 1. Acid Digestion Process schematic.

The central unit operation of the system is the oxidation vessel where effective organic destruction occurs via digestion in a bath of 14.8M phosphoric acid containing 0.5 to 1.0M nitric acid. Because of the extreme corrosiveness of the acidic solutions, the oxidation vessel should be constructed of resistant Teflon-lined steel or tantalum. To provide adequate freeboard to accommodate foaming, the vessel should also have a volume equal to three times that of the oxidation liquid. To achieve and maintain desired operating conditions for the oxidation reactions ($150 –200^0C$ and 0 to 20 psig), process monitoring of temperature and pressure is necessary, as well as cooling. Caution should be exercised in the design of heating equipment to avoid damage to the Teflon. Since the oxidation reaction is exothermic, cooling capability is also necessary for the offgas system. Ports are required to charge the vessel of process acids, feed waste organics to the process, exhaust offgases, and remove spent acids and residues for stabilization.

Several approaches exist for the recycle of nitric acid. One of the most attractive and readily implemented alternatives for radioactive service is hydrogen peroxide absorption. The nitric acid recycle or recovery system would consist of a series of gas washing bottles containing hydrogen peroxide, which is extremely efficient at absorbing both NO and NO_2 gases and oxidizing them back to nitric acid. Experimentally, three vessels in series can reduce NOx emissions to well below 100 ppm. However, hydrogen peroxide, although the most expedient option, may not be the best acid recovery approach. The hydrogen peroxide process uses a relatively expensive oxidant and produces relatively high levels of liquid effluents. More traditional acid recovery approaches use water from the oxidation process to recycle NOx, thereby reducing effluent volumes and cost for the nitric acid feed.

A second aspect of acid recovery is the removal of HCl, which is a by-product of polyvinyl chloride (PVC) oxidation. Tests at SRS have demonstrated that essentially all chlorine evolves from the oxidation vessel as HCl, which can be partially removed using a condenser that allows passage of NOx to the recovery subsystem. Additional testing is needed to determine if adequate separation of HCl and NOx is feasible.

While the recycle of nitric acid is very attractive in most applications, the specific needs related to SRS Pu-238 contaminated job control waste create opportunities for simplified offgas treatment options. The restrictions and requirements of handling waste streams with high radiation levels make it attractive to greatly reduce the number of process operations, system complexity, and maintenance issues even at the expense of somewhat higher operating costs. Because of this, several other options are being considered that involve the direct destruction and/or absorption of both HCl and NOx instead of separating the HCl and recycling the NOx as nitric acid. One method being studied involves the use of a solution of urea for HCl absorption and NO_2 destruction.

In the presence of large quantities of iron, solidification of the spent acid solution of inorganics may be nothing more than a receiving station where the liquid from the oxidation vessel is allowed to cool. Preliminary experimentation has shown that the acid, if heated to 220°C, will form a solid with no free-standing liquid upon cooling. The waste volume can be reduced further by heating to higher temperatures to drive off excess water. However, this waste form will be highly leachable.

A more stable nitrate final waste form can be achieved by either of the following approaches:

- Magnesium phosphate ceramic: The advantage of this solidified and stabilized waste form is that it is produced at room temperature and pressure and sets in a few hours. In the process, appropriate amounts of magnesium hydroxide and boric acid are added to the phosphoric acid, mixed and casted into the waste container to solidify. The magnesium phosphate produced creates a ceramic barrier and the hazardous inorganic metals are converted to their insoluble phosphate salts. Studies at the Argonne National Laboratory (ANL) have shown this to be a viable waste form capable of passing the required RCRA leachability tests for the hazardous metals.

- Iron phosphate glass: The advantage of this waste form is that it produces an extremely stable waste form for Pu bearing waste. In the process, appropriate amounts of iron oxide and sodium carbonate are added to the acid. Subsequently, the solution is melted at 1,100°C to form a high integrity glass upon cooling.

It is estimated that a production-scale acid digestion process would require up to nine technicians and engineers for operation. One or two for bringing in and opening waste drums, two to three to run the process, one or two to process secondary waste, and several others present for management, radioactive control, decontamination, maintenance, and engineering support on a part-time basis.

SECTION 3

PERFORMANCE

Demonstration Plan

The majority of the development and demonstration efforts for the Acid Digestion technology occurred in FY-96 and FY-97 at the SRS. The FY-96 tests were mainly carried out in small bench-scale units of 2–5 liter capacity, where as the bulk of the FY-97 tests were completed in the 40-liter glass pilot scale unit shown in Figure 2.

Figure 2. 40-liter Glass Acid Digestion Pilot Scale Reactor.

Tests at the pilot scale were planned to validate results obtained from the bench scale and to conduct experiments not practical at the smaller scale. Objectives for these tests were diverse and consisted of the following:

- determine applicable organic waste streams for Acid Digestion technology,
- determine oxidation conditions and rates for a variety of applicable organic waste matrices and mixtures of matrices,
- verify optimum acid recycle parameters for removing HCl from the offgas and converting NOx to nitric acid for reuse in the process,

- obtain chloride-partitioning data for the by-products produced from oxidizing chloride-containing organics, such as PVC,
- obtain data that validates that final waste forms (i.e., glass and ceramics) for spent acid solutions pass standardized waste form performance tests,
- obtain data, such as corrosion rates, to select the best material for the design of production-scale equipment;
- obtain data on the types (i.e., dioxins and furans) and quantities of undesired offgas emissions produced during the oxidation of specific compounds,
- obtain partitioning data for metals and transuranics that enter the oxidation process from the waste stream. These data would determine their distribution between the solution phase and that of the offgas and are particularly important for the SRS job control waste where containment of Pu-238 is critical.

Additional demonstration efforts are planned to optimize waste and feed handling methods, as well as to define process control and monitoring requirements for a full-scale demonstration.

Results

To establish the viability of the Acid Digestion Process, the effectiveness of oxidation and oxidation rates for the target waste stream and other applicable streams was determined. Additionally, it was necessary to determine cumulative effects of continuous oxidation on the process and equipment. Therefore, tests were conducted on cellulose, neoprene, polyethylene, and PVC. Among these materials, cellulose is the only compound containing significant quantities of inorganic material.

Initially, tests were performed to determine the amount of cellulose material that could be decomposed into a fixed volume of acid before precipitates begin to form. These data provide an estimate of expectable volume reduction resulting from acid digestion. When complete, 240 grams of KimWipes^{TM} were oxidized in 70 ml of nitric-phosphoric acid. The residual phosphoric acid was then immobilized into 43 ml of iron phosphate glass without difficulty, which results in a waste loading density of 349 pounds per cubic foot. If it is assumed that all organic in a drum is cellulose, volume reduction should be on the order of 50–100 fold depending on where the processing endpoint is established.

A series of experiments were conducted in the 40-liter pilot-scale vessel with approximately 16.5 liters of phosphoric acid. Tests were performed on individual organic based compounds, [e.g., cellulose, neoprene, and polyethylene (PE)] as a function of temperature, pressure, and acid concentration. The data presented in Table 1 reveal significant temperature, pressure, and acid concentration effects on the oxidation process for each compound.

Table 1. Pilot-scale test results.

Test	Temp (C)	[H+] (M)	P (psig)	Waste (g)	Dissolution Time (min)
1	155	0.5	4	41 cellulose	2
2	170	Acid def.	4	41 cellulose	>30
3	155	1.0	4	30 cellulose	2
4	170	0.5	5	10 PE	80
5	185	0.5	5	10 PE	35
6	170	0.8	5	10 PE	35
7	170	1.0	5	10 neoprene	30
8	170	0.6	5	10 neoprene	40
9	185	0.4	5	10 neoprene	45
10	185	0.4	8	15 PE	25
11	170	0.6	8	15 PE	20

Additional experimental data show the following estimated oxidation rates for various types of shredded waste:

- cellulose @ 150°C and 0–5 psig (95 g/L-h),
- neoprene @ 165°C psig and 0–5 psig (50 g/L-h),
- polystyrene resin @ 170°C and 5–10 psig (65 g/L-h),
- polyethylene @ 180°C and 10–15 psig (35 g/L-h),
- PVC @ 205°C and 10–15 psig (35 g/L-h).

Tests were also run with mixtures of cellulose, neoprene, polyethylene, and PVC. The oxidation characteristics of these tests were consistent with that of earlier laboratory-scale experiments. Based on these observations, it is believed that PVC dissolution rate, even when PVC is added in small quantities, will be the rate-limiting step in the process.

Difficulties were encountered with feeding solids in a continuous manner, which prevented testing of the pilot-scale facility in a continuous mode. Consequently, followup work was performed at the bench scale to evaluate throughput capabilities for different organics. Tests were conducted in a vessel containing 200 ml of nitric-phosphoric acid in a semicontinuous mode. Polyethylene bags containing 1.0 gram of simulated waste were added every 15 minutes over a 2-hour period to a process solution at 185°C and 10–12 psig. The samples entered solution readily and were oxidized. The rate of addition corresponded to a throughput rate of 220 kg of carbon per 24 hours per cubic meter (assuming 50% freeboard for the vessel).

Metal solubility is another concern in the oxidation process. Based on the expected waste composition, the metals of greatest concern are iron, aluminum, silicon, and lead. Each of these metals will have a solubility limit, and how the solution behaves at that limit can be critical. The greatest concern is iron precipitation, both because of the prominence of iron in the waste streams and iron precipitates as a water-insoluble gelatinous mass. Analysis of iron concentration in the oxidation vessel is essential to the avoidance of this condition.

Experiments were conducted to study NOx absorption into hydrogen peroxide to confirm design parameters for the pilot-scale acid recycle unit. Four key parameters were evaluated during the tests: (1) NO:O_2 ratio, (2) residence time to convert NO to NO_2 before absorption by hydrogen peroxide, (3) percent hydrogen peroxide solution required, and (4) use of oxygen versus air to convert NO to NO_2. The most important conclusions from the tests are as follows:

Figure 3. NOx distribution.

1) Tests with pure NO yield a nitric acid concentration of 4.1M compared to NO_2 and air tests that yield approximately 13M;
2) Controlled absorption conditions have consistently shown conversion of 30% hydrogen peroxide to above 13M, which is well above the 11.5M measured under less controlled conditions in FY-96;
3) 50% hydrogen peroxide does not seem to 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 before NO_2 absorption is on the order of 60 seconds; the optimum NO:O_2 ratio is 2:2, but ratios as low as 1:2 reduce NOx absorption less than 10%.
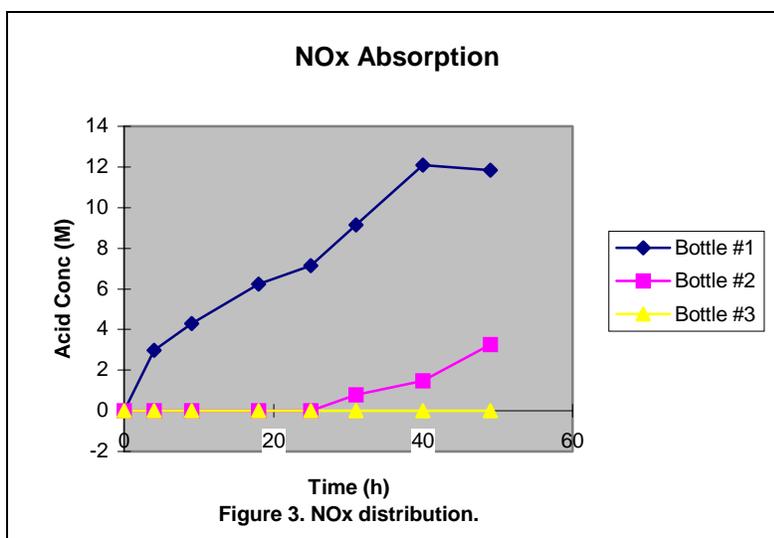
Experiments were also run using three hydrogen peroxide bottles in series and flowing a small amount of NOx through the system to demonstrate NOx distribution through the three bottles as a function of acid concentration in the peroxide. As indicated by Figure 3, the test showed that the hydrogen peroxide in the first bottle will absorb NOx completely until it is about two-thirds consumed before allowing NOx to pass through to the second bottle. Also, throughout the test, continuous monitoring of NOx emissions from the third peroxide bottle always showed 30 ppm or less as compared to the clean air standard limit of 200 ppm. Absorption efficiency is a function of geometry, but these test results are indicative of what can be expected during the proper use of hydrogen peroxide units in series to absorb NOx to recycle nitric acid.

An offgas test series was devised to identify hazardous and volatile components in the offgas that may cause problems in the process. An end-objective was to evaluate dioxin production potential. Three major pathways of dioxin formation are as follows:

1) homogeneous gas phase formation from hydrocarbon products of incomplete combustion at high temperature,
2) catalytic formation of dioxin from organic precursors similar in structure to dioxin at low temperatures (generally 300–500°C),
3) formation in the condensed phase from carbonaceous precursors that are chemically and structurally dissimilar to dioxin (this "starting from scratch" pathway is sometimes called de novo synthesis).

The first pathway was ruled out because of the low operating temperatures of wet oxidation. The last pathway is not considered likely because of required residence time and the probability of a successful completion of a number of reactions. However, the liquid batch composition in the vessel, with the major composition component being phosphoric acid, was evaluated for suspect analytes, following a series of tests, to determine if a condensed phase mechanism could produce dioxin.

The residual concentrated phosphoric acid batch liquid was analyzed following the completed series of eight wet oxidations of paper, neoprene, and other waste types. The residual batch solution contained both chlorinated pyridine and nitrochlorobenzene, but no other related compounds The amount of chlorinated pyridine was determined to be about 5 ppm and nitrochlorobenzene at 0.037 ppm. There were no phenols or dioxins identified in solution.

The value of any organic waste treatment process is strongly dependent on the ability to safely and conveniently place hazardous and radioactive inorganic metals left over into a stable final waste form. The use of a phosphoric acid matrix provides at least two final waste forms: iron phosphate (FeP) glass and magnesium phosphate ($MgPO_4$) ceramic. The ceramic sets at ambient temperatures and is stable enough to pass the new Universal Treatment Standards (UTSs) for hazardous metals. This makes it valuable for immobilizing RCRA metals and short-lived radioisotopes such as Cs-137 and Sr-90. The iron phosphate glass melts at 1,050–1,150°C and has the stability of a high-level waste glass, thereby making it valuable for immobilizing actinide metals. In comparison, the ceramic is more convenient to make while the glass provides a greater volume reduction and a more durable form.

One major concern with the ceramic, especially for Pu-238 waste, is the potential for radiolysis of the bound water to form hydrogen. It has been shown that certain cement waste forms with bound and unbound water in the matrix undergo radiolytic degradation. However, reports as early 1978 show that dried cementitious waste forms, heated to the level that unbound water is driven off, exhibit radiolytic hydrogen generation rates that are 2–3 orders of magnitude lower. This has been confirmed in later work.

Thermogravimetric analysis (TGA) was conducted on potassium magnesium phosphate ceramic ($KMgPO_4$). Samples were heated to 200, 400, and 600°C and analyzed using X-ray diffraction (XRD). TGA shows that $KMgPO_4$ readily loses water from 100–250°C and then has little or no more detectable weight loss. This is confirmed by XRD which shows $KMgPO_4$-$6H_2O$ exists at room temperature in addition to a mixture of transition products at 200°C, and anhydrous $KMgPO_4$ at 400 and 600°C. This suggests that a final waste form made from $KmgPO_4$ could be heated up to make an anhydrous form, which has acceptably low radiolytic hydrogen generation. Additional testing is required in FY-98 to verify that an acceptable waste form can be produced using KMgP.

Nonradioactive work was conducted on iron phosphate glass to identify a glass composition to be used in immobilizing radioactive solutions. Testing examined the range, which can be used for processing spent phosphoric acid solutions. The range for Fe_2O_3 is 15-45 wt%, Na_2O is 0-6 wt%, and SrO is 0-3 wt%. Glasses were consistently formed containing 20-40% Fe_2O_3 and small amounts of Na_2O and SrO. Based on the quality of glasses formed, the target glass will use 33% Fe_2O_3, 5.5% Na_2O, 2.5% SrO, and 59% P_2O_5. This composition will allow significant fluctuation in the composition without jeopardizing glass formation and quality.

The corrosive environment of the Acid Digestion Process justified considerable testing to select suitable materials of construction for full-scale operations. Hastelloy G30, quartz, Pyrex, glass-coated steel, tantalum, and Teflon coated steel were among the materials tested. Most of the corrosion testing involved exposing the corrosion coupon to a solution of $1MHNO_3$ in concentrated phosphoric acid at 175^0C for seven days. Using the success criteria that a corrosion rate of below 20mils/year is acceptable, the following materials are recommended for the oxidation vessel and/ or vessel liner: Teflon-coated steel, quartz, tantalum, and pyrolytic graphite.

TECHNOLOGY APPLICABILITY AND ALTERNATIVES

Competing Technologies

Incineration is the baseline technology for treating organic based mixed waste debris. However, due to regulatory and societal hurdles as well as limitations in accommodating some problematic radionuclides, various alternatives have been developed and advanced. Technologies that have been developed to commercial scale include steam reforming, oxidation using a char media, and a hydrogen reduction process. Others in development or near deployment include Direct Chemical Oxidation (DCO) and Catalytic Detoxification. Because all of these technologies have the capability to treat solid organic based mixed waste; they are considered competing technologies to the Acid Digestion Process. A brief description of these alternatives is given below.

The potential advantage of any one of these technologies over that of Acid Digestion will depend on the particular application. An earlier study comparing various Alternative Oxidation Technologies (AOTs) rated Acid Digestion low, since development at that time had not progressed beyond the bench scale. Since then the technology has been demonstrated at larger pilot-scale capacities, thereby better defining its applicability to certain waste streams. In general, the key attributes of Acid Digestion relative to the other candidates include equipment simplicity, a less aggressive oxidizing agent that doesn't attack the inorganic substrate, and the absence of highly combustible organic gases. The largest disadvantage is the lack of integrated demonstration data, and its unproven capability to treat a wide range of organic matrices.

Oxidation Using a Porous Char Media

In this process the waste materials undergo pyrolysis, partial combustion, steam reforming, and gasification in a moving reaction zone at 1200^0C. The reactions take place in a shaft furnace packed with a mixture of the waste and a triple reverse burn char. The char provides a porous adsorptive media that binds the waste, but allows passage of reaction and product gases. The process may be operated in a continuous mode by regulating the char/waste feed and the burned char in a manner to provide a stationary reaction zone. Appropriate size reduction and blending of debris waste would be required to ensure waste/char mixes that are acceptable for the process. A commercial company in California has an exclusive license to develop and market the technology.

HYDROGEN REDUCTION

In this process, vaporized organic wastes are mixed with hydrogen rich gas at 900^0C in an electrically heated reactor. The process is well suited for both liquid organics and aqueous wastes containing dilute organics. Because the organics must be in the vapor phase for complete hydrogenolysis of the waste components, organics from solid waste matrices must first be desorbed. As a consequence, typical combustible debris waste may be degraded too slowly for practical applications. Only debris waste containing easily desorbed contamination will be a good candidate for hydrogen reduction. A private company has commercialized the technology and has built systems with design capacities of 150 tons per day.

STEAM REFORMING

The DOE, EM-50 is supporting the demonstration of steam reforming of mixed wastes under contract with a commercial company. Nominal throughput of the demonstration is 90 lb/h of various low-level mixed waste surrogates. In nonradioactive applications, the steam reforming process usually involves two stages: (1) waste is pyrolyzed and volatilized by exposure to steam at elevated temperatures (300 to 800^0C) and (2) volatile species are further reacted with steam at temperatures up to $1,200^o$C to produce

synthesis gas. However for mixed waste treatment purposes, the primary stage effluent is oxidized to completion and the offgas scrubbed before discharge.

Concentrated or pure organic liquids pose no problems for steam reforming. In addition steam reforming should be just as flexible as incineration in handling both combustible and in organic debris. Soils and sludges may present challenging feed problems that may be solved with modifications to existing technologies.

Commercialized steam reforming gasifies organic waste in a fluidized bed of sodium carbonate that serves as a catalyst for reforming reactions. After particulate removal, the product gases from the steam reformer flow into a flameless thermal oxidizer, which converts volatiles to water, carbon dioxide, and acid gases. An offgas cleanup system removes the acid gases as dry salts; a baghouse and high-efficiency particulate air (HEPA) filter removes particulate before discharge to the environment.

Recent test runs with simulated mixed wastes containing uranium and a PCB simulant indicated that heavy metals are retained in the first stage reactor bed and destruction and removal efficiencies (DREs) of 99.9999% have been demonstrated. Follow-on efforts include detailed design and costing for a 500-lb/h system for testing with radioactive waste. Steam Reforming in contrast to Acid Digestion has the advantages of being fully developed and can handle a variety of wastes, including aqueous solutions. However, the system is more complex, creates more emissions, operates at higher temperatures and involves the use of hydrogen gas.

DIRECT CHEMICAL OXIDATION

The DCO Process, developed at Lawrence Livermore National Laboratory (LLNL) with EM-50/MWFA support, is a nonthermal, ambient pressure, aqueous- based technology for the oxidative destruction of the organic components of hazardous or mixed waste streams. The process uses solutions of peroxydisulfate salts (typically sodium or ammonium) to mineralize the organics to carbon dioxide and water, and the expended oxidant may be electrolytically regenerated to minimize secondary waste. The net waste treatment reaction is:

$$S_2O_8^{2-} + \{organics\} \Rightarrow 2HSO_4^- + (CO_2, H_2O, \text{inorganic residues})$$
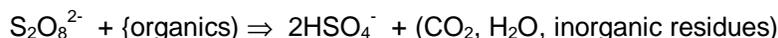
The peroxydisulfate process is an application of a well-established industrial technology. Acidified ammonium peroxydisulfate is one of the strongest oxidants known, exceeded only in oxidative power by fluorine, ozone, and oxyfluorides. The process is primarily being developed for the treatment of organic liquids, but should handle sludges if they are finely divided and slurried in to the working solution. Destruction of organic solids is possible and inorganic debris will be decontaminated The oxidation potential of peroxydisulfate is high enough to oxidize nearly all organics, and thus the process is virtually "omnivorous." Many organics are oxidized by the process at ambient pressure and temperatures in the 80 to $100^{\circ}C$ range; more recalcitrant materials, e.g., PVC polymer may require some thermal treatment ($140–180^{\circ}C$, 24 h) before oxidation by peroxydisulfate.

An integrated bench-scale system for the destruction of a wide range of chlorinated organic liquids and organic-contaminated sludges has been demonstrated at LLNL. Many chlorinated solvents require hydrolysis to offset difficulties presented by their high volatility and low solubility in water. This first step hydrolysis reaction takes place at elevated temperatures in a sealed reactor. The resultant products, generally more soluble and less volatile, are then mineralized in the DCO Process.

The integrated DCO process has been demonstrated on LLNL waste streams containing chlorinated solvents. Approximately 300 kg of low-level waste containing mixed chlorosolvents have been processed. In both industrial applications and in the LLNL tests, a broad spectrum of materials have been successfully oxidized using peroxydisulfate, including acetic acid, formamide, ethylene glycol, tributyl phosphate, methyl chloroform, carbon tetrachloride, as well as carbon residuals found in incinerator ash. LLNL is pursuing commercialization of the process through a collaborative effort with a waste treatment vendor.

The DCO process has also been demonstrated to have a greater organic destruction removal efficiency since peroxydisulfate is a stronger oxidizer than nitric acid. However, like Acid Digestion, further development is required, particularly for halogenated organics.

CATALYTIC DETOXIFICATION

This process which is being developed with EM-50 support to a private research company, is a catalytic, aqueous process that oxidizes organic materials with internal regeneration of the oxidant. The low operational temperature (150 to 250°C) and the nature of the catalyst typically does not produce regulated gases or volatile metals in the offgas. The reagent solution (containing $FeCl_3$, with Pt and Ru co-catalysts) is not consumed in the reaction, readily dissolves metals, and, therefore, can accumulate toxic and radioactive metals before recovery or disposal. Oxygen present above the reagent solution supports reoxidation of the reduced ferrous ions back to ferric.

$$Fe (II) + \tfrac{1}{2} O_2 + H_2O + e^- = Fe (III) + 2 OH^-$$
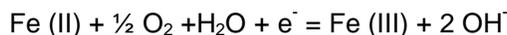
Reported destruction efficiencies range from better than 99.999% for nonchlorinated solvents to 98.9% for PCB compounds. The process is generally more applicable to liquid wastes, but can accept some solids, limited by solubility of the inert matrix in the working fluid.

Catalytic detoxification is being developed primarily for the treatment of organic liquids. However, the process should handle some solids, sludges, and particulate if they are finely divided, and suspended, slurried, or emulsified in the working fluid. In addition, feeding of any sludge, solids, or debris may quickly
expend the acid chloride process solution, requiring solution rework

The advantage of the catalytic detoxification process is that it can aggressively digest a variety of organic waste matrices, including chlorinated compounds, while at the same time continually regenerating the oxidant. In contrast, the system is more complex than Acid Digestion and may generate greater emission concerns as well as a need for greater containment and corrosion control

Technology Applicability

The Acid Digestion technology is applicable to most solid and some liquid organic mixed wastes containing a variety of RCRA hazardous metals and radiological components (e.g., actinides and fission products). The general category of wastes most amenable to this AOT method is organic based job control waste containing significant quantities of TRU material such as Pu-238. The technology may also have some success in digesting nonvolatile organic liquids (e.g. nitromethane), including oils. However, oil digestion may be slow. Specifically, the process can destroy the following organic materials at moderate temperatures: cellulose (paper), polyethylene, latex rubber, Tyvek ™, neoprene, polyvinyl chloride, polystyrene ion exchange resins, filters, munitions, and plastics. Larger nonreactive inorganic matrices mixed with the above organic debris are acceptable, and will be decontaminated in the process.

Even though treatment of halogenated organics has been shown, additional development to ensure removal of HCl from the offgas, separation of HCl from nitric acid, and elimination of the need for post treatment is necessary. The process is not recommended for aqueous wastes containing only dilute organics and has not been demonstrated for nondebris solids, including sludges and particulates. The treatment capabilities for the RCRA regulated organics has not been fully assessed.

Since surface area of the mixed waste can have a significant effect on the digestion efficiencies and rate, the Acid Digestion Process may only be applicable to specific wastes that have been sized before feeding. Continued development is recommended to define the applicable sizing range before digestion of a given waste stream.

Patents/Commercialization/Sponsor

Westinghouse Savannah River Company, the primary SRS contractor, filed a patent on the Acid Digestion Process during an early development stage in 1997. Later, two WSRC personnel who were the primary developers of the technology formed a small, for-profit company to commercialize the technology. As required, the spin-off company was able to obtain an exclusive license for Acid Digestion

from SRS. This new company has also formed a strategic alliance with ToxGon Corp. of Seattle, WA. In addition to bringing large-scale engineering experience to the venture, ToxGon provides 16,000 square feet of facility space for additional pilot and prototype testing

The immediate objective of the spin-off company is to continue the appropriate development of the technology necessary for them to compete for deployments at full scale. Even though the new firm has proposed to EM-50 the construction and testing of a 400-liter scale system, their request for continued MWFA/EM-50 sponsorship has not gone forward. Therefore potential end users and waste managers favoring Acid Digestion for their specific organic mixed waste application, may need to sponsor the additional development needed to ensure successful deployment. In addition to DOE waste markets (e.g., TRU job control waste), the new company claims commercial markets in the nuclear power industry (e.g., spent ion exchange resins, filters) as well as in laboratory and medical wastes.

SECTION 5

COST

Methodology

The Savannah River Site is currently completing a cost analysis to determine a baseline for demonstrating an Alternative Oxidation Technology (AOT) for their Pu-238 contaminated job-control waste. SRS personnel plan on competing the demonstration effort by putting a call out for proposals, and require a baseline for comparing potential bids. As a consequence, the cost estimate is based in part on the Acid Digestion Process, including waste feed handling and spent acid waste stabilization systems.

Cost Analysis

Costs for the development, design, construction and operating of an Acid Digestion system are based on a throughput of one 55 gallon barrel of debris waste per day and will also be dependent on specifics of the desired application. Large debris type waste will require sizing and chlorinated wastes will require additional offgas cleaning and monitoring. These factors will lead to considerable additional costs. Wastes containing substantial actinides in particulate form, such as Pu-238, will require containment. Ensuring this containment will also be costly. To date, very little has been done to compare the life-cycle costs between various AOTs as applied to the same waste inventory.

Cost Conclusions

The draft SRS cost estimate for an Acid Digestion demonstration on job control waste has been completed and is undergoing final SRS management review. Based on this draft, operational scale demonstration Acid Digestion systems can range between $2,000K and $8,000K in design, construction and demonstration costs. The actual costs will vary depending on the specific configuration of the demonstration equipment, the level of testing to be performed, desired throughput of the demonstration system and waste characteristics.

REGULATORY AND POLICY ISSUES

Regulatory Considerations

Major regulatory activities, including permitting and licensing, will be necessary for implementing a production scale Acid Digestion Process at a DOE complex site. In summary, these requirements are as follows.

- A National Environmental Policy Act (NEPA) review for implementation at federal facilities (categorical exclusion is likely to apply for treatability studies). At DOE facilities, this includes an initial environmental checklist that is used to assist in determining if a more detailed environmental assessment or environmental impact statement is required.

- A radioactive material license from the Nuclear Regulatory Commission (NRC) or its applicable agreement state for non-DOE facilities or for DOE facilities expected to be regulated by NRC or the agreement state.

- RCRA notifications or permit applications submitted to the regulatory agency based upon the scale and purpose of the process and the capability of the process to achieve the required treatment of Land Disposal Restriction (LDR) wastes and meet applicable LDR treatment standards.

- A notification to the applicable regulatory agency (state or EPA) for treatability studies.

- A variance or Determination of Equivalent Treatment to allow disposal of treated wastes and residues from using this technology to treat waste that currently must be treated to meet a specific technology based LDR treatment standard that is not this technology.

- Waste Analysis and Treatment Plans for wastes treated by a generator under 40 CFR 262.34 or under 40 CFR 254 or 265 for wastes to be treated at permitted facilities.

- Submittal of a permit application or modification to the applicable regulatory agency (state or EPA) for review and approval of treatments that are not treatability studies. Currently, a risk assessment for emissions and effluents is required for this.

- Treatment of hazardous waste or mixed waste to dispose elsewhere than WIPP would need to meet the applicable RCRA 40 CFR 268.40 LDR treatment standards for wastewater or nonwastewater and include treatment of underlying hazardous constituents to UTSs (Universal Treatment Standards), as applicable. NRC waste form testing requirements may also need to be met for disposal in NRC licensed sites. Individual commercial and DOE disposal sites may have site specific requirements, including specific radionuclide limitations, which may affect qualification of the final waste form. Final waste forms must meet the Waste Acceptance Criteria for the intended disposal site. For transportation to and disposal at WIPP, final waste forms in which alpha emitting radionuclides can result in hydrogen generation must not exceed a maximum allowed wattage of heat generation or hydrogen generation rate.

Requirements specific to air emissions under the Clean Air Act (CAA) are as follows:

- An air permit/NESHAPS (National Environmental Standards for Hazardous Air Pollutants) applicability review to determine need for NESHAPS permitting or air emissions monitoring for any operation that involves potential releases of hazardous air pollutants as particulates, gases (e.g., NO_x, HCl), or vapors (e.g., volatile organics), that may contain radionuclides or other regulated hazardous air pollutants.

- A National Ambient Air Quality Standards (NAAQS) and New Source Performance Standards (NSPS) applicability evaluation to determine the need for a Permit to Construct application or an air permit modification as applicable.

Other environmental areas that may require consideration by the potential end user include the following:

- Any other secondary waste stream treatment and its associated disposal requirements, e.g.,

  - spent prefilters and HEPA filters from offgas system,
  - scrubber solution blowdown from an offgas system,
  - miscellaneous wastes.

- NPDES permitting or publicly owned treatment work (POTW) limits if process cooling water effluent is released to an affected system.

- State or a locality specific requirement, e.g., siting, zoning, historic preservation, and other laws and regulations, that may require additional permits and licenses.

The AOT development and demonstration efforts conducted by the Savannah River Technology Center was an R&D activity performed under existing air permits and NESHAPs documentation. A NESHAPs evaluation was performed. A DOE-required environmental checklist for the radioactive bench scale treatability study was used to determine that the project met the requirements of categorical exclusion B3.6 under NEPA Regulation, 10 CFR Part 1021.400, Subpart D.

Safety, Risks, Benefits, and Community Reaction

The Acid Digestion technology exhibits hazards typical of many industrial treatment and chemical synthesis operations. To its advantage the process does not require the use of high voltage or amperage, and does not generate any toxic or explosive gases. However, the use of acidic solutions at high temperatures and, for some cases, in pressurized systems can lead to worker safety concerns if the proper engineering and administrative controls are not established. Proper design and the use of established procedures should mitigate of these risks. Critical to a safe design is material selection to avoid corrosion and potential breech of primary containment. In addition, procedures must address methods and monitoring required to avoid reaction rate excursions leading to rapid temperature and pressure increases. Feed rate control of easily oxidized and/or reactive organics is of particular concern if these excursions are to be avoided.

Interest in alternatives to incineration derives largely from public concern for the potential stack emissions from excess air combustion systems. Concern is with the quantities of contaminants emitted. Large gas volumes could conceivably contain a significant quantity of contaminants. Releases of concern include products of incomplete combustion (PICs), products of recombination of molecular fragments and chlorination, especially dioxins and furans, and emissions of radionuclides. Excursions in the treatment operation are also a concern due to the potential difficulty in controlling incinerator releases to the atmosphere. Excursions may occur due to increases in organic input rates or an input of organic material with an unexpectedly high heating value. Either may cause rapid reactions and overloading of the incineration system.

Stakeholders are concerned that these problems still exist after spending millions of dollars on the design, operation, and testing of a thermal treatment unit, like incineration. They do not believe that adequate attention has been directed to the nonthermal, nonflame process such as the Acid Digestion technology.

The EPA has proposed new regulations for controlling emissions from incinerators. These new rules commonly referred to as the MACT Rule, will, when promulgated, limit emissions of chlorine, particulates, volatile organic compounds, and metals. Of particular concern to DOE incinerators are the low mercury and dioxin emission standards. These new standards are based on the top performing existing incinerator systems in use today. Control technologies required for these systems may or may

not be applicable to mixed waste treatment systems. EPA and state permit writers have indicated that they intend to use their Omnibus authority under RCRA to require the same level of control for all mixed waste thermal treatment systems.

The greatest concern is with the use of incineration technology for the destruction of the targeted waste stream (i.e., SRS Pu-238 job control waste). Methods chosen for these types of waste must ensure radiological containment during oxidation. A low-temperature, low-pressure destruction technology like Acid Digestion is more likely to be accepted by the stakeholders and state regulators for the treatment of Pu-238 waste since its emissions are considerably less and more easily controlled.

The MWFA Tribal and Public Involvement Resource Team initiated activities to gather stakeholder issues, needs and concerns about alternative organic oxidation technologies. The Technical Requirements Working Group (TRWG), a stakeholder group formed to assist the MWFA, reviewed and provided recommendations on changes to the Chemical Oxidation Technology Development Requirements Document. Their comments are in the process of being reviewed and resolved.

Following are general stakeholder issues and concerns regarding high temperature treatment methods found in public reports.

- Stakeholders expressed concerns regarding the current baseline technology, incineration, to treat various mixed waste streams. These concerns range from the release of contaminants, to mechanical failure and injury. One important concern is worker safety during operation of an incinerator. That concern is due primarily to the high temperatures associated with the treatment process.

- Incinerators are becoming more complex, difficult, and expensive to permit and operate in both DOE and the private sector. Because of these combined technical and policy considerations, alternative methods are needed to oxidize organic materials in the waste. The Acid Digestion technology is an alternative. It is a moderate temperature, less complex treatment option that can destroy various types of organic materials. Stakeholders look favorably upon technologies that reduce air emissions and are less complex, thus minimizing the potential for accidents and incidents and effects on human health and the environment.

Lastly, the MWFA Tribal and Public Involvement Resource Team facilitated Tribal and public involvement by issuing an article in the quarterly newsletter highlighting the Acid Digestion technology.

LESSONS LEARNED

Implementation Considerations

To deploy the Acid Digestion technology for a particular organic mixed waste application, potential end users need to consider factors common to most waste treatment systems. These factors include the identification of the design requirements for the front-end waste feed sizing equipment and the back end waste handling methods. Decisions also need to be made in regard to the need and type of oxidant recycle methods required.

Because the primary process hazard associated with the Acid Digestion Process arises from the presence of nitric acid in contact with organic materials, potential end –users must mitigate this risk before implementation. Tests have shown that the reaction can be safely controlled through one of three ways:

1. Oxidant control will limit the potential for runaway reactions involving nitration of organics. This can be accomplished by limiting the oxidant available, i.e., feed rate control, in the reaction vessel.

2. Organic control will limit the energy source available for a runaway condition. This can be accomplished by organic feed control and reaction rate monitoring.

3. Water content control will help to destroy nitrated organics as they are formed.

Oxidation rate monitoring and water content monitoring are issues that have not been completely resolved.

It is also essential in this process to measure iron concentrations in the nitric-phosphoric waste acid mixture on a near-continuous basis. Once the iron concentration reaches the solubility limit, solidification of the mixture is initiated.

Technology Limitations and Needs for Future Development

As mentioned previously the Acid Digestion Process is limited in the variety of different organic waste matrices that it can efficiently destroy. The categories of these difficult wastes include volatile organics and sufficiently halogenated liquid organics.

In December 1997, the status of the Acid Digestion program was reviewed in detail by a panel comprised of members both from the SRS and the MWFA. The primary objective of the review was to determine Acid Digestion's limitations and further development needs.   The scope of the review included the following activities as listed below.

- determination of the technical adequacy of both the performance requirements and design criteria,
- evaluation of waste minimization, energy conservation, and as low as reasonably achievable (ALARA) practices;
- identification of the technical issues/assumptions,
- justification of the design and hazard classification selected,
- resolution of technical risk management concerns,
- determination of the adequacy of the technical risk assessment.

The specific desired goals of the review were to:
- provide a rigorous assessment and evaluation process,
- assess the technology,
- identify key needs for additional R&D,
- recommend a path forward for future development efforts.

The Board identified basic technology needs and recommended the following future development work for addressing them:

- complete larger pilot-scale testing to demonstrate complete system operation,
- determination of G values (the amount of hydrogen gas generated per 100Kev of radiation energy) as a result of radiolysis in the final ceramic waste form,
- consideration of other low-temperature final waste forms including silica gel and inorganic, anhydrous media;
- evaluation of acid recovery options and consideration of acid recovery alternatives, such as no recycle, use of urea, or use of a caustic scrub;
- creation of a reaction (digestion) rate table as a function of temperature, pressure, types of organic waste material, and waste surface area.

As listed below, the panel also had secondary recommendations concerning future testing for a pilot-scale facility:

- determine offgas species and flow rates,
- conduct tests with combined wastes to determine synergistic effects,
- develop a detailed cost for the process as a function of the mass of waste to be treated,
- explore various size reduction/segregation/feed system options.

Technology Selection Considerations

Potential end-users and waste managers in the DOE complex need to consider many factors when selecting destruction technologies for the treatment of their organic-based mixed wastes. The primary decision involves choosing between fully developed thermal and mostly undeveloped nonthermal (or AOT) technologies. This decision is not only driven by negative stakeholder perceptions of incineration, but is largely influenced by the waste characteristics. Wastes containing particulate actinides, volatile mercury and/or contain constituents that may result in significant offgas treatment challenges may be more readily treated by one of the AOT methods, such as acid digestion. After choosing to use a nonthermal technology, end users need to choose among the various AOTs available. Factors influencing this selection include, but are not limited to, the following:

1. The General Waste Matrix Category and Its Physical Properties

Some of the AOTs favor liquid organics, while others are more amenable to sludges and debris. The Acid Digestion basically favors properly sized debris. If the waste feed stream varies, acid digestion may not be the best choice. Large debris waste might require presizing to be acceptable for some of the AOT processes including acid digestion. The matrix of the waste on acid digestion may also effect throughput since development data indicates that some matrices, such as plastics, digest at a substantially lower rate than that of cellulose.

2. Waste Composition and Characteristics

Acid digestion can handle significant inorganics in the waste feed, but is limited by the pressure of significant halogenated organics including chloride. Acid digestion is particularly suited for wastes containing actinides and transuranic oxides (Pu 238) where radiological containment is critical.

3. Secondary Waste Generation

Even though development has indicated suitable waste forms for the spent oxidant solutions from acid digestion, the process requires more oxidant replacement and recycle than other AOTs. Secondary waste treatment and disposal could become excessive.

4. Desired Degree of Oxidation/Destruction Removal Efficiency

Data collected during development of the acid digestion process indicates that the degree of oxidation for some waste streams is not as efficient compared to other AOTs, such as steam reforming. This is attributed to nitric acid's lower oxidation capabilities compared to other AOT oxidants such as peroxydisulfate. The desired degree of oxidation is dependent on the requirement imposed by the end-user, as determined by the ultimate goal of the treatment. If the purpose is to only destroy enough organics in a TRU waste matrix to eliminate hydrogen generation and allow shipment to WIPP, then acid digestion may be the optimum choice. However, if the requirement is to destroy all RCRA regulated organics to meet EPA land disposal requirements, acid digestion alone may not be effective.

5. Extent of Development

Acid digestion has only been tested at the 40-liter pilot scale. Before deployment of acid digestion by an end-user, extended development at a greater pilot scale is highly recommended. These tests should involve actual wastes or surrogates and collect data to determine the following parameters needed for production scale design.

- Digestion rate to determine design throughput

- Feed size and surface area ranges needed for oxidation. This is necessary to design pretreatment and waste handling systems.

- Extent of oxidation to determine if posttreatment methods are needed and to aid in the design of process monitoring methods.

- Determination of offgas emission compositions to design oxidant recycle as well as offgas cleanup and containment systems.

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TMS Data Elements

Funding Source

This section provides cross reference information in regard to the EM-50 Mixed Waste Focus Area contract established for development of the Acid Digestion technology. The Department of Energy – Headquarters (DOE-HQ) Technology Management System (TMS) tracking number is provided as well as the specific Technical Task Plan.

TMS # 1827 Acid Digestion of Organic Waste

TTP # SR16MW32 Acid Digestion of Contaminated Organics

APPENDIX C

ACRONYMS AND ABBREVIATIONS

ALARA	As low as reasonably achievable
ANL	Argonne National Laboratory
AOT	Alternative Oxidation Technology
BDAT	Best Demonstrated Available Technology
CAA	Clean Air Act
DCO	Direct Chemical Oxidation
DOE	Department of Energy
DOE-HQ	Department of Energy-Headquarters
DRE	Destruction and removal efficiency
EPA	Environmental Protection Agency
HEPA	High-efficiency particulate air
ITSR	Innovative Technology Summary Report
LDR	Land Disposal Restriction
LLNL	Lawrence Livermore National Laboratory
MACT	Maximum Achievable Control Technology
MWFA	Mixed Waste Focus Area
NAAQS	National Ambient Air Quality Standards
NEPA	National Environmental Policy Act
NESHAPS	National Environmental Standards for Hazardous Air Pollutants
NPDES	National Pollutant Discharge Elimination System
NRC	Nuclear Regulatory Commission
NSPS	New Source Performance Standards
OST	Office of Science and Technology
PE	Polyethylene
PIC	Product of incomplete combustion
POTW	Publicly Owned Treatment Works
PVC	Polyvinyl chloride
RCRA	Resource Conservation and Recovery Act
RFETS	Rocky Flats Environmental Technology Site
SRS	Savannah River Site
TGA	Thermogravimetric analysis
TRU	Transuranic
TRWG	Technical Requirements Working Group
UTS	Universal Treatment Standard
WIPP	Waste Isolation Pilot Plant
XRD	X-ray diffraction