

# DESIGN FOR APPLICATION OF THE DETOX<sup>SM</sup> WET OXIDATION PROCESS TO MIXED WASTES

Richard A. Bell and Patrick M. Dhooge  
Delphi Research, Inc.

## ABSTRACT

Conceptual engineering has been performed for application of the DETOX<sup>SM</sup> wet oxidation process to treatment of specific mixed waste types. Chemical compositions, mass balances, energy balances, temperatures, pressures, and flows have been used to define design parameters for treatment units capable of destroying 5. Kg per hour of polychlorinated biphenyls and 25. Kg per hour of tributyl phosphate. Equipment for the units has been sized and materials of construction have been specified. Secondary waste streams have been defined. Environmental safety and health issues in design have been addressed. Capital and operating costs have been estimated based on the conceptual designs.

## PROCESS DESCRIPTION

The process is a wet chemical oxidation using a combination of iron ions with small amounts of platinum and ruthenium ions in an acidic aqueous solution (1,2). A typical composition for the solution in application to hazardous and mixed wastes is 60% iron chloride, 3-4% hydrochloric acid, 0.01% platinum and ruthenium, and 36-37% water. The ultimate oxidant in the process is oxygen, although extensive experimentation has shown that organic compounds are oxidized in the solution by iron(III) ions (3,4). Iron(II) produced during the oxidation of organic compounds is oxidized back to iron(III) by oxygen. Thus, iron ions act as a catalyst in the oxidation of organic compounds by oxygen since the iron is not consumed. Liquid wastes may be fed into the process solution with a metering pump. Solid organic wastes may be fed into the process solution with an auger. Solid wastes containing a great amount of inert material may be washed with the process solution. The products of the oxidation of organic compounds containing only carbon, hydrogen, and oxygen are carbon dioxide and water. Chlorinated compounds produce hydrogen chloride as one of the products. Organic compounds containing phosphorous, sulfur, and/or nitrogen produce phosphate, sulfate, and/or nitrogen gas, respectively. Oxidation of organic compounds with the process is typically carried out at 423. to 473.K, with measured destruction efficiencies of >99.9999% in stirred reaction vessels (5). The vapor pressure of the process solution over this temperature range is given in Fig. 1. The process solution has been shown to dissolve varying amounts of a number of heavy metals, including arsenic, mercury, chromium, lead, neodymium, and cerium (6). Due to the oxidizing nature of the process solution and the relatively low operating temperature, metals are contained in the process solution. Lead, cadmium, and other toxic metals can be selectively precipitated from the process solution, allowing these metals to be recycled or disposed of in extremely compact form. It has also been demonstrated that the process solution can destroy hazardous organic compounds in, and extract heavy metals from, soils, vermiculite, and HEPA filter material (5-7). The process may be operated in batch or continuous mode, depending on the particular application. The reaction may be carried out in a plug flow or stirred tank configuration, although a plug flow reactor may be excessively long for some applications of the process. The process is more than an alternative to incineration, since it can effectively extract, contain, and concentrate toxic and radioactive metals from the inert components of a waste, it is tolerant of wastes containing great amounts of

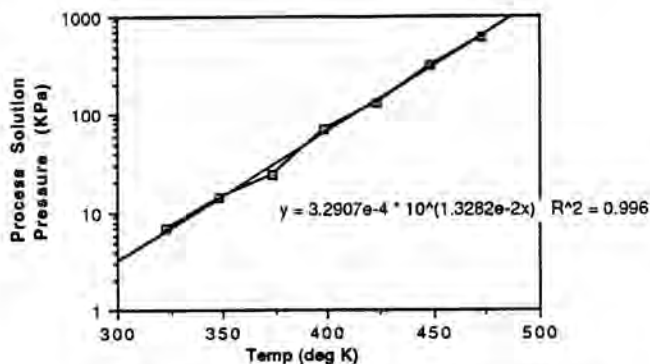


Fig. 1. Process solution pressure versus temperature.

water, and its emissions can be carefully controlled during operation.

## POTENTIAL PROCESS APPLICATIONS

Destruction of hazardous organic compounds, volume reduction of bulk organic or aqueous/organic wastes containing toxic and/or radioactive metals, and treatment of inert solids contaminated with hazardous organic compounds and/or metals are believed to be the three most useful applications of the process. A wide range of hazardous organic compounds are destroyed by the process, and proper design would allow one treatment unit to be used effectively on non-volatile, semivolatile, and volatile organic compounds. Since the process is not particularly sensitive to waste particle size, water content, or waste type, it can be described, with some reservations, as an omnivorous waste treatment method. Depending on the type of wastes to be treated, the process unit can be configured as a continuous, stirred tank reactor (CSTR), a batch, stirred tank reactor, a recycled plug flow reactor, a counter-current liquid/gas reactor, or a combination of these types.

Examples of potential applications of DETOX<sup>SM</sup> to mixed wastes are:

1. Volume reduction of waste scintillation fluids, extraction solutions, and organic solvents contaminated with toxic and/or radioactive metals.
2. Volume reduction of disposable laboratory protective wear, paper towels, etc., contaminated with solvents, toxic metals, and/or radioactive metals.
3. Volume reduction of spent transformer oils, greases, and hydraulic fluids contaminated with solvents, heavy metals, and/or radioactive metals.

4. Cleaning soils and soil residues contaminated with solvents, and heavy metals and/or radionuclides.
5. Cleaning sorbent materials and HEPA filters contaminated with hazardous organic compounds, heavy metals, and/or radionuclides.
6. Volume reduction of aqueous solutions containing radioactive and/or toxic metals.

The process is applicable to many mixed waste types, but is probably not suitable for treating great amounts of cement, concrete, or structural metals (including metallic aluminum). If a mixed waste to be treated contains significant amounts of nitrate, carbonate, iodine, cyanide, fluorine, inorganic sulfide, phosphate, or sulfate, special considerations must be made in design and operation of a process unit. The presence of significant amounts of barium, radium, lead, cadmium, arsenic, or selenium in a waste will also result in some special design considerations. The design of a particular process unit can be highly dependent on the application(s) planned for that unit.

As examples of process applications for this paper, we have concentrated on engineering design for volume reduction of two liquid organic mixed wastes. These wastes are:

- A. An oily waste containing approximately 50.% polychlorinated biphenyls and 50.% hydrocarbon oil, with trace amounts of chlorinated solvents and transuranic metals.
- B. Spent tributyl phosphate (TBP) containing trace amounts of polychlorinated biphenyls, toxic metals, uranium, and thorium.

## ENGINEERING

### Mass Balance

Table I gives the calculated mass balance for oxidation of PCB. The feed rates are assumed to be 5. Kg/hr for the PCB oil and 25. Kg/hr for TBP. It is assumed that approximately 5.% of the content of the product gases exiting the reaction vessel would be unused oxygen gas.

Oxidation of PCB/oil waste would produce carbon dioxide, water, and hydrogen chloride (HCl). These products would be removed from the reaction vessel in a controlled flow of hot gases. Water and HCl would be condensed from the gas stream. It would be necessary to neutralize the condensate with soda ash or sodium hydroxide to eliminate its hazardous corrosive characteristic. The remaining gas, primarily carbon dioxide from the oxidation reaction, could be compressed into a pressure tank and analyzed before venting. Non-product water in the neutralized condensate would be evaporated, condensed, and returned to the reaction vessel, thus minimizing the volume of brine to be disposed.

Oxidation of TBP would produce carbon dioxide, water, and phosphoric acid. Left to accumulate in the DETOX<sup>SM</sup> solution, phosphoric acid would buffer the acidity of the process solution, precipitate the iron catalyst, and fill up the reaction vessel, so phosphate must be removed from the process solution. Calcium ion could be used to remove phosphate. Reaction of calcium chloride with phosphoric acid would produce calcium dihydrogen phosphate salt and hydrogen chloride (HCl). Carbon dioxide, water, and HCl would be removed in a controlled flow of hot gases from the reaction vessel. Water and HCl would be condensed from the gas stream. The remaining gas, primarily carbon dioxide, would

TABLE I  
Mass Balance for Oxidation of PCB Oil

<b>Mass In:</b>	Aroclor 1254	2,517. g/hr
	Hydrocarbon Oil	2,483. g/hr
	Oxygen	13,179. g/hr
	Water	5,134. g/hr
	Sodium Hydroxide	1,542. g/hr
<b>Total In</b>		24,855. g/hr
<b>Mass Out:</b>	Oxygen	1,706. g/hr
	Carbon Dioxide	11,874. g/hr
	Water	9,020. g/hr
	Sodium Chloride	2,255. g/hr
<b>Total Out</b>		24,855. g/hr

be monitored before release. The condensate would be neutralized with calcium hydroxide (slaked lime) to regenerate calcium chloride for further phosphate precipitation. Precipitated calcium dihydrogen phosphate salt would be removed by a solids concentration and filtration system. Product water would be evaporated from the condensate for disposal.

### Energy Balance

Table II gives the calculated balance for the application. The energy generated by the reaction is essentially the heat of combustion of the organic materials being destroyed.

Both treatment units would require active cooling of the reaction vessel. In addition, a heat source would be required to initially bring the reaction vessel to its operating temperature. Standard jacketed reaction vessel design can be used, with a thermal fluid which will provide a heating and cooling medium.

### Process Application Schematics

Figure 2 shows the conceptual schematic for a treatment unit.

Wastes and oxygen are fed at predetermined rates into the reaction vessel. In the reaction vessel, organic components of the wastes are oxidized to water, carbon dioxide, and HCl or phosphoric acid. A metered flow of hot gases from the reaction vessel is passed through a condenser to cool the gas and remove water and HCl as a liquid condensate. For either application a simple condenser would be used, but the exit gases from the reaction vessel would be cooled to 423.K and

TABLE II  
Energy Balance for Oxidation of PCB Oil

<b>Energy In:</b>	Heat of Combustion	147,500. kJ/hr
	Heat of Solution (HCl)	2,900. kJ/hr
	Heat of Reaction (HCl + NaOH)	2,200. kJ/hr
<b>Total Energy In</b>		152,600. kJ/hr
<b>Energy Out:</b>	Reactor Vapor Condensation	40,200. kJ/hr
	Water Return Condensation	24,500. kJ/hr
	Active Reactor Tank Cooling	87,900. kJ/hr
	<b>Total Energy Out</b>	

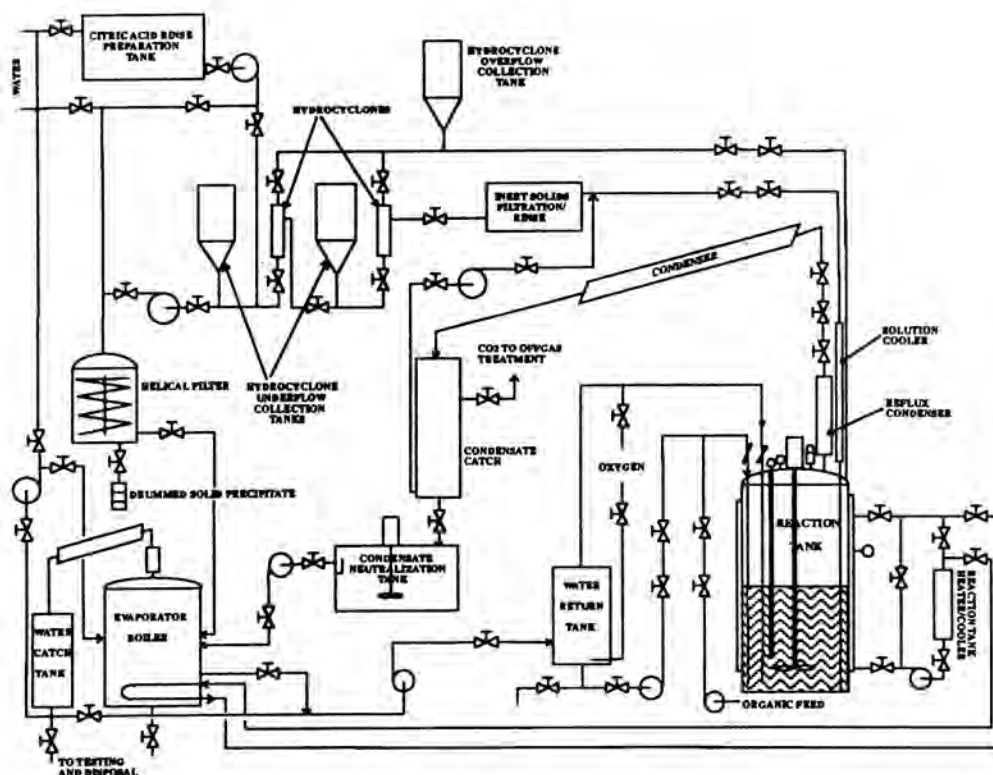


Fig. 2. Process schematic.

refluxed slightly at the exit from the reaction vessel to contain heavy organic compounds in the reaction vessel.

Condensate would be collected and neutralized, after which it would be pumped into an evaporator. For oxidation of PCB/oil, the neutralized condensate would be a secondary waste stream containing water and chloride produced in oxidation of the organic compounds; non-product water condensed from the product gas stream would be boiled off the condensate and returned to the reaction vessel. Volatile organic compounds would be boiled off the neutralized condensate and returned to the reaction vessel with the non-product water. In oxidation of TBP, the neutralized condensate contains product water which must be isolated as a secondary waste stream from the process; product water in the neutralized condensate would be boiled off for disposal and the remainder of the neutralized condensate returned to the reaction vessel. The TBP product water could be sparged with feed oxygen to return any volatile organic compounds to the reaction vessel.

In treatment of PCB/oil solids would not have to be removed from the process solution, but solids removal would be necessary in treatment of TBP. To remove solids during the treatment of TBP, a flow of the process solution would be taken from the reaction vessel, cooled to approximately 373.K, and passed into a solids concentration and filtration system consisting of two hydrocyclones and a helical filter. Underflow from the first hydrocyclone would be collected in a tank and periodically passed through the second hydrocyclone. Underflow from the second hydrocyclone would be collected in a tank and periodically fed through the helical filter. Overflows from the hydrocyclones would be collected in a tank and pressured back into the reaction vessel. The filtrate from the helical filter, and rinses of the solids with dilute citric acid and

water, would be fed to the evaporator along with neutralized condensate. Rinse water would be recycled from the evaporator to prepare additional rinses.

Both of the treatment units would be assembled on skids for ease of transport and modularity. The PCB/oil treatment unit, with the exception of the carbon dioxide holding tanks, could be assembled on one skid. The TBP treatment unit could be assembled on two skids which would be connected at the treatment site.

#### Operating Flows, Temperatures, and Pressures

Calculated flows, temperatures, and pressures in the treatment units are given in Tables III and IV. The primary points of control for the treatment units would be waste feed rate, oxygen feed rate, reactor temperature, process solution flow rate for the TBP treatment unit, and product gas flow rate.

#### Materials of Construction

Materials of construction for the treatment units would range from exotic metals to polypropylene.

The highly corrosive nature of the process solution, combined with its elevated temperature and pressure, and the need for reliable containment of the hazardous and radioactive components of the wastes, requires the use of strong, robust, and highly corrosion resistant materials for the reaction vessel and its inlet and outlet lines. For these reasons, a Grade 7 titanium pressure shell lined with tantalum has been chosen for the reaction vessel, and double-walled tantalum tubing for the vessel's inlet and outlet lines. Tantalum has an established history of successful use in chemically aggressive environments in the chemical process industry, and its corrosion rate in aggressive environments is well known. The Grade

TABLE III  
Flows, Pressures, Temperatures for Oxidation of PCB Oil

Location	Flow (L/hr)*	Temperature (K)	Pressure (kPa)
Oxygen to Reactor	632	293	1620
Organics to Reactor	4.1	293	1620
Water to Reactor from Evaporator	9.5	293	1620
Reactor Vessel		473	1500
Gases to Condenser	15500	473	275
CO <sub>2</sub> + O <sub>2</sub> to Compressor	3100	300	265
CO <sub>2</sub> + O <sub>2</sub> in Holding Tank		293	1500 Max.
Condensate (10% HCl in Water) to Catch	13.4	300	83
Neutralized Condensate to Evaporator	14.1	336	175
Water to Evaporator	5.2	293	83
20% NaCl from Evaporator	9.8	293	83

\*At the temperature and pressure given.

TABLE IV  
Flows, Pressures, Temperatures for Oxidation of TBP

Location	Avg. Flow (L/hr)**	Max. Flow (L/hr)**	Temp. (°K)	Pressure (kPa)
Oxygen to Reactor	2830	2830	293	1,620
Organics to Reactor	26	26	293	1,620
Water/CaCl <sub>2</sub> /FeCl <sub>3</sub> /Citric Acid to Reactor <u>from Evaporator</u>	27.5	27.5	389	1,620
Reactor Vessel	473	1,500		
Gases to Condenser	46,200	46,200	473	275
CO <sub>2</sub> + O <sub>2</sub> to Vent	12,300	12,300	300	265
10% HCl From Condenser Tank	34.1	34.1	300	83
13.8% CaCl <sub>2</sub> to Evaporator	35.2	35.2	339	175
Water from Water Tank ( <u>from Evaporator</u> )	56.2	56.2	300	83
DETOX to Solids Separation*	121	182	473	1,350
DETOX from Solids Separation*	102	1,653	373	1,620
FeCl <sub>3</sub> , Citric Acid, and Water Rinse <u>to Evaporator</u> *	48.5	12.1	300	175

\*Intermittent flows  
\*\*At the temperature and pressure given

7 titanium pressure shell would provide reliable secondary containment if the tantalum liner were breached. Tantalum check valves would be used on the oxygen and waste inlet lines, and tantalum or zirconium control valves on the hot gas and process solution inlet and outlet lines. The condenser which handles the hot process gases will also experience chemically aggressive conditions due to the amount of HCl in the condensate, so it would also be constructed with a process side of tantalum.

Once beyond the product gas condenser, conditions become much less aggressive. The condensate for both treatment units would be approximately 10% HCl at essentially room temperature, and will contain some amount of volatile and semivolatile organic compounds. The condensate can be collected in a glass- or plastic-lined steel vessel for neutralization. Neutralized condensate for the PCB/oil treatment unit would be pumped into a Monel™ boiler tank, where non-product water would be removed through a stainless steel condenser into a polypropylene tank for return to the reaction vessel. Brine bottoms from the boiler would be stored in a polypropylene tank until tested for disposal. Neutralized con-

densate for the TBP treatment unit would be passed into a Grade 7 titanium boiler, along with process solution and rinses from the solids filter, to remove product and rinse water through a stainless steel condenser to a polypropylene tank for reuse and disposal. The boiler bottoms would be returned to the reaction vessel through a Grade 7 titanium tank.

For treatment of TBP, parts of the solids removal system exposed to the process solution would be constructed of Grade 7 titanium and fluorocarbons.

#### Cost

A list of estimated parts was prepared for the two units and quotes obtained from suppliers. From the quotes, capital costs are estimated to be \$600,000. to \$800,000. for the 5. Kg/hr unit and \$900,000. to \$1,200,000. for the 25. Kg/hr unit with solids removal. The units have relatively small throughputs and thus do not benefit from the economics of scale a larger unit would enjoy. From these estimates, a set of capital and operating cost estimates were made for a range of units for mixed waste treatment. A 1. Kg/hr unit would have an estimated capital cost of \$230,000. to \$300,000. If the 1. Kg/hr unit

was used for ten years to treat 1000. Kg of waste per year with one operator, its estimated total operating cost, including depreciation of the unit, would be approximately \$150. per kilogram. Capital cost for a 10. Kg/hr unit is estimated to be \$800,000. to \$1,000,000. Treatment of 15,000. Kg of waste per year for ten years with this unit, assuming two operators, would result in a total operating cost of approximately \$25. per kilogram. A 100. Kg/hr treatment unit has an estimated capital cost of \$2,100,000. to \$2,800,000. Over a ten year lifetime with 200. sixteen hour days of operation per year, total operating cost is estimated to be approximately \$3.50 per kilogram of waste treated. These costs do not include any post-treatment of the residues, or any ultimate disposal costs for the residues.

### SECONDARY WASTE STREAMS

Secondary waste streams from the process will be of three types: product water, solids, and spent process solution.

Product water from oxidation of hazardous organic materials would be a secondary "solid" waste from the process. If the organic material were chlorinated, the product water would also contain product HCl and would have to be neutralized with a basic material such as soda ash to eliminate its corrosive characteristic. With proper design, condensed water from the process should contain environmentally compliant amounts of volatile organic compounds, but would have to be tested and de-listed before it could be released as non-hazardous or non-LDR waste. The nature of the radioisotopes in the primary waste will determine whether the condensate will be radioactive. Radioactive metals and other heavy elements will remain in the process solution, and so would not be present in the condensate. Tritium is the radioisotope which would be of primary concern in the condensate, since tritium would be incorporated in the product water if present as a contaminant in the waste. If tritium is present in the waste to be treated, special design considerations would have to be made to ensure capture and safe handling of the product water from the process. A costs/benefits analysis would be required to determine whether it would be preferable to treat a particular tritium-containing waste with the process or to use an alternative scheme to prepare the waste for ultimate disposal.

Solids from the process can be of four types: "inert" solids, precipitated solids, "separated" solids, and carbonate solids. Inert solids would be those materials which are not destroyed or dissolved by the process solution, examples of which would be silica, glass, some clays, and fluoropolymers. Precipitated solids would be those materials which would form or be purposefully formed as precipitated solids in the reaction vessel during waste treatment, examples of which would be calcium dihydrogen phosphate and calcium sulfate. Inert and precipitated solids could be filtered from the process solution, rinsed, and isolated as non-hazardous materials for disposal. Separated solids would be those materials which have been purposefully separated from the process solution by manipulation of the process solution temperature, concentration, and/or acidity, examples of which would be ferric arsenate, lead chloride, and cadmium chloride. Separated solids would be filtered from the process solution, rinsed, and isolated as low volume hazardous materials for disposal. Carbonate solids would be a special case for wastes containing carbon 14. Carbon 14 will be incorporated in the carbon dioxide product gases, so these gases must be absorbed in some reasonably permanent form for disposal. We propose absorption in

slaked lime to form calcium carbonate, which could then be disposed of as a radioactive waste. All solids isolated from the process would be considered hazardous solid wastes if the primary waste were a hazardous waste, and would have to be tested and de-listed before they could be disposed as non-hazardous or non-LDR wastes.

The process solution would accumulate amounts of soluble foreign materials as waste was treated in it. At some point, it would be desirable to treat or dispose of the process solution. It has been found that much of the iron in the process solution will be precipitated if the solution is adjusted to a pH of 3.0. The liquid would then contain a large fraction of the contaminant metals and anions. The liquid could be removed by filtration and its water content evaporated to isolate the contaminants in a low volume form, then new acid added to the iron precipitate to regenerate the process solution. When it is necessary to dispose of the entire process solution, the solution may be neutralized to pH 7.0, de-watered, and solidified for ultimate disposal. The contaminants from a great volume of waste can be concentrated into the relatively small volume of the process solution before ultimate disposal. The process solution residues would be a radioactive waste, and probably a hazardous waste due to its toxic metal content. Proper solidification techniques would eliminate the hazardous characteristic, although the solidified residue would have to be tested and de-listed to be disposed of as a radioactive waste.

### ENVIRONMENTAL SAFETY AND HEALTH ISSUES

The DETOX<sup>SM</sup> process involves the treatment of radioactive and hazardous materials at elevated temperature and pressure. The combination of these factors results in environmental safety and health concerns related primarily to containment of the process solution and the hot gases from the solution. In response to these concerns, preliminary design has been conservative in the areas of the treatment unit which would contain the process solution and vapors. Secondary containment is required on waste treatment systems, but a further goal of this effort is to design in a high degree of containment reliability. A high level QA/QC program would be incorporated as part of a treatment system's detailed design and fabrication effort to insure high initial treatment unit quality. High quality, redundant sensors and controls would be used to improve the reliability of process control. Redundant valving on all reaction vessel inlet and outlet lines would provide high shut off reliability. Sensitive, redundant primary containment breach sensors would give high reliability detection of any primary containment breach at an early stage. The treatment unit would be configured such that crucial parts could be accessed easily. A cold water quench would be incorporated into the design to provide positive shut down in the event of a major upset; the advantage of a cold water quench is that it will work quickly with little or no damage to the system. A thorough test, inspection, and maintenance routine would be incorporated into the operations manual for the treatment unit to help ensure continuing safe and effective operation. While no system can be made 100.% reliable, containment reliability values can be established which make the risk of material release over the expected lifetime of a unit extremely low. Finally, all personnel involved with operating a unit would be equipped with, and trained in the use of, all appropriate safety and handling equipment for hazardous chemicals and low level radioactive materials.

### CONCLUSIONS

Preliminary engineering design demonstrates that the DETOXSM catalyzed wet oxidation process can be applied to a variety of organic, aqueous, and soil-like mixed wastes to achieve volume reduction and destruction of hazardous organic components. Typical applications would be destruction of organic liquids or solids contaminated with radionuclides, and hazardous organic compounds and/or toxic metals. Exotic metal construction will be required for areas of treatment units exposed to the process solution and its vapors. Treatment costs using the process are estimated to range from \$150. per kilogram for a 1. Kg/hr unit to \$3.50 per kilogram for a 100. Kg/hr unit, with the largest single cost item being operator labor. Secondary waste streams from the process would be product water or brine, inert or precipitated solids from the waste, and the process solution after it has been used to treat a quantity of waste. Proper precautions during design, fabrication, and operation will provide acceptable environmental safety and health characteristics for waste treatment operations.

### ACKNOWLEDGEMENTS

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