Description of Recommended Non-Thermal Mixed Waste Treatment Technologies Version 1.0

August 1995

**U.S. Department of Energy
Assistant Secretary for Environmental Management
Office of Technology Development**

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**U.S. Department of Energy
Assistant Secretary for Environmental Management
Office of Technology Development
Germantown Md, 20874**

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FOREWORD

This document contains description of the technologies selected for inclusions in the Integrated Nonthermal Treatment Systems (INTS) Study . These descriptions are reproduced totally from the following works:

- Schwinkendorf et al., *Alternatives to Incineration Technical Status Report*, DOE/MWIP-26, U.S. Department of Energy, Washington, DC 20585, April, 1995
- *SITE Superfund Innovative Technology Evaluation Program, Technical Profiles, Seventh Edition*, EPA/540/R-94/526, U.S Environmental Protection Agency, Office of Research and Development, Washington, DC 20460, November, 1994
- Overview of Non-Thermal Mixed Waste Treatment Technologies, U.S. Department of Energy, Office of Science and Technology, Washington, DC 20585, June 20, 1995.

The major fraction of these descriptions come from the work of Schwinkendorf et al.

The purpose of these descriptions is to provide a more complete description of the INTS technologies. It supplements the summary descriptions of candidate nonthermal technologies that were considered for the INTS and described in the Overview (third work, above). Schwinkendorf et al. and EPA SITE report contain numerous technical references if more information is desired.

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Source Documents

DOE/MWIP-26, Alternatives to Incineration Technical Area Status Report, April 1995

Overview of Non-Thermal Mixed Waste Treatment Technologies, June 20, 1995

Superfund Innovative Technology Evaluation Program, Technology Profiles, Seventh Addition, November, 1994

SECTION 2

LOW-TEMPERATURE OXIDATION PROCESSES

For the purposes of this report, low temperature processes are those that take place at temperatures less than 350°C. This is sufficiently below the temperature at which dioxins and furans are thought to form and reactions at or below this temperature should preclude the formation of these toxic species.

Direct chemical oxidation of organic compounds has been practiced in the water and wastewater industries for several years. This technique usually involves converting the target compounds into less toxic compounds by exposing them to strong oxidizing agents such as oxygen or air (as in wet-air oxidation), ozone, hydrogen peroxide, potassium permanganate, hypochlorite, and/or chlorine dioxide. Recently, ozone and hydrogen peroxide have become popular oxidizing agents for application to aqueous solutions because they do not introduce additional salts or chlorine compounds into the treatment streams.

Chemical oxidation with ozone and hydrogen peroxide is commercial technology used to treat various waste problems. Ozone appears to have received the greatest attention; however, it has been found that O_3 can have two reaction modes: direct ozonation reactions and free radical (such as hydroxyl radical) decomposition reactions. The direct O_3 reaction involves molecular O_3 which produces a highly selective and relatively slow reaction resulting in incomplete mineralization and the formation of various intermediate compounds. The hydroxyl radical formed during ozone decomposition reacts more rapidly with organic compounds than molecular O_3 , and is much less selective. Thus, a major thrust for low-temperature destruction of organics has been the direct generation of hydroxyl radicals in sufficient quantity to effect organic destruction either through the use of H_2O_2 or other oxidant, irradiation, or a combination of the two methods.

Most low-temperature oxidation processes used in waste treatment systems involve the production of free radicals in sufficient quantity to oxidize and destroy organics. However, these processes vary in the methods used to generate the radicals and often use a combination of strong oxidants (e.g., O_3 and H_2O_2), catalysts (e.g., transition metal ions or photocatalysts), and irradiation (e.g., ultraviolet, ultrasound, or electron beam). Chemical oxidation is a general category that contains many options for converting combustible organic wastes into gaseous effluent, liquid effluent, and stable solid residues. Such options include generation of hydroxyl radicals as well as direct oxidation by an acid medium or other strong oxidant (e.g., $Ag(II)$ in the MEO process or Fenton chemistry). Radiation induced or enhanced oxidation processes use an

external radiation source to generate radicals which may destroy organics in contaminated water. High-energy radiation (e.g., x-rays, gamma-rays, and even low-wavelength UV radiation) may also break the molecular bonds of organic molecules directly.

Low-temperature oxidation is most commonly used to destroy dilute organic contaminants in aqueous wastes; however, oxidation processes such as mediated electrochemical oxidation (MEO), wet oxidation, acid digestion and the Delphi DETOXSM process are being developed for treatment of waste sludges, and organic liquids and solids, and have been tested for decontamination of inorganic matrices such as soil and vermiculite. These oxidation processes may also be used to solubilize RCRA metals and radionuclides to decontaminate soils and debris.

Oxidation processes are generally appropriate for treatment of wastes with relatively low levels of contamination. When high concentrations of contaminants are present, oxidation rates in low-temperature oxidation systems may be slow although fine dispersion of the organic into the aqueous media will help speed the process. Oil and grease in contaminated media may lower the oxidation process efficiency. However, residence time in the reactor may be increased significantly by controlling the waste feed rate, the size of the organic solids in the waste stream may be reduced, and insoluble organic liquids in the reactor solution may be dispersed to increase the surface area available for chemical oxidation.

This document divides oxidation technologies into three groups as follows:

"Conventional" Chemical Oxidation:

- Wet Air Oxidation
- Catalyzed Wet Chemical Oxidation
- Acid Digestion

Electrolytic/Electrochemical Oxidation.

Radiation Induced or Enhanced Oxidation:

- Photolytic Ultraviolet Oxidation Processes
- Ultrasonic Detoxification

- Electron Beam Oxidation
- X-Ray and Gamma-Ray Destruction of Organics.

Each of these technologies will be briefly described in the following sections.

2.2 CATALYZED WET CHEMICAL OXIDATION

The catalytic wet oxidation process uses an oxidant in a catalyzed solution to enhance the destruction of organic wastes. There are two processes being developed, one by Delphi Research, Inc. called the DETOXSM process, and similar wet oxidation processes by JGC Corporation and AEA Technology.

2.2.1 Delphi DETOXSM Process

2.2.1.1 Technology Description

The DETOXSM process uses iron(III) in a hydrochloric acid solution as the primary oxidant to oxidize waste organics to CO₂ while solvating and concentrating heavy and/or radioactive metals in the acidic catalyst solution. A set of homogeneous cocatalysts increase the oxidation rate for organics, and the rate of oxidation of iron(II) formed in the oxidation process back to iron(III) by a second catalyzed reaction with oxygen. Typically, these cocatalysts are copper ions and one or more of the ions platinum(IV), palladium(II), and ruthenium(III) (Ref. 1). The process typically takes place at 373°K to 573°K (100°C to 300°C), depending on the waste form and composition and at pressures of 20 to 200 psig. The standard DETOXSM solution consists of 60 wt% ferric chloride, approximately 3.6 wt% HCl, and water. Catalyst concentration is approximately 0.001 M.

For treatment of bulk wastes, the DETOXSM solution is maintained in the oxidation reactor vessel at a constant temperature of about 200°C. The DETOXSM solution is agitated by recirculated headspace gases and/or by a mechanical stirrer. Waste is added to the vessel continuously through a solid or liquid-feed assembly. This is an exothermic reaction so the waste needs to be metered into the reactor to prevent a runaway reaction, and larger systems will require active cooling for temperature control (Ref. 2).

Oxidation of organics occurs principally at the surface of contact between the organics and the DETOXSM solution. Carbon dioxide generated by the oxidation reaction is carried out of the oxidation vessel with the headspace gases (Figure 2-2). The headspace gases, which are primarily water vapor, CO₂, O₂, and HCl, are passed through a condenser to remove most of the water vapor and HCl. The condensed acidic water is typically returned to the DETOXSM

Figure 2-2. DETOX Process Flow

solution, but can be neutralized and disposed of as excess water, or used to rinse residual solids before being returned to the reaction chamber. The remaining gases, principally CO₂ and O₂, are recirculated to aid in agitation of the solution and to accelerate oxidation of any volatile organic materials. Excess pressure due to CO₂ generation is vented in the recirculation loop, or the CO₂ may be removed by a membrane separator or captured in a basic solution. Oxygen levels in the recirculated gases are monitored continuously, and gaseous oxygen added as necessary. Volatile organics may also be carried over in the headspace gases. The gases can be injected back to the reactor to contain and destroy the organics or passed through an activated carbon adsorption unit to remove the VOCs from the gas stream. At the end of the treatment process, the activated carbon may be fed to the DETOXSM solution to complete the destruction of organic wastes.

The DETOXSM solution is used until analysis indicates an accumulation of metallic contaminants or residual solids. Residual solids can be filtered from the solution, rinsed, and disposed, or further treated as required. Metal and radionuclide salts can be selectively precipitated from the DETOXSM solution by cooling, precipitated as hydroxides or oxides by neutralization of the DETOXSM solution, or concentrated by evaporation (Ref. 2). The resulting sludge can then be rinsed with dilute HCl and water to remove remaining acid and soluble metals. The resulting sludge typically passes TCLP tests and may be disposed directly, or stabilized in a final form for disposal.

In application to the treatment of soils, the DETOXSM solution would be pumped from a main tank into a reaction chamber containing the soil to oxidize the organics and remove toxic metals. After treatment, the DETOXSM solution would be pumped back to the main tank, and the soil rinsed with DETOXSM condensate and then with water; all rinses would be returned to the main tank.

The best combination of materials for construction appear to be a Grade 7 titanium reactor shell with a tantalum liner. The tantalum liner would give superior resistance to chemical attack, and the titanium shell would act as a corrosion-resistant secondary containment and pressure vessel. Valves and piping exposed to hot vapors from the DETOXSM solution should also be constructed from tantalum. Teflon-lined valves may be used for the inlet feed lines. The gas outlet line may be hardened zirconium, if it is not exposed to iron from the process solution, or tantalum. The condensate catch tank may be a commercial glass-lined steel vessel or it can be fabricated of EPDM-lined steel (Ref. 3).

2.2.1.2 Input and Output Stream Characteristics

The process is highly tolerant of waste composition, form, water content, and particle size. It is applicable to a variety of waste types, including mixed solvents, sludges or bottoms containing hazardous organics and/or metals, hazardous organic liquids, shredded organic solids, and soils and other inorganic materials that may be contaminated with hazardous organics and/or metals. Many toxic metals are dissolved and concentrated in the solution; however, some toxic metals are converted to insoluble forms depending on the composition of the waste stream. The low-temperature process produces no NO_x , SO_x , dioxins, or furans (Ref. 4). Neither heavy metals (including mercury) nor radionuclide surrogates have been found in the exhaust gases (Ref. 2).

Secondary waste streams from the process include the neutralized process solution at the conclusion of the waste processing; heavy metal and radionuclide hydroxides or oxides, and the hydrated oxide of iron precipitated from solution upon neutralization; and salts resulting from the destruction of organic compounds. These may include chlorides from the destruction of halogenated hydrocarbons or phosphates from the destruction of tributyl phosphate. Trace amounts (in the mg to μg /liter range) of residual volatile and semi-volatile organics, including chlorinated hydrocarbons, have been found in the condensate and process solution (Ref. 5).

Studies in which the process oxidation reactions were interrupted have shown the presence of both oxygenated and chlorinated intermediates. However, the formation of chlorinated intermediates represents a minor reaction pathway for the process. Typical chlorinated intermediates seen in this study included chlorinated ethanes in very small amounts. Chlorinated benzenes have also been found as intermediate reaction products during the oxidation of Aroclor 1260 (a polychlorinated biphenyl). Release of these compounds can be minimized during the reaction by refluxing the outlet of the reaction vessel to contain the organics. Most of the intermediates have boiling points greater than water and can be concentrated in the bottom of the column and kept in the reaction vessel until they are destroyed. However, small amounts of trichloroethane, bromodichloromethane, and chloroform have been found. These lighter compounds may escape the reaction vessel but will be dissolved in the much larger volume of the condensate. These organics can be removed from the condensate by sparging it with oxygen, and returning the lighter organics to the reaction vessel with the oxygen until they are destroyed.

2.2.1.3 Technology Status

The process is currently at the bench-scale level of development. Most tests have been conducted in static, unmixed reaction vessels; however, several tests have been performed in a 4-liter (1-gallon) mixed-reaction vessel. In the unmixed vessels (bombs), DREs are limited by the lack of mass transfer and volatility of some of the compounds. Tests in the mixed-reaction vessels indicate reaction rates one to two orders of magnitude greater than those in the unmixed vessels. Several test programs have been performed including a series of tests at Los Alamos National Laboratory (LANL), tests performed under a PRDA for Morgantown Energy Technology Center (Ref. 6), and tests performed for EG&G Rocky Flats Plant (Refs. 3 and 5).

As part of the PRDA, conceptual design studies were performed for two wastes: PCB transformer oil and hydraulic fluid at Rocky Flats Plant, and tributyl phosphate located at Weldon Springs Site. Savannah River and Weldon Springs have been identified as sites for the demonstration of a prototype system under Phase IV of the PRDA.

Oxidation studies on simulated LANL mixed waste were conducted by LANL and Delphi Research, Inc. Vacuum pump oil, trichloroethylene, and two scintillation cocktails were tested to determine the viability of the process for the destruction of hazardous organics. Blank vermiculite was loaded with these organics to determine the effectiveness of the DETOXSM process in removing organics from an inorganic matrix. These organics were also spiked with metals and tested for metal solubility using mercury metal, mercuric oxide, neodymium isopropoxide (as a surrogate for plutonium), and cerium naphthanate (as a surrogate for uranium) (Ref. 4).

These studies demonstrated that the DETOXSM solution oxidized the simulated wastes in approximately 3 hours with temperatures ranging from 200°C to 225°C in the mixed reactor. The reaction rate was superior by a factor of ten in a concentrated chloride-based solution versus a sulfate-based solution, and was proportional to the contact area above about 2 wt% loading of organics. Reaction rates achieved in the mixed bench-top reactor were one to two orders of magnitude greater than in the unmixed reactions. The reaction rate constants obtained in these preliminary studies indicated that a thoroughly mixed reactor could oxidize 10 to 100+ grams of organics per liter-hour (Ref. 4). It was found that the ratio of iron(III) to iron(II) had little effect on the apparent reaction rate or the formation of reaction intermediates, and reaction intermediate compounds had no significant effect on oxidation reaction rates. The reaction rates increase with the addition of small amounts of sulfate and phosphate, decrease in the presence of ammonium ions, and decrease when the acidity of the DETOXSM solution exceeds 1M

(Ref. 7). Because acids will be formed when halogenated organics are oxidized, a pilot plant will require a neutralization system to maintain acidity levels.

When organics containing cerium and neodymium were oxidized in the catalyst solution, no amounts of these metals were found in the solid residues. The detection limits for these two metals give a minimum solvation of 97%, but the actual values may be considerably higher. Neodymium solubility was adversely affected by the presence of sulfate anion. Mercury is soluble in the chloride-based DETOXSM solution to the extent of about 400 g/l, and is not affected by minor changes in acidity or the presence of sulfate anion up to 0.2M. The amount of mercury found in the solids resulting from organic oxidation indicate a minimum solvation of 99.98% (Ref. 4).

The 4-liter (1-gallon), titanium bench-top reactor was equipped with a gas entrainment impeller. Oxidation tests using the original simulated wastes indicate that use of the gas entrainment impeller increases the apparent reaction rate by a factor of two, and the reaction is organic concentration dependent. The organic concentration in the present reactor configuration is limited by the amount of oxygen that can be preloaded into the reactor. Future development work should use a system that operates continuously with the ability to replenish oxygen.

The test program performed for Morgantown Energy Technology Center (METC) (Ref. 6) used only unmixed reaction vessels. In this test program, the destruction efficiency for various organic compounds and the solubility of various metals were determined. The ability of the DETOXSM solution to dissolve metals and destroy organics adsorbed onto various soil types was also determined. The organic compounds picric acid, poly vinylchloride, tetrachlorothiophene, pentachloropyridine, Aroclor 1260, and hexachlorobenzene were oxidized in 125 ml reaction vessels at 473°K.

The metals arsenic, barium, beryllium, cadmium, cerium, chromium, lead, mercury, neodymium, nickel, and vanadium were tested for solubility in the DETOXSM solution. Barium, beryllium, cerium, chromium, mercury, neodymium, nickel, and vanadium were all found to be very soluble (>100 g/l) in the solution. Chromium(VI) was reduced to chromium(III) with 90% efficiency with 100% Fe(III). When Fe(II) was added the reduction of chromium(VI) was complete. The solubilities of arsenic, barium, cadmium and lead are in the range of a few grams per liter. Metal levels in any residual solids after rinsing with DETOXSM condensate (dilute HCl) and water were all sufficiently low to make the residuals nonhazardous by the RCRA TCLP test.

Six soils were contaminated with arsenic, barium, beryllium, chromium, lead, and neodymium oxides at approximately 0.1% by weight, and benzene, trichloroethane, mineral oil, and Aroclor 1260 at approximately 5% by weight. The metals were removed by the DETOXSM solution and rinsed to levels that made the soils nonhazardous by the TCLP test. The more volatile organics, which were not protected by the soil, were well oxidized. In the 24-hour tests no benzene was detected in any of the soils and good trichloroethane destruction was achieved with the maximum amount remaining being 7 µg in clay soil. Aroclor 1260 was the most resistant to oxidation; only half was oxidized in the 24-hour tests, and the amount remaining was highly dependent on the soil type. In these unstirred tests it was apparent that the nonvolatile and semivolatile organics were protected from oxidation due to poor contact between the soil particles and the DETOXSM solution. Stirred reaction vessels should provide improved reaction rates and DREs.

Tests have been performed on Rocky Flats' wastes to develop a bench-scale solids feed system and investigate the destruction of organic wastes (Refs. 3 and 5). These wastes included shredded, solid, combustible material (sawdust, paper, cotton, wood, contaminated HEPA filter media, polyethylene, poly vinylchloride, latex, and Tyvek), and mixed-waste cutting oils (Trim Sol and Regal). The HEPA filter media was contaminated with Trim Sol, trichloroethane, and carbon tetrachloride. The solids were shredded to increase the surface area and reaction rate. Reaction rate constants, activation energies, and DREs were measured in unstirred reactors for these materials (Refs. 3 and 5).

2.2.1.4 Destruction Efficiency

In the LANL studies, oxidations in unmixed reactors were performed for 24 hours to obtain fairly complete oxidation of the organics. Results showed that greater than 99.9997% of the o-xylene and 1,2,4-trimethylbenzene had been destroyed, and 99.995% of the TCE had been destroyed. Some amounts of other organic intermediates were observed, giving absolute DEs of about 99% in these tests. For the vermiculite loaded with organics and oxidized for 24 hours in an unmixed reactor, 99.55% of the trichloroethylene and over 99.98% of the 1,2,4-trimethylbenzene was destroyed (Ref. 4).

Organic oxidations in the 4-liter stirred batch reactor were conducted over 1 to 3 hours and with significantly greater amounts of organics. Oxidation of the vacuum pump oil was complete, and the absolute destruction efficiency for all the organic material in the reactor was 99.96%. For the scintillation cocktails, oxygen consumption indicated complete oxidation with

an absolute destruction efficiency for all organic material of 99.5% after 3 hours. A destruction efficiency of 99.95% was achieved for TCE after 3 hours, with an absolute destruction efficiency for all organic material of 99.5% (Ref. 4). The destruction efficiency (DE) was lower than expected because of an unforeseen erosion/corrosion mechanism of the Grade 2 titanium impeller and impeller shaft that consumed oxygen needed to completely oxidize the TCE (Ref. 7).

Additional studies have been performed for LANL on chlorinated aromatics (PCBs and hexachlorobenzene), chlorinated heterocyclics, and a chlorinated plastic (poly vinylchloride). The solubility of various contaminant metals was also investigated (Ref. 6). These studies were performed in unmixed reactors for 24 hours to achieve fairly complete oxidation of the organics. Absolute oxidation efficiencies were obtained by summing all of the organic material in the catalyst solution at the end of the reaction period and dividing this sum by the amount of organic added. Except for hexachlorobenzene, absolute DEs ranged from 99.7% to 98.1%, and specific DREs were greater than 99.5%. Destruction of hexachlorobenzene requires extended oxidation times at higher temperature (250°C) and the reaction vessel was not suited for these conditions.

Results of the tests performed for METC are shown in Table 2-2 where the absolute destruction efficiency is for all organic compounds in the reaction vessel. DEs developed for Rocky Flats' waste in unstirred reaction bombs are shown in Table 2-3. Reaction rates are expected to be much higher with higher organic loadings and in stirred reaction vessels.

In unstirred reaction vessels the reaction rate for oily liquids was limited because these materials will float on the surface of the DETOXSM solution thereby limiting the surface area for reaction. Similar effects were found for polyethylene and Tyvek (a spun polyethylene fiber) because this material becomes liquid (or very soft) and, due to its low density, floats on the DETOXSM solution. Paper and cotton undergo the fastest oxidation. Various residual organic compounds remained in solution in the 10 to 100 µg range after these tests were completed. Test results indicate that the optimum combination of reaction rates for a variety of organic materials and operating temperature is in the range of 423°K to 443°K. In this range, the pressure is relatively low (20 psia vapor pressure at 423°K) and can be easily contained.

Table 2-2. Organic Oxidation Times and DEs in Unstirred Reactors

Organic Material	Absolute Destruction Efficiency (%)	Oxidation Time (hrs)
Hexachlorobenzene	99.97	216
Polychlorinated Biphenyl (Aroclor 1260)	98.9	216
Picric Acid	99.7	24
Poly vinylchloride	99.8	24
Tetrachlorothiophene	98.1	24
Pentachloropyridine	99.5	24

Table 2-3. Oxidation Conditions and Efficiencies in Unstirred Reaction Bombs for Organic Material in DETOXSM Solution

Organic Material	Temperature (°K)	Time (hrs)	Absolute Destruction Efficiency (%)
Trim Sol	408	240	53
	473	24	>80
Texwipes	408	240	92
	473	24	>93
Cotton	408	240	88
	473	24	>92
Latex Rubber	408	240	58
	473	24	>80
Poly vinylchloride	408	240	87
	473	24	85
Polyethylene	408	504	29
	473	24	>75
Tyvek	408	504	Note 1
	473	24	69

Note 1: An apparent negative destruction efficiency, probably due to weight gain of the Tyvek from partial oxidation.

Treatment of the contaminated filter material in an unstirred reactor resulted in complete destruction of trichloroethane and carbon tetrachloride. This seems to indicate that hazardous organics can be effectively removed from HEPA filter material by the DETOXSM process. Again, various residual organic compounds remained in solution in the 10 to 100 µg range. Particle size tests were performed with wood at 408°K and indicated no significant difference in the reaction rate for particle sizes between 0.1 cm and 1.0 cm.

2.2.1.5 Required Development

- Demonstration of a complete system with offgas treatment, residuals treatment, and acid recovery.
- Demonstration of a larger scale system that operates continuously with the ability to replenish oxygen.
- Evaluation of large-scale system corrosion issues and development of system corrosion protection and corrosion monitoring.
- Development of an acid recovery process and demonstration of a recovery/recycling system.
- Evaluation of destruction of hexachlorobenzene and other difficult organics and solids in mixed reaction vessels.
- Evaluation of destruction of various organic solids as a function of process parameters, solid composition, and particle size.

2.2.1.6 Cost of Technology or Equipment

The treatment system can be engineered as a truck- or skid-mounted unit for on-site treatment, or may be designed as a larger fixed facility for centralized treatment. A small, highly mobile 50-gallon reactor vessel should be capable of oxidizing 4.5 to 22.7 kg (10 to 50 lbs) of hazardous organics per hour. A larger, centralized 5,000-gallon reactor would oxidize 450 to 2,270 kg (1,000 to 5,000 lbs) of hazardous organics per hour (Ref. 2). Costs for mixed waste treatment units have been estimated in Reference 3. Capital costs for a 10 kg/hr mixed waste transportable treatment unit are estimated to be between \$800,000 and \$1,000,000. Treatment of 10 kg/hr for a total of 1,500 hrs/yr over 10 years (with two operators) results in an estimated

operating cost of \$15/kg. Capital costs for a 100 kg/hr mixed-waste treatment unit at a fixed installation is estimated to be \$2,100,100 to \$2,800,000. The operating cost of a 100 kg/hr unit is approximately \$2.50/kg. The cost of treatment per weight of soil or other inorganic material will be considerably less than the per weight cost of organic material. These costs do not include any pre-treatment of the waste, post-treatment of residues, or ultimate disposal costs for the residues. The DETOXSM process can also be used to treat waters containing low levels of contaminants, subject to increased capital and operating costs related to evaporation and condensation of water in the treatment system.

2.2.2 Wet Oxidation Processes

2.2.2.1 Technology Description

Two similar wet oxidation processes have been developed by commercial entities: one by the JGC Corporation of Japan, and the other by AEA Technology of the United Kingdom (UK). Lawrence Livermore National Laboratory. (LLNL) is modifying the AEA design for use in their Mixed Waste Management Facility (MWMF). The principle differences between these processes and the other non-thermal processes are that these operate at low temperature (80°C to 100°C) and atmospheric pressure, and the reaction mixture is relatively non-corrosive. Except for wastes with high chloride content, stainless steel reaction vessels are adequate; where chloride content is high, Hastelloy C or a glass-lined vessel can be used (Ref. 8).

Wet oxidation uses Fenton chemistry to oxidize organics dispersed in water. It operates under mild temperature and pressure conditions and a pH ~ 3, using hydrogen peroxide and iron as the oxidant and catalyst, respectively. The JGC process may also use copper as a catalyst. Under these conditions, hydroxyl free radicals are produced from the hydrogen peroxide. These are strong oxidizing agents that initiate oxidation of the organics.

The decomposition reaction rate depends on the concentration of the waste mixture and the waste constituents, the reaction temperature, the concentration of catalyst, the pH of the reaction mixture, and the hydrogen peroxide supply rate. The liquid or slurry waste is supplied to the reactor, and FeSO₄ and/or CuSO₄ catalyst is added. Sulfuric acid is added as necessary to adjust the pH of the mixture. After heating the reactor to the operating temperature, the oxidation reaction proceeds by continuously supplying hydrogen peroxide. The pH must be controlled to maintain the activity of the catalyst, and it is important to monitor and control the hydrogen peroxide supply. If the percentage of H₂O₂ is too high, the oxidizing efficiency

decreases because excess peroxide scavenges hydroxyl radicals; when the supply is too low, the decomposition rate is impractically low (Ref. 9).

The process will treat liquids, sludges, and solids; however, the solids must be in a form capable of being dispersed and suspended in water. A generalized flow sheet for the process is shown in Figure 2-3. Waste feed is introduced into the reactor bottom and an in-tank mixer maintains the liquid and solid wastes having $< 50 \mu\text{m}$ particle size in an aqueous dispersion. The feed system uses hydraulic transfer of wastes because there would be little advantage to dry solid feed since the waste must be suspended in water during the reaction. The steam and gases produced by the wet oxidation reaction, primarily CO_2 and oxygen with traces of CO and VOCs, are passed through a heat exchanger and cooled. Condensed water may be stored in a distillate tank, and non-condensables pass through an acid scrubbing column and HEPA filter before discharge to the atmosphere. The process can be carried out under distillation or reflux, however, the distillation option is usually preferred if radionuclides are to be retained and concentrated (Ref. 8). On completion of oxidation, the mineral residue is neutralized using calcium oxide or sulfuric acid and the batch evaporated to a thick but mobile slurry of 30-40 wt% which is discharged for drying and/or stabilization (Ref. 10).

The liquid condensate contains volatile and moderately volatile organic compounds in solution or organic phase. A phase separator removes the non-aqueous phases which are returned to the reactor. A fractionator separates the aqueous phase into two streams: the stream high in organics is sent back to the reactor, and the stream low in organics (20 to 2000 mg/liter of low molecular weight organics) is transferred to a downstream aqueous phase destruction process. In LLNL's MWMF, this is a UV photo-oxidation process (Ref. 11). Because of relatively low destruction rates, and the presence of intractable organics in the waste, some organic materials will accumulate in the system. These are periodically purged and discharged with the batch residual to a water treatment process if non-volatile, or returned to the liquid feed system if volatile.

In the case of the JGC process, the pH of the mixture is neutralized by adding NaOH after decomposition of the organic waste (Ref. 9). The reaction mixture is then concentrated by evaporation until the Na_2SO_4 concentration is approximately 25 wt%. The concentrate is then drained, dried, or solidified, and packaged for storage or disposal.

Figure 2-3. Wet Oxidation Process Flow

2.2.2.2 Input and Output Streams

The general categories of organic material which can be treated directly by this process include (Ref. 8):

- Any organics that are water soluble or partially water soluble.
- Organic compounds containing unsaturated carbon bonds.
- Organic compounds containing functional groups, e.g., carbonic acids, esters, sulphonate, phosphate, chloro- and nitro-substituted compounds, etc.

The only pretreatment requirements are to insure that the waste is in a physical form that can be transferred through the feed system, and can be readily suspended and dispersed by the mixer in the reaction vessel. The presence of inorganic solids or intractable organic polymeric materials within the reaction mixture has no detrimental effect on the destruction of the treatable organic species. For some intractable organics, such as PCBs, chemical pre-treatment may be considered.

The following waste have been studied and have been identified as suitable for treatment by this process by either the JGC Corporation (Ref. 9), AEA Technology (Ref. 8), or LLNL (Ref. 11):

Radioactive Wastes

- Organic ion exchange resin (chelate resin, spent bead resin, spent powdered resin)
- Mixed organic/inorganic reactor sludge
- Organic decontamination liquors
- Organic scintillants
- Spent reprocessing solvents (tri-butyl phosphate)
- Cellulosic-based solid waste (paper, cotton, filter aid)

Hazardous Organics

- Glycolic Acid
- Alcohols
- Tributyl Phosphate
- Diethylene Glycol
- Acetone
- Toluene
- Carboxylic acids
- Formaldehyde
- EDTA
- Dimethyl Formamide
- Tetrachloroethane
- Ketones
- Phenol, nitrophenols and chlorophenols
- Formic Acid
- Acetic Acid
- Trimethylamine
- Ethylene Glycol
- Xylene
- Trichloroethylene
- Thioacetic acid
- Pyridine
- Thiophene
- PCBs (after pre-treatment)
- Pesticide effluents
- Aldehydes

Wastes that have very slow kinetics or are unsuitable for this process include alkanes (motor oil), haloalkanes (trichloroethane), poly vinylchloride, rubber, and polyethylene.

Generally, the organics are converted to CO_2 , H_2O , and inorganic salts while inorganics and intractable organic compounds are largely unaltered. However, there may be some oxidation of inorganic components (e.g., Fe(II) to Fe(III) , sulfite to sulfate, etc.). Effluents from the process include:

- Primary product - mixture of inorganic salts, intractable organic compounds, and water as a solution or sludge depending on the waste being treated.
- Distillate - an aqueous solution containing some low molecular weight organics at concentration of 20 to 2000 ppm.

- Gaseous discharge - CO₂ and O₂ (generated from a secondary H₂O₂ degradation reaction).
- Scrubber liquor - used to remove acid or alkali gases; depending on the feed, it may contain some VOCs.

2.2.2.3 Technology Status

JGC has conducted bench-scale testing and development, and in 1987 built and placed in service a full-scale demonstration wet oxidation facility at its Garai Research Laboratory in Japan. The daily process capability of this facility is 400 kg of powdered or bead resin on a dry basis. JGC and ADTECHS, JGC's wholly owned U.S. subsidiary, are beginning to commercialize this process for nuclear power plants and centralized mixed and radioactive waste-processing facilities (Ref. 9). A system is being installed at the 200 Area Effluent Treatment Facility at Hanford Site to process 150 gpm of aqueous waste.

LLNL has selected a modification of the AEA Technology process for inclusion in their Mixed Waste Management Facility. This system is now in the design phase.

The wet oxidation process has been under development by AEA Technology since 1987, initially for the treatment of spent ion exchange resins and organic-containing reactor sludge. In parallel with the radioactive waste treatment program, a parallel program was initiated in 1991 for the treatment of hazardous waste.

A mobile pilot facility has been built which is fully contained in a single ISO transport container for the treatment of radioactive waste. The design waste throughput is 50 - 100 kg/day with a maximum activity within the containment glovebox of 2.7 Ci. This throughput corresponds to approximately 120 liters/day of ion exchange resin based on an 8-hour day. The upper limit of a mobile plant is about 400 kg of organics per day. Above this, the size of the system becomes too large to be accommodated within a transportable container. For a fixed installation, limits are determined by the ability to provide adequate mixing in the reaction vessel and heat removal from the process.

AEA has recently completed a second demonstration plant for the treatment of toxic organic wastes in aqueous effluents. This plant is designed to operate on a continuous basis and potentially has a throughput in the range of 1 to 5 m³/hour (265-1325 gallons/hour) of effluent

containing up to 5% organics. A conceptual design for a continuous plant processing 100 m³/day has been developed.

2.2.2.4 Destruction Efficiency

JGC Corporation reports typical degrees of decomposition of 90% in 4 to 6 hours for bead resins; 90% in 5 to 6 hours for powdered resins; and 98% in 2 to 4 hours for filter sludges (Ref. 9). The weight of the reaction residue for powdered resin is 40% of the dry sludge weight, and the reaction residue for filter sludge is 10% of the dry sludge weight.

Volume reductions are as follows:

- 2.5 for spent resin at a rate of 60 cf/day.
- 13.2 for filter sludge at a rate of 75 cf/day.
- 5.2 for chelate waste at a rate of 1,100 gal/day.

Because this is a low temperature and pressure process, DREs for many of the hazardous organic compounds do not reach the 99.99% level, and are typically less than those reached by the DETOXSM process (Ref. 12). However, the process can be adjusted to achieve distillate concentrations to meet most required technical specifications.

AEA has published results of tests performed using the mobile system for the treatment of organic radioactive waste (Ref. 10). These were non-radioactive tests on ion exchange resin and decontamination solution (consisting of 7% EDTA dissolved in a dilute ammonia solution). The results are shown in Table 2-4. These tests demonstrated >95% total carbon removal, and significant waste volume reduction factors.

2.2.2.5 Required Development

- Evaluation of the DREs for hazardous organic wastes, the reaction rates and times required for destruction, and the fate of inorganic materials in the waste.
- Demonstration of the process and system on DOE mixed waste.

Table 2-4. Results of AEA Tests in Mobile Wet Oxidation System (Ref. 10)

Waste Type	Feed Vol. (L) ¹	% Total Carbon Removal	Peroxide Used (kg/m ³) ²	Volume Reduction (% dry)	Volume Reduction (% wet)	Reaction Time (hrs)
IX Resin	25	96	3,600	82	43	3
IX Resin	103	99.2	2,700	87	60	10
IX Resin	125	98	2,900	92	74	12
IX Resin	125	97	2,700	92	74	11.5
IX Resin	165	96	3,200	86	57	18
Decon Sol'n.	116	99.1	480	n/a	n/a	3

1. For IX resin, feed volume refers to flooded volume.

2. Peroxide used is kg of 50% H₂O₂ (aq) per m³ of waste.

2.2.2.6 Cost of Technology or Equipment

No cost data was available.

2.2.3 Technology Comparison

2.2.3.1 Advantages

- The primary benefit of the catalyzed wet oxidation process is the ability to catalytically oxidize organic constituents of a waste stream in a contained reactor. This technology is potentially more convenient to use than other forms of wet oxidation because of its ability to accept a wide variety of waste streams and sizes.
- Lack of NO_x, SO_x, dioxin, or furan formation.
- Relatively low-power usage.
- Containment and concentration of heavy metals and radionuclides.
- Ability to operate at moderate temperatures (100°C to 225°C) and near atmospheric pressures (atmospheric to 40 psig). Because these are low-temperature processes, and can be operated as a closed or confined system, there is less potential for the escape of toxic materials in exhaust gases.

The catalyst solutions can remove organic and inorganic contaminants from mineral and sorbent materials. DETOXSM DREs have shown 99.9999% destruction in well-mixed reactors for many organic contaminants without build-up of byproducts, and gas analysis has shown complete oxidation to carbon dioxide.

The JGC and AEA wet oxidation processes operate at low temperature and pressure and are therefore less hazardous. They are less aggressive and therefore material compatibility is a lesser issue. These processes have been commercialized and are at the full-scale level for implementation.

2.2.3.2 Disadvantages

- The DETOXSM technology is at the bench-scale level of development and will require scaleup and pilot-scale testing and demonstration before it can be implemented.
- The spent acid solutions will require processing to recover the dissolved heavy metals for subsequent disposal. A regeneration and recycling process for the acid solution, with catalysts, needs to be developed and demonstrated. Otherwise, the acid solution will be a secondary waste requiring disposal. If this is the case, a process may be required to recover the expensive cocatalysts.
- There are material compatibility issues with the highly corrosive DETOXSM solution that require resolution.
- Compared to incineration, wet oxidation is a slower process and there are fewer types of waste that can be processed.
- Depending on the organic contaminant, DREs may be less than 99.99%. This is particularly true for the less aggressive JGC and AEA wet oxidation processes. Thus, there is a potential need for post-processing to achieve the required destruction efficiency, depending on contaminants and local discharge requirements.
- In order to destroy solids, they need to be reduced in size causing a potential dust problem and introducing a pre-processing step.

2.2.4 References

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2.3 ACID DIGESTION

There are two acid-digestion processes that have been considered for application within the DOE complex. These are the sulfuric-acid digestion process developed by Westinghouse Hanford Company (WHC) in the 1970s and 1980s, and the phosphoric-acid process being developed by Westinghouse Savannah River Company (WSRC). The sulfuric acid or the phosphoric acid are used in concentrated amounts to enable increasing the working temperature of the mixture to well above the boiling point of water, and to dehydrate and carbonize organic matter. Both processes use nitric acid as the primary oxidizer of organic waste.

2.3.1 Sulfuric-Acid Digestion

2.3.1.1 Technology Description

This acid-digestion technology is an oxidation process carried out in a concentrated sulfuric-acid medium which functions to break carbon-hydrogen bonds in organic waste, and also acts as a corrosive on metallic and nonmetallic inorganic waste. The sulfuric acid carbonizes and partially oxidizes the waste; but the primary oxidant is nitric acid, which is added continuously to the digester at a rate proportional to the waste addition rate. In this process, the organics are converted to carbon dioxide, water, and other gaseous products, and the nonvolatile inorganics form insoluble oxides and/or sulfate salts.

A process diagram for the acid-digestion process is shown in Figure 2-4. The waste material is fed into the digester vessel which contains the acid solution. Oxidation and corrosive destruction takes place in the digester. Sulfuric and nitric acid are fed in the proper proportion to maintain the required acid concentration ratios (sulfuric-acid/nitric-acid ratio > 100) to ensure the waste is charred and oxidized rather than nitrated. An external electric heater is used to maintain an operating temperature of 250°C to 300°C. Metal catalysts can be used to increase the rates of oxidation (Ref. 1).

Figure 2-4. Diagram for Sulfuric-Acid Digestion Process

The composition of the offgas consists of CO_2 , CO , H_2O , and HCl from oxidation of the waste; entrained acid solution; and SO_2 , NO_2 , NO , N_2 , and H_2O from decomposition of the acids. This offgas flows to an offgas treatment system designed to remove water vapor, nitrogen oxides, entrained acid aerosols, and particulate matter. Reaction endproducts are removed from the offgas with an aqueous alkaline scrubber, and the acidified scrubber solution can be distilled to recover the acids for recycling to the digester vessel. Recovery and recycling of the acid solution is important to minimize vapor emissions and decrease the amount of new acid that must be added to the process. The solid residue is separated from the acid medium by periodically withdrawing a portion of the acid slurry from the digester, and distilling the acid back to the digester.

The three most important factors affecting the processing rate of the digester system are heat input, acid concentration, and vapor disengaging space (Ref. 1). The heat rate is limited by the allowable temperature differential across the vessel wall to avoid thermal stress-related damage to the glass lining. The processing rate is also affected by the offgas flow rate; very high offgas rates may convey part of the waste into the offgas system and plug the demister and the offgas line. This is primarily a problem with certain reactive materials, such as plastic film with

high surface area to volume ratios, and with high feed rates. The rapid evolution of gas that occurs with oxidation of some reactive organics can also cause severe foaming which can be alleviated by agitation with air, controlling the feed rate, and/or operating at a higher temperature.

In addition to oxidation reactions, nitration reactions may occur under some conditions leading to unstable nitro compounds. However, the degree of nitration depends on the temperature of the reaction mixture and on the ratio of sulfuric-acid to nitric-acid. Nitration falls off rapidly both at high temperature ($>100^{\circ}\text{C}$) and at high sulfuric-acid/nitric-acid ratios (>100). Thus, the normal operating temperature range should be held to 220°C to 260°C . The upper limit prevents an exothermic reaction from damaging the glass liner due to a rapid temperature rise, although temperature control is relatively easy due to the thermal inertia of the acid inventory.

Tests at Hanford included a tray digester and an annular digester. The annular digester design (shown in Figure 2-5) provided more intimate waste-acid contact and improved heat transfer, yielding significantly higher digestion rates than the tray digester design. The annular design consisted of two vessels: a digester and a heat exchanger. Each vessel, in turn, consisted of two vessels: an inner vessel with the glass coating on the outside of the shell, and an outer vessel with the glass coating on the inner surface. This construction provided a favorable geometry for nuclear criticality safety and permitted a much higher inventory of fissile material in the digester. Due to the corrosiveness of the acid solution, acceptable materials of construction include glass-lined steel for the reactor vessels, teflon for vessel and pipe liners and gaskets, and ceramics for internal hardware.

In the annular digester system, waste was introduced and digested in the annulus of the digester vessel. Two internal gaslift recirculators located on either side of the feed inlet sprayed incoming waste with acid. Vigorous agitation of the waste-acid slurry, and wetting the waste as it fell into the digester, prevented small plastic particles from melting and fusing together into large particles that would require longer digestion times. The second vessel acted as a heat exchanger, providing added heat-transfer surface area to boil away excess water in the system. The two vessels were connected at the bottom by a glass-lined steel settling chamber to trap heavy, undigested solids and at the top by a glass-lined steel recirculation line.

Figure 2-5. High-Rate Digestion System Schematic

Mechanical damage to portions of the glass liners occurred due to localized overstressing caused by inadequate support or over-torquing of clamps holding the vessel covers. In addition, localized excess heating caused a layer of tightly adhering residue to buildup on the glass. Differential thermal expansion between the glass and residue damaged the glass; however, the residue layer protected the underlying steel vessel and prevented any serious damage (Ref. 1).

Laboratory tests were also conducted using hydrogen peroxide as the oxygen source, which minimized NO_x in the offgas (Ref. 1). Organic ion-exchange resins were readily digested in a hydrogen-peroxide/sulfuric-acid digestion process. This process takes place in two steps: 1) initial carbonization reaction with sulfuric acid, and 2) subsequent oxidation of the carbon with H_2O_2 . Although direct oxidation of carbon by H_2O_2 is possible, the peroxide can also react with sulfuric acid to produce peroxomonosulfuric acid, which in turn reacts with carbon to produce either CO or CO_2 . The peroxomonosulfuric acid can also decompose unproductively to sulfuric acid and oxygen. Tests indicated that H_2O_2 utilization depended on the amount of undigested carbon in the sulfuric acid, and this was adversely affected by both the presence of

metal catalysts and the presence of metal sulfates. Though apparently successful, the nitric-acid process was too well developed to proceed with peroxide studies and system development.

2.3.1.2 Input and Output Stream Characteristics

Acid-digestion systems are able to treat a wide variety of waste streams containing hazardous organics. The process works especially well for cellulosic materials (e.g., glovebox-type materials), and is suitable for chlorinated nonvolatile organics such as PCBs and polymers such as polyethylene. Lubricating oils could probably be handled by injection under the liquid surface to prevent flash-off and increase residence time.

Wastes should be sorted to remove noncombustible materials, and the remaining combustibles shredded into approximately 3-cm pieces before feeding to the acid-digestion system. Based on the results of the demonstration conducted at Westinghouse Hanford, the process is also able to handle a wide variety of radioactive waste forms.

The Westinghouse Hanford process generated NO_x and SO_x in the offgas, and if chlorine-containing waste was treated (e.g., PVC), hydrochloric acid was also generated. This offgas required treatment (scrubbing) before release to the atmosphere. The offgas was quenched and scrubbed with cooled, recirculated acid in the presence of added air to oxidize and recover SO_2 and NO_x as dilute sulfuric and nitric acids. The offgas leaving the primary scrubbing tower passed through a wet, packed, fiberglass filter to remove entrained acid mist, then through a secondary scrubber to remove residual NO_x before it was heated above the dew point, then through three stages of HEPA filters before being discharged. In this process, no detectable radionuclide carryover was observed in the exhaust offgas.

An acid fractionation module was used to recover and concentrate the dilute acids from the scrubbers for recycling to the digester. The fractionator offgas contained most of the water and HCl generated during the digestion process plus some volatilized nitric acid. This offgas was heated and filtered through HEPA filters before being discharged.

Virtually all the sulfuric acid lost in the digester offgas was recovered in the first scrubber, about 20% of the nitric acid introduced into the digester was recovered in each scrubber for a total recovery of about 40%, and none of the chlorine in the waste was detected in the final scrubber offgas. Although the nitric-acid recovery was low, offgas samples showed little or no NO_x in the final offgas. Presumably, much of the missing nitric acid was reduced to N_2 in the digestion process.

The dilute mixed acids recovered in the process offgas system were concentrated about twofold by the acid fractionator in the acid recycle system before being returned to the digestion system. The fractionator recycled all the sulfuric acid input to the system and about 40% of the nitric acid. Any absorbed chloride in the fractionator feed was exhausted to the stack. Tests indicated that HCl in the exhaust would be accompanied by an equimolar amount of HNO_3 bound with the HCl. The lack of a rectifying section on the fractionator also meant that the offgas would contain free nitric acid as well in the amount of 7 to 9 moles per kilogram of waste processed.

A Belgian group's design (Ref. 2) included an offgas system to separate all acids quantitatively and recycle sulfuric and nitric acids into the process. To separate the acid gases, conventional scrubbing columns were used. A two-step rectification process was then used to separate reusable sulfuric acid (85%) and nitric acid (55%). This separation process required the use of two stripping columns, the first operated at 225°C and the second operated at 120°C.

In the Westinghouse Hanford process, acid digestion of dry combustible waste resulted in the generation of a solid noncombustible residue at about 10 to 15 wt% of the incoming waste. The residue was primarily composed of sulfates and oxides; silicates of calcium, magnesium, and iron; and other minor constituents. These inert materials were either present in the waste as fillers, or came from digestion of tramp metals that escaped the sorting process. Plutonium, if present, also ended up in the residue as plutonium sulfate, which could be readily leached from the sludge with dilute nitric acid with >99% recovery, provided the residue was not dried first. The inert residue was kept low by continuously removing a bleed stream, passing it through a centrifuge to concentrate the slurry, and transferring the resulting sludge to drying pots. Sulfuric acid that evaporated from the drying pots was routed back to the digester for recovery.

The dried product was a friable cake with 30 wt% consisting of materials volatile below 450°C, presumably mostly sulfuric acid and thermally unstable sulfate salts. The sulfate fraction accounted for at least 50 wt% of the residue. Sulfate materials tend to limit the fraction of residue that can be immobilized in concrete and still have good waste-product characteristics. Also, sulfates are incompatible with glass and will cause secondary phase formation if present in any appreciable concentration. The acid-digestion residue can be immobilized in both the portland cement and borosilicate glass waste forms, and the volume significantly decreased if the sulfate is removed by heat and a reducing agent. Cementation of a desulfated residue will result in a volume comparable to the original residue volume, and vitrification of a desulfated residue can decrease the waste volume to 50% of the original residue volume.

The Hanford pilot-plant reactor vessel was emptied only about once each year. The digester acid (about 20 wt% solids) was evaporated to recover sulfuric acid for reuse. Sulfuric acid was totally recovered and recycled in the process. Nitric-acid recovery was typically 25 to 40%. Losses were due to the formation of free nitrogen during digestion, reaction with chlorides in the waste to produce NO_2Cl in the fractionator offgas stream, and other process losses.

The process does not work well for high-ash waste because of the large volume of residual that is created. Wastes containing significant quantities of metals (electronic weapons components), particularly aluminum, may generate sulfates that produce a larger volume of secondary wastes than that initially entering the system (Ref. 4). Also, highly volatile materials may not be appropriate for treatment, because a deep vessel would be needed to provide sufficient contact time. Fiberglass waste also proved to be a problem. It tended to float in the acid medium and became distributed throughout the digestion system. Screens placed in the recirculation lines were reasonably effective in removing the fiberglass, but had to be cleaned frequently.

2.3.1.3 Technology Status

Acid-digestion treatment of radioactive/transuranic combustible wastes was initiated in 1972 at Westinghouse Hanford Company and continued until the early 1980s, when successful completion of the program's objectives were met and funding was no longer available. This system has recently been dismantled. At the Karlsruhe Nuclear Research Center in Mol, Belgium, an acid-digestion demonstration plant was built to treat about one ton of combustible waste remaining from former plutonium conversion operations, with recovery of about 7 kg of plutonium.

The Westinghouse project focused on treatment of transuranic wastes, and the research in Belgium focused on combustible waste with high-plutonium content. However, the fundamental principles of these developments would be applicable to treatment of low-level mixed waste.

Westinghouse Hanford cold tested an acid-digestion pilot plant in the late 1970s. A tray digester was tested in this plant and found to provide inadequate contact between waste and acid. In response to this, Westinghouse developed an annular digester, which better satisfied the requirements for treating high levels of nuclear materials.

Over 5,000 kg of synthetic and actual wastes were processed starting in December 1979 in the annular radioactive acid-digestion pilot plant. Special tests were conducted to assess the system's ability to process particular waste forms, including ion-exchange resins, decontamination rags, HEPA filter frames, wooden structural materials, high plutonium sludge, and plastic shipping bottles. Also, over 500 kg of waste containing large quantities of plutonium were processed during a 2-week run in 1980. Laboratory tests demonstrated the removal of plutonium from the treatment residue.

The acid-digester pilot plant was constructed in modular glovebox units, including:

- A waste storage and assay area
- A feed preparation module
- The acid-digestion module, including the annular digestion and heating vessels, and an air-cooled wire-mesh mist eliminator
- An offgas treatment module, where offgas was condensed and scrubbed
- An acid fractionation module, where recovered dilute acids from the scrubbers were concentrated for recycling to the digester.

The annular digester had instantaneous processing rates ranging from 5.2 to 13.5 kg/hr. Average processing times including shutdown (e.g., the system was shutdown and allowed to cool over weekends and holidays) was 5 kg/hr; predominantly cellulosic wastes were processed at rates around 10 kg/hr. Downtime was typically caused by equipment maintenance (18%), low temperature or low liquid level (29%), waste feed problems or plugs (26%), and miscellaneous (27%). The screens placed in the recirculation lines to remove the fiberglass in some of the glovebox wastes were effective, but had to be cleaned frequently. A greater heat input was required because the recycled acid contained 40% water that needed to be evaporated so that the production rate was not as great as had been predicted.

2.3.2 Phosphoric-Acid Digestion

2.3.2.1 Technology Description

This process is being developed at Savannah River, with design principles very similar to the sulfuric/nitric acid-digestion process that was developed at Hanford in the 1970s and 1980s.

Nitric acid is used as the oxidant, and is regenerated by air in an acid recovery system. The Savannah River team has replaced the sulfuric acid of the Hanford system with a concentrated phosphoric-acid medium, which acts as a dehydrating agent and allows nitric acid to be retained in solution at atmospheric pressure and temperatures up to 190°C—well above its normal boiling point of 121°C. Many organics will not decompose below 150°C, and preliminary results indicate that a 30°C increase in temperature increases reaction rates by an order of magnitude. Thus, by raising the temperature at which nitric acid remains a liquid, complete oxidation of organic intermediates which do not decompose below 150°C is ensured. Also, the phosphoric acid aids in the decontamination of the noncombustible materials in the waste since many actinide oxides are soluble in concentrated phosphoric acid at temperatures near 200°C.

The system is being developed by Westinghouse Savannah River (WSR) to operate below 200°C at moderate pressures (0-15 psig). It consists of five primary unit operations: feed preparation, nitric/phosphoric acid oxidation and decontamination, acid recovery and recycle, metal precipitation and recovery, and solids vitrification (Figure 2-6). The feed preparation step involves shredding the solid organics to increase their surface area because experimental data indicate a strong surface area dependence for the dissolution and reaction rates. The solids are then placed in oxidation vessels where they are oxidized and dissolved in the nitric- and phosphoric-acid mixture.

Direct oxidation of most organic compounds by HNO_3 is energetically favorable but very slow due to its inability to break the carbon-hydrogen bond. The oxidation of organic compounds is usually initiated by the production of organic radicals generated by dissolved $\text{NO}_2\bullet$ and $\text{NO}\bullet$ radicals in solution (Ref. 6). For aliphatic compounds, high concentrations of $\text{NO}_2\bullet$ and $\text{NO}\bullet$ are needed requiring a pressurized system. The organic radicals are then oxidized by nitric or nitrous acids, or nitrated by $\text{NO}_2\bullet$. As the organic molecules gain more oxygen atoms, the organic molecules become increasingly more soluble. Once in solution, the molecules are quickly oxidized to CO_2 , CO , water, and HCl if the original compound contains chlorine.

Most organic chemicals, with the exception of aliphatic and resonant-stabilized compounds, can be oxidized at moderate temperatures (below 180°C) and at ambient pressure. Oxidation of aliphatic and resonant-stabilized compounds requires moderate pressurization to attain higher concentrations of $\text{NO}_2\bullet$ and $\text{NO}\bullet$ in solution. As the reaction progresses, NO and NO_2 are released from solution, and nitric acid is depleted. As a result, the NO and NO_2 need

to be recovered as nitric acid in order to continue initiating the reactions. The net oxidizer for the process would then be oxygen from the air added to the acid recovery system. At the same time, HCl gas from the oxidation of chlorinated hydrocarbons must be allowed to pass through to be recovered in a subsequent step.

Many organic materials have been completely oxidized to CO₂, CO, and inorganic acids in a 0.1M HNO₃/14.8M H₃PO₄ solution (see Table 2-5). Addition of 0.001M Pd⁺² reduces the CO to near 1% of the released carbon gases. Minimizing CO in the gas phase is important because CO and NO and/or NO₂ can form explosive mixtures. To accomplish complete oxidation the solution temperature must be maintained above 150°C. The oxidation is usually complete in a few hours for soluble organic materials (Ref. 6).

Table 2-5. Carbon Balance for Oxidation of Various Organic Compounds in a 0.05-0.1M HNO₃/14.8M H₃PO₄ Solution, 120°C to 160°C

Compound	Co-catalyst Metal (conc.)	Percentage Carbon Released as CO ₂ and CO	Percentage CO of CO ₂ and CO
Cellulose	none	98±2 ^a	20±1
Cellulose	Pd (0.0012M)	99±2	0.9±1
Cellulose	Rh (0.003M)	97±3 ^a	6.3±1.5
EDTA	none	99±2	25±1
EDTA	Pd (0.0012M)	>91±2	0.9±1
EDTA	Rh (0.003M)	>84±3 ^a	19±1.5
TBP	none	103±3 ^a	43±1 ^b
TBP	Pd (0.0012M)	-	1.3±1
Nitromethane	none	101±2	60±1
Nitromethane	Pd (0.0012M)	-	2.3±1
Tartaric acid	none	>96±2	15±1
Neoprene	Pd (0.001)	101±10	<17

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

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

The materials that have been oxidized at atmospheric pressure and below 180°C include neoprene, cellulose, EDTA, tributylphosphate, tartaric acid, and nitromethane. More stable compounds such as paraffinic and naphthenic oils, benzoic acid, ion-exchange resin, PVC, and polyethylene have been successfully decomposed below 200°C and 15 psig (Ref. 6). In addition to dissolution of plastics, hot concentrated phosphoric acid has been shown to efficiently dissolve plutonium oxide.

Microwaves have been used to enhance the dissolution and oxidation of insoluble organics. Oxidation of aliphatic compounds can be accomplished under microwave digestion conditions of 180°C and 4 atmospheres pressure. High-density polyethylene (HDPE) can be, within experimental error, quantitatively oxidized to CO₂ and CO under typical microwave digestion conditions (approximately 100 Watts) in relatively dilute nitric acid. However, the microwave energy is used to heat the solution because the energy is insufficient to cause bond breakage.

Observation of the effect of microwaves on dissolution and reaction rates indicate the following (Ref. 6): (1) they provide a higher liquid surface temperature (sometimes up to 20°C-30°C higher) than the bulk of the solution; and (2) they appear to heat partially-reacted plastics that are not normally susceptible to microwave energy absorption thereby increasing temperatures and reaction rates at the plastic surface. Additional work is needed to determine the effect of microwaves on the process and to determine if they play a sufficiently advantageous role in the dissolution and destruction of plastics and other organic materials.

Dissolution appears to be the key process that will control the system throughput. Although good results for dissolution have been achieved at elevated pressures, work is continuing to initiate dissolution at low pressure due to the presence of radionuclides. For the enhancement of dissolution of insoluble organics, the benefits of microwave heating are still considered important although the effect of microwaves is unclear. Oxidation is another critical aspect of the process. If the surface area of the plastics can be increased by dissolution, the temperature of the oxidation reaction may be lowered and still maintain an acceptable reaction rate. It is felt that dissolution will be the rate-limiting step in the process. This combination of dissolution and oxidation as separate steps may improve the effectiveness and throughput of the entire process.

Initiation of the reaction by NO• and NO₂• is also an important step. Once initiated, it is expected that the reaction will proceed at an acceptable rate until all solids are in solution because the reaction itself generates NO• and NO₂•. Research is still required to determine the preferred method for reaction initiation. Using NO_x gas, nitrous acid, or a nitrite salt are the most obvious approaches, but further research on reaction initiation will identify the preferred method (Ref. 7).

As the reaction progresses, NO and NO₂ are released from the solution and nitric acid is depleted. Thus, the NO and NO₂ need to be recovered as nitric acid to maintain the reactions. At the same time, HCl evolved from the oxidation of chlorinated hydrocarbons must be allowed

to pass through the nitric acid recovery process to be recovered in a subsequent step due to the highly corrosive nature of the combination of HCl and HNO₃. Acid recovery units for converting NO_x to nitric acid are a commercially available technology, and methods for recovering HNO₃ separately from HCl are being evaluated. An approach is to take advantage of the solubility of nitric acid in phosphoric acid relative to the solubility of HCl. Recovery data indicates that much of the NO_x reabsorbs back into the phosphoric acid, thereby reducing the size of the required acid recovery system.

Metals and radionuclides will accumulate in the acid solution. However, heavy metals are highly insoluble in phosphoric acid at room temperature. Thus, upon cooling, these metals can be recovered by precipitation either as phosphates or oxalatophosphates. The precipitate can be separated by an appropriate separation process, rinsed, dried, and immobilized for disposal. Immobilization may be performed by use of polymers, vitrification, or phosphate-bonded ceramics depending on the metal compounds.

Materials need to be considered for two applications: room temperature and 200°C. One advantage of a phosphoric-acid system is that the phosphate passivates the surface of many metals, including stainless steel, even in the presence of chloride (Ref. 7). This is particularly advantageous at room temperature where common stainless steel can be employed wherever the equipment will experience only room-temperature acid streams. This includes equipment associated with cold feed, filtration, and solution handling following oxidation.

At elevated temperatures, the passivation effects are less pronounced resulting in greater attack on a wide variety of materials. Vapor phase corrosion data (Ref. 8) indicate that 317L SS and Hasteloy C-22 are good candidates for the acid recovery system. Because the system will operate near atmospheric pressure, glass and Teflon[®] linings are good candidates for the oxidation vessel and will keep the capital cost of equipment and replacements lower than if tantalum were used. All other equipment subject to low temperatures can be constructed from inexpensive materials such as 304L or 316L stainless steel, or Hasteloy C-276.

2.3.2.2 Input and Output Stream Characteristics

This technology is being developed for the treatment of heterogeneous waste streams by converting hazardous liquid and organic solids to inorganic gases and salts while performing a surface decontamination of the noncombustible items. The process is intended to oxidize the combustibles (cellulose, rubber, plastics, oils, resins and sludges, and miscellaneous organics)

without requiring separation from the noncombustibles. In addition to dissolution of plastics, hot concentrated phosphoric acid has been shown to efficiently dissolve plutonium so that the solution should be effective in decontaminating non-combustibles. The system has been tested on combustibles such as plastics, neoprene, cellulose, and tributylphosphate, with cellulose and tributylphosphate oxidizing more readily than neoprene and plastic. Reaction rate reflects a strong surface-area dependence, and shredding will be a necessary feed-preparation step. It has also been observed that the oxidation of plastics progressed more rapidly in the presence of microwaves.

The offgas will depend on the feed composition, but will consist of large amounts of NO, NO_x, nitric-acid mist, phosphoric-acid mist, and halogen acids if halogens are present in the waste feed. As the reaction progresses, NO_x is released from solution and the nitric acid is depleted. Thus, the offgas system design will be very important because of the potential for high levels of offgassing and the need to recover nitric acid. Preliminary experiments with EDTA indicate that approximately 2.5 moles of NO_x are generated per mole of carbon. Commercial nitric-acid absorption/recovery columns exist which are capable of recovering 150 lb/hr of NO_x gas as nitric acid. This level of nitric-acid recovery is expected to be capable of supporting organic oxidation rates of 200 to 500 lb/hr. Acid recycle and HCl capture have been examined mostly from a theoretical standpoint based on the literature and personal experience. A test unit is being constructed at Savannah River to verify the proposed arrangement for separating HCl from the other gases while minimizing nitric-acid losses.

Inert materials and soluble products of oxidation, such as salts, will require removal from the acid-digestion system through neutralization/precipitation, ion exchange, complexation/precipitation, or other techniques. The residual low-level waste, TRU, and hazardous metal components can be collected and placed in a safe form for storage or disposal. Metals can be recovered by precipitation as either phosphates or oxalatophosphates. The precipitates can then be separated using filtration and stabilized in a ceramic or glass matrix. Water will be mostly treated and recycled.

2.3.2.3 Technology Status

The phosphoric-acid system is currently at the lab/bench-scale and requires additional development and testing before scale-up to pilot-scale. Preliminary work has demonstrated a high level of promise for handling the solid TRU waste on-site. Most of the hardware components of the system are commercially available, streamlining the necessary remaining

work. The basic chemistry is understood and demonstrated, but has not yet been optimized or tested on an engineering scale.

Several approaches are being developed to simplify the process as much as possible. One approach would recover the nitric acid using the actual oxidation solution instead of separating the acid in a different process stream, taking advantage of the solubility of NO_x gases and nitric acid in phosphoric acid relative to the solubility of HCl .

The results of these investigations appear promising, especially for low-volume generators. Metal removal from the acid is considered the most significant area of development remaining for treating mixed wastes (Ref. 9).

2.3.3 Destruction Efficiency

Much of the research on the sulfuric-acid process was done before the establishment of destruction efficiency requirements, but DREs have been measured at 99.99% (Ref. 2). This destruction efficiency is considered likely for the nitric/phosphoric acid-digestion process as well.

The feed processing rate for the nitric acid/phosphoric acid process is rapid for soluble materials, where the reactions can take place homogeneously in the acid medium, and moderate for readily dissolved materials, neoprene, and plastics with microwave assistance. The reaction rate is slow for plastics without microwaves. Assuming 1 liter of nitric/phosphoric acid, throughputs have been estimated for EDTA, cellulose, and polyethylene as 140 g/hr, 90 g/hr, and 15-40 g/hr, respectively (Ref. 9). These throughputs are based on the maximum oxidation rates observed over the first 5-10 minutes of reaction. Polyethylene is stated as a range because this work is incomplete; 15 g/hr represents experimental observations while 40 g/hr reflects experience with other compounds (Ref. 9).

Figure 2-7 (Ref. 8) shows the oxidation of cellulose, polyethylene, and polyvinyl chloride (PVC). Because polyethylene dissolves faster than PVC, it has a faster reaction rate due to the increased surface area in the dissolved state. Experiments on Trimsol (a water soluble oil) indicate that reaction rates increase with both temperature and nitric acid concentration, and that reactions at temperatures less than 150°C do not appear to go to completion. Based on these experiments, it is believed that optimum conditions for easily oxidized compounds (cellulose) involve lower temperatures and higher acid concentrations due to rapid reactions and

Figure 2-7. Oxidation of Primary Organics

corresponding rapid acid depletion. However, cellulose reaction rates increased significantly as the temperature was increased from 140°C to 165°C (Ref. 9). Optimum conditions for plastics use elevated temperatures where the dissolution of the plastic and oxidation of the more stable, long-chain intermediates is more important.

Pressure alone has no observable effect on plastic oxidation. However, pressurized systems permit both higher reaction temperatures and acid concentrations instead of forcing the selection of one or the other. The effect of having both higher temperature and acid concentration is shown in Figure 2-8. Thus, the optimum system for plastics will be a safe way to maximize temperature and nitric acid concentration using elevated pressures.

Figure 2-8. Oxidation of Polyethylene

Experiments on a 15% EDTA solution indicated that reaction rates at 140°C, 160°C, and 170°C were essentially identical (Ref. 10). Results of subsequent experiments, performed at 140°C and with the batchwise addition of solid EDTA to vary the concentration, are shown in Table 2-6. The highest concentration of EDTA caused the reaction temperature to increase to 168°C indicating a runaway reaction was possible. However, this may not be a major safety issue because the system may be self-correcting, since the nitric acid will boil off as the temperature rises, thereby stopping the reaction.

Table 2-6. Oxidation of EDTA at 140°C (Ref. 10)

Time (Minutes)	EDTA Concentrations			
	0.33 g EDTA in 28 ml	0.68 g EDTA in 30 ml	1.38 g EDTA in 32 ml	2.15 g EDTA in 34 ml
5	—	—	—	50.4
10	50.3	62.5	57.7	72.8
15	69.1	72.2	70.2	82.7
20	78.9	80.5	77.3	90.4
30	87.4	86.3	85.3	94.7
40	91.1	91.6	89.8	96.8
50	93.9	93.5	92.6	96.5
60	95.4	95.1	95.6	97.0

These experiments with EDTA (Ref. 9) show that high throughputs generate large amounts of offgas. Thus, a reaction vessel will require a large head space or means of controlling foaming.

2.3.4 Technology Comparison

Both processes have been demonstrated to effectively treat such combustible organics as cellulosics and glovebox materials, with very little ash generation. However, waste streams containing significant quantities of metals may produce a larger, secondary waste stream than the initial feed stream. Therefore, this technology would be suited to a well characterized organic combustible feed stream or contaminated inert material. The acid-digestion process is relatively low temperature (compared to incineration), but may have significant offgas treatment system concerns.

Currently there are no commercial manufacturers of acid-digestion systems. Disadvantages include acid handling, removal of the radionuclides from the acid after digestion, and disposal of the acid after it has been depleted. In addition, the feed requires sorting and shredding, and acid gases are produced requiring acid recovery and recycling. Additional advantages and disadvantages of acid digestion are as follows:

2.3.4.1 Advantages

- Can achieve relatively rapid, efficient destruction of a wide variety of organics at lower temperatures than incineration.
- Small offgas flowrates and low-temperature operation reduces volatile metals in the offgas.
- Performs well on low ash, dry wastes.
- Can treat a wide variety of wastes including decontamination of inorganic debris.
- A soluble residue is produced that allows actinide recovery.
- Provided the appropriate geometry, it can process high levels of radioactivity.

2.3.4.2 Disadvantages

- Capability for DOE waste is not demonstrated: development and demonstration required especially for particle sizing, solids processing, and system operation and reliability.
- Not well-suited for wastes containing significant amounts of metals.
- High levels of acids and NO_x in the offgas must be recycled or disposed.
- Technology is emerging with no treatment units presently in operation.
- The solid products, offgas products, and spent acids require further treatment to meet disposal criteria.
- Very acidic solutions are not compatible with many materials of construction.

- Safety and operational concerns are more complex with such high concentrations and quantities of acids.
- All effluent materials including unreacted feed, inorganic solids, sludges of dissolved and precipitated inorganic material, and offgas system solids will require further treatment to immobilize fine particles, metals, and radionuclides. Waste water will require processing for recycle or disposal.
- The acid-digestion system is fairly complex with feed and acid preparation and mixing, digestion, solids recovery, acid fractionation, and offgas treatment.

2.3.5 Cost of Technology or Equipment

The system cost is expected to be comparable to that of other chemical oxidation options. Cost/benefits and acceptability of secondary waste-stream generation would be different for high- versus low-level waste, and will also vary with amount of metals and noncombustibles fed to the system. Explicit cost estimates have not been developed.

2.3.6 References

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2.4 ELECTROLYTIC/ELECTROCHEMICAL OXIDATION

There are two electrochemical processes being investigated within the DOE complex; the mediated electrochemical oxidation (MEO) process, and the persulfate process. These processes are applicable to the destruction of organic liquids and the removal of mixed wastes from surfaces of heterogeneous or homogeneous solids.

In these processes an electrochemical cell is used to generate an oxidizing species at the anode in an acid solution (typically nitric acid), which then migrates into the bulk electrolyte to oxidize and destroy the organic compounds. A microporous membrane is usually placed between the electrodes to prevent the oxidizer produced at the anode from being reduced by cathode-generated species. The oxidizer will produce hydroxyl free radicals from water; and the oxidizer and free radicals both attack organic compounds converting most of them to CO_2 , water, and inorganic ions. The oxidizer is reduced in these reactions and is regenerated (oxidized) at the anode. The oxidizers and acid destroy hazardous organic compounds and dissolve inorganic compounds which may contain radionuclides, including PuO_2 which is not soluble in nitric acid alone. To keep waste generation to a minimum, the chemicals that are added are recycled. Recovery/recycle processes have been developed or are under development for the materials used in the MEO process.

Because of the corrosive nature of the electrolytes, special attention must be paid to the materials of construction. In the Pacific Northwest Laboratory (PNL) tests (Ref. 1) all materials that come in contact with the anolyte solution are titanium, PVDF, Teflon, or glass. The catholyte is also corrosive, but stainless steel has provided adequate corrosion protection.

2.4.1 Mediated Electrochemical Oxidation (MEO) Process

2.4.1.1 Technology Description

The MEO process is being studied and developed at LLNL, PNL (where it is called the catalyzed electrochemical oxidation (CEO) process), AEA Technology in the UK, and LANL. This process uses strongly oxidizing cations (or mediators) such as Ag(II) , Co(III) , Fe(III) and Ce(IV) in supporting electrolytes of HNO_3 or H_2SO_4 . These mediators oxidize organic materials at low temperature ($<80^\circ\text{C}$) and atmospheric pressure directly and indirectly by first reacting with water to generate OH radicals. In contrast to Ag(I) , Co(II) , Fe(II) and Ce(IV)

remain soluble in the presence of halide anions generated during the destruction of halogenated organics. However, Ag(II) is a more powerful oxidizer than Co(III) or Fe(III). PNL has also tested cerium as an oxidizing agent in HNO₃ and, at higher temperatures (~ 100°C), found it to provide the same or better oxidation rates for Trimsol as did silver (Ref. 1).

LLNL has performed tests with both the silver-nitric acid system and the cobalt-sulfuric acid system. In the silver-nitric acid system, Ag⁺ is oxidized at the anode producing Ag²⁺ which, in the absence of organics, complexes with the nitrate ion to produce AgNO₃⁺. The Ag(II) also reacts with the nitric-acid solution to produce hydroxyl and NO₃ radicals which are highly reactive, and the complex reacts with organic material according to the following example reaction with ethylene glycol (Ref. 2):

Carbon dioxide and carbon monoxide may both be formed, the ratio depending on the organic material in the waste stream and the oxygen atoms arising from the water in the anolyte. Inorganic products (e.g., sulfates, phosphates, and metal cations) may also be formed depending on the waste composition.

The catholyte is similar in composition to the anolyte but typically has a higher Ag concentration due to the migration of Ag⁺ and hydronium ions across the membrane. The principal cathode reaction is the reduction of nitric acid to nitrous acid:

Microporous glass or a nanoporous polymeric cation-exchange membrane were found to be effective in preventing reduction of Ag(II) by HNO₂ produced at the cathode (Ref. 2). As the nitrous acid concentration increases, it decomposes to NO_x. Contacting the nitrous acid with oxygen will regenerate nitric acid and prevent NO_x build-up. Because oxygen has limited solubility in the solution, LLNL developed a turbo-aerator (Refs. 3 and 4) which achieves very high conversion efficiencies in a small volume. The turbo-aerator is installed in the catholyte loop and draws the gas and fluid together, and passes them through a row of stator blades which disperses the gas into very small bubbles. The intimate mixing and high surface area produce measured conversion efficiencies of 95 to 99%.

An integrated flowsheet for an MEO system is shown in Figure 2-9. An integrated system would consist of an anolyte and a catholyte loop. Organic waste plus make-up water is fed to the anolyte loop. The CO , CO_2 , etc., formed during organic destruction is vented through an offgas treatment system to ensure no acid fumes or volatile organics are discharged. To achieve good mass transfer and uniform reaction across the anode, tests were performed using a rotating cylindrical anode, and in a larger system the anode contained turbulence promoters so that turbulent flow was maintained throughout the anode cell.

94-0320-TR-G-36

Figure 2-9. Flowsheet for Integrated Mediated Electrochemical Oxidation System (Ref. 3)

The catholyte loop is more complex because this loop involves the recovery of nitric acid from the nitrous-acid offgas. In addition, the water produced in the catholyte from the oxidation of the organic waste, or from the migration of hydronium ions across the membrane, must be distilled and returned to the anolyte as make-up water or discharged. This excess water is removed from the system by using an evaporator in conjunction with a fractionating column. The electrolyte is passed through the evaporator and a small amount is evaporated off, enough to remove the excess water. The concentrated electrolyte is returned to the cells. The vapor from the evaporator contains both water and nitric acid, which are separated in the fractionating column that produces sewerable water and reusable acid.

To be applicable to waste treatment, this process will require an integrated system design in which the electrolyte is bled off to limit the concentration of ions resulting from the waste stream and the destruction process (e.g., metal ions and anions produced from compounds containing sulfur, phosphorus or chlorine), and to recycle the Ag and HNO₃. Recycle of silver will be necessary for economic reasons, and because it is a RCRA metal. When chlorinated organics are destroyed in the anolyte, chloride ions combine with silver ions to form insoluble silver chloride. The silver chloride precipitate is removed from the electrolyte by settling or centrifuging. It is then introduced into a hot solution of sodium hydroxide and hydrogen peroxide to reduce the silver chloride to silver (Ref. 3):

The silver is filtered or centrifuged and dissolved in nitric acid for reuse. The chloride remaining in solution in the form of NaCl is dried and disposed.

Since silver chloride is almost insoluble, it affords a method for removal of silver from the electrolyte, when desired. When the electrolyte becomes loaded with dissolved radionuclides and metals they must be removed, but the silver in solution must be removed first for reuse. By adding chlorides to the electrolyte, the silver precipitates out and is separated. The solution is boiled off until almost dry by passing it through a thin film evaporator, and the bottoms are removed for disposal or further treatment.

2.4.1.2 Input and Output Streams

The operation of the process overall has been reported to be unaffected by the organic concentration in the feed stream (Ref. 5). The organic content of the waste feed can vary between 100% to 5% without materially affecting the process. A wide range of water content in the feed stream can be accommodated by changing the ratio of the volume of water recycled back to the anolyte to the volume of water discharged. However, recent tests (Ref. 1) indicate increased rate of destruction with increased oil content in the electrolyte when cerium was used as the electro-catalyst.

The organic content may consist of soluble or insoluble organic liquids, or solids that have been size reduced to increase the surface area for the reaction to take place. A significant number of compounds have been identified which can be destroyed by the Ag/nitric acid process. These include aliphatic and aromatic hydrocarbons, phenols, organophosphorus and organosulfur compounds, and chlorinated aliphatic and aromatic compounds (Ref. 5). The

oxidation of several real and surrogate organic wastes, including ethylene glycol (EG), isopropanol, 2-monochloro-1-propanol, 1,3-dichloro-2-propanol, benzene, and Trimsol cutting oil have been studied at LLNL, using various mediators in supporting electrolytes of HNO_3 or H_2SO_4 (Ref. 2).

Cellulosic solids have been destroyed by both the Co/sulfuric acid and the Ag/nitric acid systems, and ion-exchange resins have been readily destroyed by the Ag/nitric acid process (Refs. 5 and 6). Preliminary tests at LLNL indicate that latex gloves, Tyvek coveralls, plastic bags (polyethylene), and biomass were destroyed with good destruction efficiency (Ref. 6). However, the plastics required a long time for destruction, and trials at AEA Technology with flaked polyethylene showed almost zero reaction because of the hydrophobic nature of the material and the restricted surface area available for reaction (Ref. 5). AEA Technology reports that the Ag/nitric acid system has been used to destroy 20% n-tributyl phosphate in kerosene, rubber gloves, polyurethane manipulator gaiters, epoxy resins, hydraulic fluid, and lubricating oil at a rate greater than 5 liters/day (Ref. 2).

Tests at PNL demonstrated destruction of non-cellulosic solids in a Ag/ HNO_3 solution (Ref. 1). As shown in Figure 2-10, wood was destroyed by approximately 80% in one hour, paper by 60%, and cloth by 50%. The remaining material tested, such as surgeons gloves, polyethane plastic, vinyl plastic, and fire retardant tape, showed no significant reduction in mass.

Figure 2-10. Comparison of Different Combustible Materials and the Extent of Oxidation During a One-Hour Period

Metals and radionuclides may be distributed in the waste stream, or may exist as surface contaminants on debris in various forms. The combination of hot nitric acid and the strong oxidizing conditions will result in dissolution of the metal compounds in the anolyte and oxidation to the highest stable state. However, for decontamination applications, this process can be applied inappropriately resulting in dissolution of the bulk solid rather than separating it from the surface contaminant.

The output streams consist of CO₂ and CO in the anolyte offgas which may also include acid vapors. The catholyte offgas consists of NO_x and HNO₂, which requires recovery and regeneration of HNO₃. The solution must be processed to remove excessive metal ions and/or anions, and any insoluble inorganics that may be in the waste feed, through a continuous bleed or by periodic batch processing. As the solution is removed from the reaction vessel for processing, silver is removed in the solution. As indicated previously, a method has been proposed to recover the silver and recycle it back to the reactor.

2.4.1.3 Technology Status

This technology is under development at three national laboratories (LLNL, PNL, and LANL), and by AEA Technology in the UK. The work at LLNL has included bench-scale tests on a variety of organic compounds, and tests on a large bench-scale facility using an industrial electrochemical cell. LLNL is currently developing a design for a pilot-scale integrated system (Figure 2-9) to be installed in their Mixed Waste Management Facility. The system is expected to be ready for demonstration in 1998. The effort at PNL and LANL is at the bench-scale level and is proceeding to develop optimum operating conditions for the wastes of interest. The work at PNL is progressing to the design and build phase of a modular pilot-scale unit. AEA Technology uses the same principle as the MEO process developed by LLNL, and has reported on bench-scale testing at their laboratory in Scotland (Ref. 5). They hold patents for the use of the process for organic waste destruction, including U.S. patents, and have engineering designs for a full-scale plant (100 tons/yr) for treating radioactive waste. Issues regarding the importation of waste into the UK have prevented the signing of a contract with a European company to process radioactive ion exchange resin and solvent. During testing, AEA successfully treated chemical warfare agents (e.g., mustard gas, lewesite, and nerve gases) and they will be using the process for commercial recovery of enriched uranium. AEA has a licensing agreement with a U.S. company to use the process for treatment of military and industrial waste.

This technology appears to be proven and ready to be commercialized for destruction of a variety of organic materials including liquids and some solids, for treatment of mixed waste, and for decontamination of inorganic debris.

2.4.1.4 Destruction Efficiency

The parameters that can be controlled in the MEO process are system temperature, strength of the electrolyte, type of mediator and electrolyte, current density at the electrodes, and residence time in the solution. Control of these parameters will determine destruction efficiency and, in turn, coulomb efficiency and cost.

Experiments were performed at LLNL on Trimisol, which contains 11% chlorine by weight, and cellulose with the Ag/nitric acid system and the Co/sulfuric-acid system (Refs. 2, 4 and 6). Batch tests were performed in the small bench-scale rotating cylindrical electrode device, and continuous flow tests were performed in the larger bench-scale system. The destruction efficiency reported in this work refers to the total destruction of the organics to the extent of complete mineralization of carbon to carbon dioxide. The best performance was obtained with the highest possible current density below the limiting current density at which oxygen begins to be produced at the anode.

Destruction of Trimisol with Co(III)/sulfuric acid in the small-scale system proved to be very inefficient due to the insufficient oxidizing power of Co(III) and the low solubility of Trimisol in the acid solution. Trimisol is a cutting oil composed of a mixture of various oils and other organics. When it is fed into a strong acid, the emulsifier is attacked immediately by the acid causing the oils to separate out with a tendency to coalesce into larger droplets and float to the surface. These oils then become difficult to destroy because of their limited contact with the mediator. Although the solution was mixed to entrain the oils in the bulk of the solution, the oxidizing power of Co(III) is insufficient to destroy the oils before they coalesce into larger droplets.

For Trimisol, the best results were obtained under high-oxidation conditions and in the presence of high mixing and shear conditions. High-oxidation conditions include a Ag/nitric-acid solution, 8 to 10M nitric-acid concentration, 0.5M Ag, and 50°C to 70°C system temperature. The high mixing and shear conditions require fully turbulent flow throughout the system, and a mixer anywhere the oil can separate and float to the surface. As expected,

destruction efficiency increased, or time to reach a given destruction efficiency decreased, as the nitric acid concentration or temperature increased.

In the batch reactor, DEs for Trimsol ranged between 95% to over 99% in 11 to 20 hours depending on the molar concentration and temperature of the nitric acid. In the continuous flow system, DEs for Trimsol ranged from 96% to 99.8% for feed rates between 290 and 100 grams/hr, respectively. This system had two anodes with an active surface area of 0.85 m² per anode (Ref. 6).

For batch destruction of reagent grade cellulose, DEs of 99.8% were achieved in 5 hours in Co/sulfuric acid with 6M sulfuric acid, 0.5M Co, at 70°C. Decreasing the concentration of sulfuric acid to 4M and the temperature to 50°C increased the time to reach 99% destruction efficiency to almost 18 hours. For the Ag/nitric acid system with 4M nitric acid and at 70°C, 99.4% destruction efficiency was achieved in 9.6 hours. In 8M nitric acid and at 70°C, a 98.5% destruction efficiency was reached in 5.5 hours. Although the mediator/acid combination does not appear to have a major effect on the destruction efficiency for cellulose, the Ag/nitric acid system has better coulombic efficiency. Batch tests were also performed on wipes and cloth rags with a destruction efficiency of 94% to 98% over a period of 2 to 8 hours. Only the Ag/nitric acid combination was used in the continuous flow reactor which provided DEs of over 99% for reagent grade cellulose with feed rates of 150 to 400 grams/hr (Ref. 6).

For both Trimsol and cellulose, DEs of 99% or higher can be achieved at coulomb efficiencies of 70%. To obtain DEs of 99.99%, coulomb efficiencies are required in the range of 40 to 50% (Ref. 3). The coulomb efficiency refers to the theoretical amount of electric charge needed to destroy the organics versus the actual amount required.

Work in the United Kingdom (Ref. 5), using the same Ag/HNO₃ based electrolyte, has shown that a variety of organic materials can be destroyed. In these experiments, oxidation of a solvent (tributyl phosphate/kerosene) from 2,000 to 3,000 ppm to 100 ppm with the generation of CO₂, H₂O, and phosphoric acid was achieved at low temperature and little generation of secondary waste. Several ion-exchange resins were also destroyed with the oxidation of the organic component nearly complete as judged by the low organic content of the anolyte (typically < 100 ppm). The success with these ion-exchange resins was attributed to their porosity, which ensures that the reaction occurs within the body of the resin beads rather than only on the surface, and to the chemical reactivity of the resins. Comparative trials with flaked polyethylene showed almost zero reaction because of the hydrophobic nature of the material and the restricted surface area available for reaction (Ref. 5).

PNL is also evaluating the MEO technology for the treatment of TRU-contaminated and mixed-combustible waste materials (i.e., Pu contaminated cutting and lubricating oils and solid combustible materials) for the Rocky Flats Plant (RFP). Tests initiated in FY91 determined that this process could destroy the oils with reasonable efficiency, and currently PNL is developing a pilot plant to be delivered to RFP for further evaluation and demonstration (Refs. 1 and 7). The $\text{AgNO}_3/\text{HNO}_3$ electrolyte is used in the PNL system where the cycle between Ag(I) to Ag(II) at the anode, and Ag(II) to Ag(I) in the reaction with organic material, is repeated continuously to maintain a supply of oxidant and minimizing the consumption of Ag.

PNL tests have achieved DEs for RFP cutting oil of >99.9% of the organic carbon at temperatures in the range of 60°C to 90°C. A key to this process for immiscible organics in water is the use of an ultrasonic generator, thereby producing a micro-emulsion that greatly increases the surface area and the oxidation rate of the organic material. A side reaction at the anode evolves O_2 which reduces the current efficiency of the process. At the cathode, the electrolysis of HNO_3 or water produces NO_x or H_2 , respectively. Additional studies have been performed to evaluate the process for the destruction of solid combustibles such as cloth, paper, wood, plastics, and filter media (Ref. 1).

LANL is investigating the Co(III) /nitric acid system for the destruction of cheesecloth wipes used in the general cleanup in radioactive glovebox environments (Ref. 8). The cheesecloth is made from cotton that is about 90% cellulose. As with the Ag system, Co(II) produced during the oxidation reaction migrates to the anode where it is oxidized back to Co(III) in a continuous regeneration process. Preliminary tests in a small flow-through reactor indicate that these wipes can be completely dissolved in the solution, that varying the particle size of the cloth did not affect the dissolution rate, and that no hazardous organic intermediates were found. To date the maximum dissolution rate achieved is approximately 10 grams/hr, which corresponds to a destruction efficiency of 20%. However, since the dissolution rate continues to increase with increasing current density, the maximum dissolution rate has not been reached for this system. An interesting phenomena with this system is the decrease in dissolution rate and current efficiency with increasing temperature. One explanation may be an increase in parasitic reactions (e.g., reaction of Co(III) with solvent) at elevated temperatures.

2.4.1.5 Required Development

Additional tests are required to determine parameters for the destruction of mixtures of organic liquids which are typical of organic mixed wastes. Parameters expected to affect

destruction rate and efficiency include temperature, electro-catalyst type and concentration, current density, and waste type and concentration. Since organic liquids are a small percentage of the mixed waste stream, this process should be tested on organic sludges and aqueous/organic mixtures to determine its effectiveness, and tested on contaminated soils and inorganic debris. Optimum parameters need to be determined to scale up to pilot scale for demonstrations on real waste streams. The balance of plant (i.e., anolyte offgas treatment, catholyte offgas treatment and acid recovery, extraction of anions and cations from the oxidizing solution, and recovery of the mediator) should be designed and demonstrated at the pilot scale. This process should also be compared to alternatives to determine their relative performance, cost, and reliability.

2.4.1.6 Cost of Technology

An estimated cost of approximately \$1.78/kg for destroying aniline has been made (Ref. 2) for an assumed cell efficiency and power cost. Experimental data collected at PNL (Ref. 1) indicate a cost of approximately \$1.50 to destroy a pound of paper based on an electric rate of \$0.05/kWh. Operating cost will depend on the material to be treated, the cell coulomb efficiency, and the local cost of power. Capital cost data is not currently available.

2.4.2 Persulfate Process

The persulfate process is being investigated at LLNL primarily for the purpose of destroying chemical warfare agents (CWAs). It consists of a coupled direct-chemical-oxidation process in which the organic fraction of an aqueous waste is alternately subjected to catalyzed peroxydisulfate ("persulfate") and catalyzed hydrogen peroxide (Fenton's reagent) in an ambient temperature, closed system (Ref. 9). The alternating treatment is designed to destroy the weaker bonds with the less expensive Fenton's reagent, while the more expensive reagent (persulfate) is used to destroy the more resistant species. Membraneless bipolar cells are used for electrolysis of sulfate to peroxydisulfate ion which is a very strong oxidizer. The process for making peroxydisulfide ion is commercially available and using it to raise the valence of a mediator ion to destroy organics has been demonstrated on a laboratory scale. The persulfate is produced by the following reaction with incidental production of hydrogen peroxide at an oxygen depolarized electrode (Ref. 10):

Sulfate resulting from the persulfate reaction is recycled through the electrolysis cell, and persulfate and H_2O_2 are coproduced by electrolysis of the sulfate solutions. Distilled water from the reaction, and tramp water, are secondary wastes. Studies of the oxidation of organic ion exchange resins and other wastes indicate that most (90 to 95%) of the intermediate species arising in the oxidation of chemical warfare agents can be oxidized using Fenton's reagent. Thus, the overall reaction kinetics for chemical warfare agents are such that 90% of the oxidation may be accomplished by low-cost commercial peroxide (Ref. 10). Tests have shown 98 to 99% of the surrogates used for chemical warfare agents (CWA) detoxification were oxidized to CO_2 in 3 minutes with commercially available peroxydisulfate salts.

Use of peroxydisulfate salts as an oxygen source produces a very large waste stream of sulfate and sulfuric acid which can be recycled for electrolytic regeneration of the peroxydisulfate. However, methods for the removal of byproducts containing phosphorus and halogens need to be developed.

The applicable waste streams include concentrated or dilute halogenated and nonhalogenated organic liquids, CWAs, and ion-exchange media. This process is currently at the laboratory-scale level of testing and additional design or destruction data is not available. The goal is to achieve economic destruction of CWAs in an ambient temperature, totally contained process with no secondary waste streams other than distilled water, CO_2 offgas, and inorganic components of the waste feed.

2.4.3 Technology Comparison

Since electrochemical oxidation is an aqueous process, it is primarily applicable to mixed wastes that are soluble in the electrolyte. However, insoluble liquids can be treated by emulsifying and dispersing them in the electrolyte using mechanical mixing or ultrasonic devices. Solid wastes can also be treated after size reduction and by agitating the solution. This technology is not suitable for destroying all types of organics. Plastics and other highly polymerized organics may be attacked by the oxidizer, but at very slow rates.

As an alternative to incineration, this process has some advantages:

- The process operates at low temperature thereby reducing the possibility of volatilizing and discharging unreacted waste and noxious offgases.
- The process operates at atmospheric pressure.

- The process can be stopped quickly by turning off power to the cells.
- Nearly the same operating conditions can be used for a wide variety of organic materials negating the need for process modifications as the waste stream changes.
- Tests indicate little or no volatilization of low molecular-weight species formed as intermediates during the reaction.

Potential problems with the Ag(II)/HNO_3 process include precipitation of Ag as a halide salt by anions liberated by the destruction of halogenated organics. However, a silver recovery concept has been developed. Problems with electrochemical oxidation in general include excessive corrosion of the anode in the presence of concentrated acids; generation of HNO_2 and NO_x at the cathode when nitric-acid solutions are used; leakage of cations and anions through the electrode separator; and rupture, fouling, chemical attack, and radiation-induced degradation of polymeric membrane separators. In addition, MEO is more expensive than other treatment methods such as biological treatment and incineration.

2.4.4 References

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Mixed Oxidants (MIOX) Process

Description The Mixed Oxidants (MIOX) process generates a mixed oxidant solution electrolytically from a sodium chloride brine. The uniqueness of this system is the patented method of separating the solutions generated at the anode (oxidants) and at the cathode (reductants) before substantial recombination can occur. The anode solution contains a mix of oxidants (chlorine, hypochlorite, and ozone) rather than solely hypochlorite, which would be the case if the flows were allowed to recombine. The anode solution containing the mixed oxidants is then injected into raw water for the purpose of organic destruction or disinfection. (Company literature provided by the Mixed Waste Working Group of the Western Governors Association)

Waste Treated Aqueous waste containing pathogenic organisms, and a wide range of industrial wastes such as VOCs, aromatic hydrocarbons in fuel, and cyanides. The process is also being suggested for the passivation of uranium metal and uranium hydride in spent nuclear fuel or metal shavings. The concept is to react the surface of the uranium or UH_3 particles with the mixed oxidant solution to produce a safe oxide and prevent pyrophoric reactions with the air.

Residue Hydrogen and sodium hydroxide from the electrolysis of NaCl. The mixed-oxidant solution produces from 20% to 50% of the total trihalomethanes produced by hypochlorite on an equal chlorine basis. Passivation process water containing radionuclides.

State of Development This process has been patented, commercialized and demonstrated by Los Alamos Technical Associates, Inc. (LATA) for treatment of wastewaters. The passivation application has been tested at LANL on uranium chips/shavings, and requires further testing and demonstration.

Cost Data Not available at this time.

Issues Organic destruction efficiencies and reaction by-products need to be determined for DOE wastes.

25 PHOTOLYTIC ULTRAVIOLET DESTRUCTION PROCESSES

Photolytic reactions (reactions induced by exposure to light) can destroy certain hazardous organic wastes at room temperature. In general, the processes require the UV light source to emit wavelengths in the regions absorbed by either the contaminant to be destroyed or an oxidant and/or catalyst to produce free radicals. While various systems differ in details, they share a common method of operation. Typically, they destroy the waste compounds through an indirect photochemical process that uses UV energy provided by a small number of high-energy lamps, or large numbers of low-energy lamps such as in the Ultrox unit, to photolyze either hydrogen peroxide or ozone to generate hydroxyl radicals ($\text{OH}\cdot$) in the bulk fluid. These radicals then react with the organic species in the water. One process, discussed later, uses UV energy and a catalyst to produce hydrated electrons which reduce organic contaminants.

Many organic compounds have broadband absorption characteristics in the absorption region of these oxidants. Thus, when UV radiation is used to produce $\text{OH}\cdot$, the UV radiation may also photolyze some organic contaminants, such as tetrachloroethane (PCE), aromatic halides, and pesticides thereby increasing their removal efficiency (Ref. 1). However, applications of these technologies in large-scale hazardous waste remediation has been limited, largely due to small throughput rates and an inability to completely mineralize the targeted wastes. For aqueous waste streams, these problems have been partially addressed by using indirect photochemical reactions involving a highly reactive oxidant and/or catalyst. Although UV oxidation processes are being used to destroy VOCs in soil and contaminated water, the best application of this technology appears to be for final treatment of dilute solutions of organic compounds.

UV light-induced oxidation of organic contaminants in an aqueous waste stream has been commercialized and is under investigation by the EPA and at several DOE facilities to determine its applicability to specific waste streams. Several processes can be found that use UV radiation; the differences lie in the use of different wavelength light sources and different oxidants or catalysts. Light sources typically include mercury, xenon, and excimer lamps, and potentially excimer lasers. However, due to the high cost of laser systems, those companies that have investigated this technology have reverted to high-energy UV lamps (Ref. 2). Hydroxyl radicals are generated through UV photolysis of various oxidants such as H_2O_2 , O_3 , or Fenton's reagent. In addition, catalysts and other energy sources, such as heat and hydrodynamic

cavitation, are used to enhance the production of $\text{OH}\cdot$ or hydrated electrons and the destruction of organic bonds.

Several photolytic processes are applicable primarily to destruction of organics in the vapor or gas phase. These systems will be discussed in Section 6. The processes described in this section are applicable to destruction of dilute organics in an aqueous phase.

2.5.1 Oxidizer Enhanced

In a photochemical reaction, only the light absorbed is effective in producing a photochemical change. Therefore, there must be an overlap between the emission spectra of the light source and the absorption spectra of the reacting species, whether it be the oxidizing agent (H_2O_2 or O_3) or the organic substance to be destroyed.

Low-pressure mercury-vapor UV lamps are typically used in commercial applications because of their low cost and long life. However, the dominant emission wavelength is about 254 nm, whereas the maximum absorptance by H_2O_2 occurs at 220 nm. Also, the molar extinction coefficient of H_2O_2 is low at 254 nm so that a high concentration of H_2O_2 is required to generate sufficient hydroxyl radicals. However, an excess of H_2O_2 is harmful because it can scavenge the hydroxyl radicals that were formed to react with the organics present. UV photolysis of O_3 is not expected to have the same limitations with these lamps because the molar extinction coefficient of O_3 is 170 times that of H_2O_2 at 254 nm (Ref. 1). However, the solubility of ozone in water is only 70 ppm (Ref. 3) which would be the upper limit for producing hydroxyl radicals. Thus, the application of ozone to streams containing reasonably high concentrations of organics is not practical, and large-scale destruction of organics is better accomplished by photolysis of H_2O_2 because it is fully miscible with water and commercially available in concentrations up to 70%.

To overcome the limitations with H_2O_2 and O_3 , some technology developers (e.g., Purus, Inc.) use xenon lamps which emit higher intensity, shorter wavelengths more readily absorbed by organic contaminants and H_2O_2 . The broadband emission of xenon lamps in the UV region (240 to 300 nm) can excite most simple organic compounds to enhance their reactivity with oxidants. In addition, the higher intensity of the Xe lamp in the region near 230 nm will decompose H_2O_2 into $\text{OH}\cdot$ more effectively than the Hg lamp (Ref. 4). However, the main application of this system is currently for organics in a vapor or gaseous state. LLNL is attempting to extend this technology to higher concentrations of hazardous organic materials in

aqueous streams by developing reliable lamps that produce the proper wavelength for either direct activation of organic molecules, and/or very high efficiency conversion of H_2O_2 to OH radicals (Ref. 3). Direct photolysis applied to an aqueous stream would require a high-intensity, broadband light source to break the bonds of the variety of organic compounds in DOE waste streams, or the light source would have to be tailored to specific compounds, and would require a wavelength that is not readily absorbed by the window material or water.

In addition to the lamp wavelength, adjustable operating parameters include hydraulic retention time, oxidant dose, radiation intensity, pH level, and gas-to-liquid flow rate ratio (Ref. 1). In general, increasing the retention time will increase destruction efficiency up to an equilibrium value. Increasing the retention time beyond this point will not increase the treatment efficiency.

Increasing the oxidant dose generally increases the destruction efficiency. However, there are limitations. Excess hydrogen peroxide can act as a free radical scavenger, thereby decreasing the hydroxyl radical concentration. Ozone can react directly with hydroxyl radicals consuming both ozone and radicals. Also, ozone and $\text{OH}^\bullet$ may be consumed by scavengers in the water to be treated. Therefore, the optimum proportion of oxidants for maximum destruction or removal efficiency cannot be predetermined, but must be determined by tests on a case-by-case basis.

Low pH will decrease the concentration of carbonate and bicarbonate scavengers by shifting the equilibrium toward carbonic acid. However, if carbonate and bicarbonate alkalinity is low, high pH should improve the treatment efficiency by increasing hydroxyl radical formation. If ozone is used as an oxidant, the gas flow rate can also influence the treatment rate (Ref. 1). The ratio of gas flow rate to liquid flow rate dictates the hydraulic characteristics of the reactor. At low gas-to-liquid flow rate ratios, the mixing regime in a reactor is close to that of plug flow; whereas, at high ratios the mixing regime is close to that of a mixed reactor. Since plug flow mixing characteristics produce higher treatment rates for reactions with a positive reaction order, low gas-to-liquid flow rate ratios should be used. In addition, a low gas-to-liquid flow rate ratio minimizes stripping of VOCs.

In the following sections, descriptions of systems using various oxidants and energy sources are provided along with the results of system tests.

2.5.1.1 Technology Description

UV/Ozone

Photolysis of aqueous ozone produces hydrogen peroxide and subsequently hydroxyl radicals in a chain reaction. As a result, compounds normally refractory to ozonation alone may be rapidly converted to CO₂ and water. PCBs, which are very stable to ozone, are rapidly destroyed to less than 0.1 ppm with UV and ozone. This process has been specified by the EPA as Best Practicable Control Technology Currently Available for the treatment of PCBs in water (Ref. 5). However, only one commercial system, marketed by Solarchem Environmental Systems (Ref. 6), has been found that uses only ozone as the oxidant. Most systems that have been commercialized, and that are being developed and tested by DOE laboratories and EPA use direct photolysis, H₂O₂, or a combination of H₂O₂ and ozone as oxidants. This is because the hydroxyl radical typically has a reaction rate constant 10⁶ to 10⁹ times that of ozone (Ref. 6).

Based on operating cost, the use of ozone can be attractive, especially for waters with high UV absorptance. However, capital cost, stripping of volatile contaminants, ozone destruction, and health, safety, and environmental considerations can make ozone less desirable than other oxidants. One case where ozone is cost effective is in the destruction of trinitrotoluene (TNT) contaminated water (Ref. 6). The treatment of TNT with UV/peroxide generates a toxic byproduct, trinitrobenzene (TNB), which is refractory and difficult to treat. UV/ozone treatment of water contaminated with TNT can avoid the production of TNB.

UV/H₂O₂

UV photolysis of H₂O₂ generates OH•. Studies have shown that this system can destroy a wide variety of hazardous compounds in water at low-concentration levels (Ref. 5) including aromatic and haloaromatic compounds, chloroalkenes and alkanes, ethers, alcohols, carboxylic acids, and ketones (Ref. 6). Organic chlorine in chlorinated aliphatic compounds has been converted to chloride ion, indicating destruction of the chlorinated structures. In the case of aromatic compounds, many intermediates are formed which could be eliminated by extending the residence time in the reactor. It has been found that the oxidation rate increases with increasing hydrogen peroxide, up to a point where excess peroxide scavenges hydroxyl radicals, and decreases with increasing organic concentration.

This technology has been commercialized by Peroxidation Systems, Inc., Purus, Inc., Solarchem Environmental Systems, and several national laboratories have used these

commercial systems, or modifications thereto, to perform tests and evaluations of the technology on waste streams of interest to DOE.

Peroxidation Systems, Inc.

The Peroxidation reactor is annular in configuration with the lamp in the center and the waste stream circulated through the annular region around the lamp. The lamp is a medium-high pressure, broadband, mercury-arc lamp. Several lamps may be used in series as shown in Figure 2-11 (Ref. 1), and lamps are available with different power levels, depending on the application. Hydrogen peroxide may be injected at multiple points to make it available throughout the reactor. Peroxidation systems range from small, straight-through designs operating at less than 100 gpm and approximately 30 kW, to large systems operating at over 5,000 gpm with recycling and over 800 kW (Ref. 7).

Figure 2-11. Schematic of PSI UV/Oxidation System

Although most contaminants are rapidly destroyed by hydroxyl radicals, some compounds, such as low molecular weight chlorinated alkanes, are resistant to $\text{OH}^\bullet$ attack and require large systems with recycling to achieve adequate destruction, or direct photolysis. W.J. Schafer Associates, Inc. has developed a new surface-discharge (SD) UV lamp that generates two to four times the UV energy with the same electrical input as conventional high intensity UV lamps. Much of this UV light is generated below 250 nm where it has enough energy for direct photolysis of chlorinated alkanes. This lamp was integrated with the Peroxidation system and tested on groundwater at the K-25 site at Oak Ridge National Laboratory (ORNL) in 1993 (Ref. 8) resulting in a factor of two increase in the destruction rate of TCA over destruction by $\text{OH}^\bullet$ radicals. A combination of UV peroxide with UV photolysis can be effective for aqueous wastes containing a variety of organic contaminants, and can decrease the treatment cost by a factor of two below the cost of a UV/peroxide system alone.

This SD lamp uses a pulsed plasma discharge along a dielectric surface between two electrodes and produces UV light from the dielectric material that is generated in the plasma. The radiant emission from the surface discharge can be enhanced in a specific spectral region by choosing a substrate material with constituents that have emission lines in the desired region. A gas recirculation system is required to filter and cool the gas from the discharge region, and a liquid cooling system is required to cool the electrodes and substrate.

Purus, Inc.

Purus, Inc. uses pulsed xenon arc-lamps which are more efficient than Hg lamps for direct photolysis of organics in the vapor or aqueous phases, and more efficient in decomposing H_2O_2 in the aqueous phase. This system is used for destruction of organics in both the vapor and aqueous phases (Ref. 9). Vapor-phase organics may be produced by vapor extraction from soils or groundwater, air stripping from groundwater, or thermal desorption of soils.

The UV source is a xenon arc-lamp that operates in a pulsed mode. The company reports that the source is intense enough to destroy highly stable compounds including carbon tetrachloride, and destruction is 50% faster than other systems (Ref. 10). Problems with fouling the lamps are minimized by a mechanical wiping device that cleans the lamp's surface twice a day. The pulsed mode of operation reduces the total input cost by converting over 20% of the electrical energy into UV energy in the spectrum below 300 nm. The system is reported to be suitable for destroying organics in aqueous waste in concentrations less than 500 ppm. It can process hundreds of gallons per minute, depending on influent concentration, effluent concentration requirements, and the rate of reaction with water.

Solarchem Environmental Systems

This company markets various treatment processes based on UV oxidation chemistry, including the UV/ H_2O_2 process; the option selected depends on the particular contaminants to be treated and the characteristics of the water. Solarchem has developed a proprietary, 30 kW high-temperature mercury lamp with over 30% efficiency. The lamp has 30% of its output between 200 and 300 nm, and a wiper is used periodically to clean the quartz sleeve.

One variation on the UV/ H_2O_2 process is the UV/visible/peroxide process for waters with a high background UV absorptance (i.e., COD > 500 ppm). Peroxide is a relatively weak absorber in the 200-300 nm wavelength band and, in waters with high COD, the H_2O_2 must compete with other UV absorbers for photons (Ref. 6) and the production of $\text{OH}^\bullet$ becomes less efficient. Solarchem has developed a proprietary catalyst that strongly absorbs both UV and visible light from 200 to 500 nm thereby making more use of the lamp energy. Absorbing the

radiation, the catalyst is excited to a higher energy level. The excited catalyst reacts with the peroxide to produce hydroxyl radicals and is de-excited to its ground state.

UV/Ozone/H₂O₂

A combination of UV radiation, ozone, and hydrogen peroxide is used by Ultrox International to oxidize organics in water. The major components of the system are the UV/oxidation reactor module, hydrogen peroxide feed system, and catalytic ozone decomposition (Decompzon) unit (Figure 2-12). The UV/oxidation reactor is available in various sizes. The unit used in an EPA SITE program (Refs. 1 and 11) had a reactor volume of 150 gallons which was divided into 6 chambers with three 65-watt UV lamps per chamber (Figure 2-13). Each chamber had a sparger to uniformly diffuse ozone gas from the base of the reactor into the water. Hydrogen peroxide was added to and mixed with the contaminated water in the influent line. The Decompzon unit uses a nickel-based proprietary catalyst to decompose ozone to oxygen in the reactor offgas.

The maximum initial concentration of organic material is 10,000 ppm with a system throughput dependent on the compounds to be treated and the final decontamination level required (Ref. 12). Typical throughputs vary from less than 10 gpm to over 1,000 gpm.

Tests have shown that in the Ultrox system using ozone, stripping is a significant removal method for those compounds that are difficult to oxidize. However, though the Decompzon unit's primary function is to remove ozone, significant removal of VOCs also occurred. For example, the Decompzon unit removed TCE, 1,1-DCA, 1,1,1-TCA and vinyl chloride (present in the reactor offgas at levels of approximately 0.1 to 0.5 ppm) to below detection levels (Refs. 1 and 11).

Oxidation using the Ultrox system has been tested in a full-scale plant at the DOE Kansas City Plant for treating groundwater contaminated with TCE and other chlorinated VOCs (Ref. 11). In addition to VOCs, the contaminated groundwater contained bacteria, suspended solids, iron, manganese, and oil and grease at levels that would reduce the effectiveness of the operation. Results indicated that the effluent from the system met applicable discharge standards, nitrogen (as ammonia and nitrite) was oxidized to nitrate, and about 98% of the bacteria was removed. However, very little of the oil and grease was removed, and precipitation of the iron and manganese within the system caused plugging of the ozone spargers and coating of the UV lamps. This indicates that effective pretreatment of the waste stream is required for proper, long-term functioning of the system and to minimize downtime and maintenance requirements.

Figure 2-12. Isometric View of the Ultrox System

Figure 2-13. Ultrox System Flow Diagram

UV/Fenton's Reagent

The hydroxyl radical can be efficiently generated from H_2O_2 and catalysts such as transition metal ions without an external energy source, such as UV radiation. One such system is Fenton's reagent in which H_2O_2 is decomposed into a hydroxyl radical and hydroxide ion in the presence of $Fe(II)$ ions. The use of Fenton's reagent to oxidize toxic organics began in the late sixties and has been widely applied to the treatment of hazardous organic compounds (Ref. 5). The major advantages of Fenton's reagent as a hazardous waste treatment technology are: 1) there are no chlorinated organic compounds formed during the oxidation process as in chlorination or ozonation; 2) both iron and H_2O_2 are cheap and nontoxic; 3) there is no mass transfer limitation due to its homogeneous catalytic nature; and 4) there is no external energy source required as a catalyst so the reactor system is much simpler.

Fenton-type reactions can also be enhanced by light at wavelengths >300 nm in acidic solutions of $Fe(III)$ and H_2O_2 by photoreduction of $Fe(III)$, photolysis of an $Fe(III)$ peroxide compound, and photo-oxidation of ferric-coordinated organic compounds. These processes produce OH radicals directly or indirectly, or contribute to oxidation of the organic (Ref. 13). Batch studies at LLNL on powdered fibrous cellulose indicate that Fenton's reagent will enhance the destruction efficiency of insoluble fibrous cellulose (Ref. 14). Solarchem Environmental Systems markets a process using UV/Fenton chemistry and reports up to a 5-fold enhancement in treatment rate for aromatic and olefinic compounds (Ref. 6).

Laser-Induced Photolytic Oxidation

This technology is the same as UV/ H_2O_2 oxidation except that the UV light is generated using an Excimer laser. The organic compound and H_2O_2 both absorb the beam energy, which makes them reactive. The technology as developed by UV Technologies (formerly Energy and Environmental Engineering, Inc.) is reported to reduce saturated concentrations of organics in water to nondetectable levels (Ref. 15). The system operated by UV Technologies for EPA's SITE program was able to treat a solution containing 32 ppm of TOC at a rate of 1 gpm. Typically, contaminated groundwater is first pumped through a filter unit to remove suspended particles. Reaction products were CO_2 , water, and a halogen acid if halogenated hydrocarbons were treated.

UV Radiation with Hydrodynamic Cavitation (CAV-OX Process)

The CAV-OX process (developed and patented by Magnum Water Technology) uses the synergistic effects of hydrogen peroxide, hydrodynamic cavitation, and UV radiation to produce hydroxyl radicals and oxidize organic contaminants and cyanide in aqueous waste streams (Ref. 16). This technology induces hydrodynamic cavitation through the shape of its cavitation chamber which causes pressure variations in the flowing fluid. The waste stream can be recycled through the cavitation chamber to control the hydraulic retention time before it is transferred to the UV reactor (Figure 2-14). The UV reactor houses low-pressure mercury-vapor lamps housed in UV-transmissive quartz-tubes. Two systems are manufactured: the low-energy CAV-OX I system containing six 60-watt lamps per reactor; and the CAV-OX II system containing two UV reactors with one lamp each and operating at 2.5, 5.0, 7.5, or 10 kilowatts.

Figure 2-14. The CAV-OX Process

The process is designed to treat aqueous waste contaminated with organic compounds. It cannot handle free product or highly turbid waste streams because they lower the efficiency of the UV reactors; although the cavitation chamber is unaffected by these conditions. Test results indicate that scaling of the quartz tubes has not occurred in these systems. These systems are available in various sizes from less than 10 gpm to 250 gpm, and can be grouped in modules and operated in parallel for large applications.

2.5.1.2 Input and Output Stream Characteristics

Photolytic and UV oxidation systems are generally designed to remove organic pollutants in plant process water, groundwater, and drinking water to below regulatory requirements. These systems are generally limited to waste streams that have been diluted or wastes pretreated by other means to allow for sufficient penetration of the UV light and to remove contaminants that might cause scaling or fouling of the UV windows. Typical removal characteristics would lower contamination levels from 10 ppm in the influent down to 0.5 ppb in the effluent. However, some systems are being developed to accept influent streams with contamination levels up to 10,000 ppm. In general, the processes cannot handle free product or highly turbid waste streams, because these conditions tend to lower the efficiency of UV reactors. Reaction products are primarily carbon dioxide and water; however, when treating hydrocarbons with a halide, sulfur, or phosphorous the corresponding anion will be produced in the effluent.

The contaminant removal efficiencies depend on the type of contaminant to be treated. For example, organics with double bonds, such as TCE, PCE, and vinyl chloride, and aromatic compounds are easily removed because they are easily oxidized. In systems that use ozone, organics without double bonds and with high Henry's law constants are also removed. However, since they are difficult to oxidize, removal is most likely due to stripping. Organics without double bonds and with low Henry's law constants would be difficult to remove because they are not easily oxidized or stripped (Ref. 1). In general, VOCs have not been found in the offgas from these systems; with ozone as a stripping agent VOCs have been destroyed in the ozone destruction unit.

Any species in the waste stream that scavenges the oxidants diminishes the ability of the system to destroy the organic contaminants. Such scavengers include anions such as bicarbonate, carbonate, sulfide, nitrite, bromide, and cyanide. Metals present in their reduced state are likely to be oxidized to a more toxic form (e.g., trivalent chromium to hexavalent chromium), or to a less soluble form which may precipitate and cause scaling of the UV lamp or window, or produce suspended solids. Suspended solids and oil or grease will reduce UV transmission and may foul the windows, thereby decreasing the treatment efficiency. Thus, pretreatment may be required for proper functioning of the UV/oxidation system depending on the waste characteristics.

2.5.1.3 Technology Status

UV photolytic oxidation is a well-developed technology that is available from several manufacturers at the commercial scale for various applications. These systems may be modularized and skid mounted for portability, and range in size from a few gallons per minute to several thousand gallons per minute throughput.

Most of the developed systems have been tested at the pilot- or full-scale level as part of EPA's SITE program and are continually being improved upon. Peroxidation Systems, Inc. has fielded over 40 systems for groundwater and wastewater treatment, and was tested in an EPA pilot-scale study at a site on the Aberdeen Proving Grounds in Maryland (Ref. 1). This system is also being studied at the bench-scale at LLNL (Ref. 3 and 4), and an improved surface-discharge lamp is under development (Ref. 8). Ultrox International has fielded several pilot and full-scale systems, and was tested as part of EPA's SITE Program (Ref. 11 and 12). Several case studies are described in Reference 11, including the results of testing a 725-gallon unit at the DOE Kansas City Plant. Solarchem has over 50 installations at industrial facilities and superfund sites, with several case studies described in Reference 6.

The CAV-OX process has been tested at several private and public sites and was accepted into the SITE Demonstration Program in 1992 with a demonstration at Edwards Air Force Base (Ref. 16). Recent tests at a Superfund site treated leachate containing 15 different contaminants. In other tests, the process has successfully treated cyanide contamination. Two small systems are being used to treat gasoline contaminated groundwater at gas stations (Ref. 17).

The system developed by Purus, Inc. has been used for treating contaminated groundwater and wastewaters, and for destruction of organic vapors. Purus has been working with ANL to investigate treatment of vapor-phase organics derived from soils by the soil vapor extraction process in continued demonstrations at DOE's Savannah River Site. The system was accepted into EPA's SITE Program in 1992 for a demonstration at LLNL. This demonstration involved treating trichloroethylene in the vapor phase at 200 to 350 cfm extracted from soil and groundwater using air stripping and vacuum extraction. The Purus system has also been tested on a bench-scale at LLNL for the destruction of Trimsol in water (Ref. 18).

The bench-scale Purus system used for treating Trimsol consisted of a 6-inch, 3,675 W pulsed-xenon lamp contained in a 7-cm-diameter, cylindrical quartz housing concentric to the reactor cylinder, leaving an effective light pathlength of 9 cm through the solution. Trimsol was diluted to 25% v/v in water and flowed through the reactor at 14 ml/hr. The sum of TOC and

TIC (HCO_3^-) accounted for 73% of the TOC added; a thin oil film was detected on the top of the water at the end of the reaction which may account for the missing TOC. These tests demonstrated the ability to destroy 2 to 3 grams per hour of TOC derived from Trimsol.

The laser-induced photolytic oxidation technology developed by UV Technologies was accepted into the SITE Emerging Technology Program in 1987. However, laser systems were found to be too expensive to operate, and the vendor abandoned this technology in favor of high-power mercury lamps coupled with a photocatalyst (Ref. 2). With new lamps having a power output of 3 kW/ft and H_2O_2 as the oxidant, the flow rate was increased to 100 gpm. This company is attempting to address higher contaminant concentrations on the order of 100 to 1,000 ppm. This technology is currently capable of performing treatability studies but is not yet at the pilot scale.

To successfully convert mixed waste containing hazardous organics to low-level radioactive waste, the UV photolysis process must convert all the toxic organic compounds to nontoxic compounds (i.e., all carbon atoms converted to CO_2 , all hydrogen atoms to H_2O , and other nonmetallic elements to corresponding anions). However, this process has not yet been demonstrated as an incineration alternative for treating this class of mixed waste. Also, further research is needed on the effectiveness of dry or wet scrubbers for removing acidic photo-oxidation products, methods for pretreatment and post-treatment of undesirable products, and the possible use of shorter-wavelength UV lamps or catalysts.

2.5.1.4 Destruction Efficiency

UV/ H_2O_2

Tests using the Peroxidation Systems, Inc. process were performed at the Aberdeen Proving Grounds at a site containing VOCs, organosulfur compounds, and explosives in the range of 10 $\mu\text{g}/\text{l}$ to 500 $\mu\text{g}/\text{l}$ (Ref. 1). An 80-gallon reactor was used with four chambers each containing a 15-kw UV lamp. The tests were conducted at a flow rate of 15 gpm resulting in a retention time of 5 minutes. The test results are shown in Table 2-7 where, for most compounds, the effluent levels were below detection levels, and the removal efficiencies were greater than 82 to 99%.

Additional data for the Peroxidation system was obtained from company literature for bench-scale and full-scale tests and is presented in Table 2-8.

Table 2-7. Performance Data for the Peroxidation System (Ref. 1)

Compound	Influent µg/l	Effluent µg/l	Percent Removed
Chloroform	41	1.2	97
1,2-dichloroethane	22	<1.6	>92
1,2-dichloroethylene	195	<1.6	>99
Methylene Chloride	8	<1.1	>86
Trichloroethylene	21	<1.4	>93
Benzene	52	<2.0	>96
Thiodiglycol	477	<10.0	>97
1,4-Dithiane	200	<2.2	>98
1,4-Oxathiane	82	<2.14	>97
Benzathiazole	20	<3.47	>82
1,3,5-Trinitrobenzene	15	0.53	96

Table 2-8. Destruction Data From Peroxidation Systems, Inc. Literature

Contaminant	Influent µg/l	Effluent µg/l	Oxidation Time min.	Percent Removed
TCE	150	<1	0.3	>99.3
1,2-DCE	3480	<1	0.55	>99.97
PCE	24990	<1	1.5	>99.99
TCA	940	89	4.0	90
Methylene Chloride	2510	<20	4.0	>99
Phenol	100,000	<100	1.0	>99.9
Pentachlorophenol	5600	<0.1	1.5	>99.99
2,4,6-Trichlorophenol	2310	<0.1	2.0	>99.99
2,4-Dinitrophenol	250	<0.1	1.0	>99.96
Napthalene	891	<2	1.0	>99.7
Acenaphthene	205	<0.1	1.0	>99.9
1,2-DCA	5500	0.2	4.0	99.99
Dichloropropane	110	4	2	96.4
Benzene	12900	2	1.3	99.98
Toluene	7600	2	2	99.97
Ethyl Benzene	3000	0.6	2	99.98
Xylenes	18500	8	2	99.96

Bench-scale studies have also been performed at LLNL using a 2-kw mercury lamp to evaluate the performance of the UV/H₂O₂ oxidation process for treating water-soluble organics such as ethylene glycol, low-level waste oils such as Trimsol which is a water-dispersible lubricant, and cellulosic material (Ref. 4 and 14). Ethylene glycol was reduced to essentially zero TOC in approximately 80 minutes in 30% H₂O₂. Trimsol, which is a mixture of more than ten organic compounds, was substantially mineralized to nearly zero TOC. To maintain the dispersability of Trimsol in the water and prevent the immiscible components from separating, the pH of the solution was maintained above eight.

Water-soluble cellulosic material was destroyed to nearly zero TOC in approximately 120 minutes. It was found that Fenton's reagent doubled the destruction efficiency of water-insoluble powdered fibrous cellulose. However, the highest destruction efficiency achieved was only about 60%. This study indicates that the UV/H₂O₂ process can effectively mineralize the nonhalogenated organic compounds in aqueous waste streams; however, the process is much less effective for dispersible but insoluble organic liquids or insoluble fine-powdered celluloses (Ref. 14).

Tests with a 90kW Solarchem system at Kelly Air Force Base for the treatment of contaminated groundwater exhibited the following results (Ref. 6):

Contaminant	Flow Rate (gpm)	Influent	Effluent
DCE	130	1200 ppb	<70 ppb cis, <100 ppb trans
TCE	130	130 ppb	<5 ppb
Vinyl chloride	130	120 ppb	<2 ppb

The operating cost for this system was \$1.34/1000 gallons. Applying a 270 kW Solarchem system with an operating cost of \$1.98/1000 gallons provided the following results:

Contaminant	Flow Rate (gpm)	Influent	Effluent
1,1 DCA	250	60 ppb	< 3.5 ppb
DCE	250	300 ppb	<70 ppb cis, <100 ppb trans
PCE	250	200 ppb	< 5 ppb
Vinyl chloride	250	240 ppb	< 2 ppb

UV/Ozone/H₂O₂

The Ultrox system was tested in a pilot-scale study to treat groundwater at a site in San Jose, California (Ref. 1 and 11). The site was used for drum recycling operations and the

groundwater contained high levels of VOCs including TCE (280 to 920 $\mu\text{g/l}$), vinyl chloride (51 to 146 $\mu\text{g/l}$), and 1,2-trans-dichloroethane (42 to 68 $\mu\text{g/l}$). The system used a 150-gallon UV/oxidation reactor with 24 64-watt UV lamps. Several tests were performed in which the operating parameters were varied to determine the optimum operating conditions. These conditions were as follows: influent pH of 7.2; hydraulic retention time of 40 minutes; ozone dose of 110 mg/l; hydrogen peroxide dose of 13 mg/l; and all UV lamps operating.

Results at these operating conditions were total VOC removal of 90%, while removal efficiencies for TCE were about 98% and those for 1,1-DCA and 1,1,1-TCA were about 60% and 85%, respectively. Analysis of the treated water did not indicate the formation of new compounds. Because the Ultrox system treated groundwater by bubbling ozone through it, some VOC removal occurred due to stripping in addition to oxidation. The percentage of removal by stripping was high for 1,1-DCA and 1,1,1-TCA because these compounds are difficult to oxidize, whereas TCE and vinyl chloride were removed primarily by oxidation even though vinyl chloride has a higher Henry's law constant than the other compounds. Thus, for a UV/oxidation process using ozone, stripping is a significant removal pathway for compounds that are difficult to oxidize. Although these VOCs were removed by stripping and were present in the reactor offgas in measurable quantities, the ozone destruction unit (Decompzon unit) removed them from the offgas to below detection limits.

Other tests with a 150-gallon Ultrox system demonstrated removal levels of 98 to 99.9% of benzene, toluene, ethylbenzene, and xylene from groundwater (Ref. 11). Residence times and other operating parameters were not identified.

An 18 kW Solarchem system was used to treat pesticide contaminated water from a soil washing operation. The water contained 400-600 ppm of Dinoseb which was destroyed to less than 100 ppb in 1000 gallon batches using ozonation followed by UV peroxide treatment. Greater than 99.9% destruction of Dinoseb and other contaminants was achieved at an operating cost of \$40/1000 gallons (Ref. 6).

UV/Fenton's Reagent

Application of Fenton's reagent with UV oxidation of insoluble cellulose by LLNL was discussed previously. Other studies on the enhancement of Fenton-type reactions by UV light (a 300 to 400 nm fluorescent black lamp) have been performed on pesticides and halogenated hydrocarbons (Ref. 13). These studies demonstrated destruction of metolachlor, atrazine, and methyl parathion in less than 10 minutes; however, reaction products remained for up to 6

hours—except for methyl parathion, which was completely mineralized in 30 minutes. Halogenated aliphatic compounds, dioxins, and furans were also degraded.

Application of a Solarchem 60 kW system at a wood treating facility to treat PCP contaminated ground water resulted in the following: with an influent concentration of 1000 ppb, the PCP was reduced to < 100 ppb at a flow rate of 90 gpm, and to < 10 ppb at a flow rate of 30 gpm. The operating cost for this system was \$1.30/1000 gallons.

Laser-Induced Photolytic Oxidation

SITE tests on industrial groundwater indicated DREs greater than 95% for chlorophenol and phenol in 72 hours, and for chlorobenzene in 114 hours. A reaction time of 96 hours was required for 91% DRE for benzene (Ref. 15).

CAV-OX Process

The CAV-OX process was demonstrated at Edwards Air Force Base (Ref. 16) on groundwater containing TCE (1,475 to 2,000 ppb), benzene (240 to 500 ppb), toluene (8 to 11 ppb), and xylene (0 to 100 ppb). Several tests were performed varying the hydrogen-peroxide level and flow rate for the CAV-OX I system operating at 360 watts, and the CAV-OX II system operating at 5-kw and 10-kw. Both systems achieved up to 99.9% destruction of these compounds depending on the flow rate and H₂O₂ levels. For the CAV-OX I system, DREs of 99.9% were achieved at a flow rate of 0.5 to 0.6 gpm and H₂O₂ levels of 30 mg/l. The CAV-OX II system achieved over 99% destruction at flow rates of 1.5 to 2.0 gpm and 30 mg/l of H₂O₂. The lamp power had little effect on the results.

The CAV-OX process can treat organics such as benzene to nondetectable levels; others such as 1,1-dichloroethane are typically treated to 96% removal efficiencies. In addition, organisms such as salmonella and E. Coli are significantly reduced (Ref. 19). Data from Reference 16, using a 20 gpm CAV-OX I system with 36 low-pressure lamps (2,160 watts) are shown in Table 2-9.

2.5.2 UV Reduction

Halogenated alkanes, such as carbon tetrachloride, chloroform, methylene chloride, dichloroethane (DCA), TCA, pentachloroethane (PCA), and chlorofluorocarbons (Freons) are

Table 2-9. CAV-OX I Destruction of BTEX and TPH (Ref. 16)

Compound	Inlet Concentration ppb	Outlet Concentration ppb
Benzene	450	6.0
Toluene	44	1.9
Xylene	100	1.5
Ethyl Benzene	25.0	ND
TPH	0.8	ND

treated slowly with UV/oxidation (Ref. 6). Solarchem Environmental Systems has developed a patented UV/reduction process that they report is able to treat saturated halogenated organics with improved performance over UV/oxidation. This process involves the photochemical generation of hydrated electrons (e_{aq}^-) via a proprietary catalyst. The hydrated electron reacts with halogenated organics to generate inorganic halide ions with rate constants for chloroalkenes 1000 to 16,000 times greater than the hydroxyl radical. This process may also be effective in treating halogenated alkenes (e.g., TCE, DCE, and vinyl chloride).

Details regarding destruction efficiency, industrial applications, and cost were not available.

2.5.3 Catalyzed (TiO_2) UV Oxidation

2.5.3.1 Technology Description

In aqueous systems, complete mineralization of many organic compounds is possible when a sufficient $OH^\bullet$ flux is available *in situ*. The various UV treatment technologies described in the previous section produce quantities of $OH^\bullet$ on the order of $<10^{-12}$ M, whereas steady-state $OH^\bullet$ concentrations of the order of 10^{-9} M can be generated in aqueous solutions over immobilized particles of UV-irradiated titanium dioxide (Ref. 20). The illumination of TiO_2 in water with light of wavelength < 400 nm generates excess electrons in the conduction band (e^-_{cb}) and positive holes in the valence band (h^+_{vb}). At the surface, the holes react with either adsorbed H_2O or surface OH^- groups to form $OH^\bullet$ radicals:

Excess electrons in the conduction band react with molecular oxygen to form superoxide ions which further disproportionate to form more $OH\bullet$ radicals:

Thus, the efficiency of the UV/oxidation process can be increased with the addition of titanium dioxide catalysts. Studies have demonstrated that the addition of titanium dioxide can improve the efficiency and loading capacity of UV/oxidation systems dramatically, and increase the range of application of the system. Titanium dioxide excited by UV light generates hydroxyl radicals which break the carbon bonds, eventually degrading the organic material to CO_2 and H_2O , and halide ions if the molecule contains halogen atoms. In some cases, efficient destruction within 30 seconds to 2 minutes is achieved depending on the contaminant.

One practical problem in using TiO_2 as a photocatalyst is the "electron-hole" recombination process. In the absence of efficient electron acceptors, this process is very efficient. For high concentrations of organics or more refractive contaminants, additives that are electron acceptors such as hydrogen peroxide, ozone, ammonium persulfate, and potassium bromate may be added in small quantities (0.003 M) to inhibit the "electron-hole" recombination process and accelerate reactions (Ref. 21). The use of these additives may increase the processing rate within this system by 3 to 6 times. However, the destruction efficiency achieved for each of these additives depends on the organic contaminant. For some organics, the degradation rate was greater with potassium bromate than for ozone; whereas, for other organics the reverse was true. For 1,1,2-TCA the degradation rate was increased with the addition of ozone, but decreased with the addition of H_2O_2 (Ref. 21).

The rate of photocatalytic removal of organic compounds depends on various parameters such as initial concentration, pH, radiant flux, wavelength, mass and type of photocatalyst, type of photoreactor, and other material (such as metal ions) in the waste stream (Ref. 22 and 23). The rate of removal of pollutants increases with increasing amounts of TiO_2 up to a limit corresponding to complete absorption of photons. The removal of an organic compound was found to be slower at wavelengths > 290 nm than at wavelengths > 340 nm, despite the greater number of photons available. This is due to the direct photolysis of the contaminant at lower

wavelengths and the competition of resulting intermediate compounds with the primary contaminant at adsorption sites. Because of this, direct photolysis has a detrimental effect on photocatalytic degradation. Consequently, the wavelength range must be carefully chosen when using photocatalysis to decontaminate water (Ref. 22).

Since this method of treatment involves a surface, its efficiency decreases for low concentrations of pollutant, and the rate of degradation of a given pollutant can be modified by competition for the surface sites. This competition may be due to intermediate compounds and other organic or inorganic material in the waste stream.

In addition to the oxidation of water by the positive holes to produce $\text{OH}\cdot$, and the subsequent oxidation of organic material in an aqueous solution, the electrons, which are reducing agents, can react with oxidizing chemicals on the semiconductor surface (e.g., $\text{Hg}^{2+} + 2\text{e}^- \rightarrow \text{Hg}^0$). Investigations at Sandia National Laboratories/New Mexico (SNL/NM) (Ref. 23) on TiO_2 photocatalysis for treating water contaminated with dissolved metals and a variety of organics demonstrate a synergism between the oxidation and reduction processes, and efficient design must consider both processes. Thus, a dissolved metal in a positive valence state is reduced and usually plates out onto the photocatalyst in the form of dispersed metallic crystallites (Ref. 24), while simultaneous oxidation occurs to retain electroneutrality. Consequently, organics may be destroyed by photocatalytic oxidation while metals are removed by reduction.

The rate at which the organic material disappears depends on the nature of the organic compound and the metal in solution (Ref. 23 and 24). The presence of oxygen accelerates the disappearance of the organics, but the rate of oxidation is controlled by the rate of reduction of the metal. In some cases (e.g., Hg(II)) O_2 competes for conduction-band electrons thereby decreasing the reduction rate; however, when treating organics and metals simultaneously, dissolved oxygen may be necessary if the concentration of the metals is insufficient for complete oxidation of the organics. In these studies, the low molecular-weight acids, alcohols, and aldehydes produced reduction rates of Cr(VI) similar to those observed without organic material present. In contrast, EDTA, salicylic acid, and citric acid all produce rapid reduction. In addition, with the exception of phenol, all the singly substituted benzenes experienced only slight mineralization at the low pH used.

These results point out the need to characterize the waste stream, and the need to tailor the process characteristics for the contaminants present in order to achieve optimum destruction and minimize generation of toxic end-products.

2.5.3.2 Input and Output Stream Characteristics

The efficiency of the photocatalytic process depends on the various parameters identified above. As with noncatalyzed UV oxidation, the input stream must be filtered to remove suspended particulates and other material that may hinder the transmission of UV radiation, and radical scavengers must be eliminated. Nonhazardous organic material in the waste stream, as well as destruction intermediates and inorganics, may compete with adsorption sites, thereby affecting the destruction rate. Because the oxidation of organics and the reduction of metals are intrinsically related, detailed characterization of the waste stream is required to select the process parameters.

Toxic organic compounds found in contaminated groundwater can be decomposed by this process; however, the end-products tend to be other organic compounds which may, or may not, be hazardous depending on the original contaminants and the details of the destruction process (i.e., light intensity and wavelength, residence time, presence of oxidizing agents, solution pH, etc.). Although most simple small hydrocarbons are easily oxidized completely to CO_2 and H_2O , the reaction of larger, more complex compounds involves many intermediates and requires a much longer time for complete mineralization versus simple removal of the original compound.

During the reduction of heavy metals, the metals plate out onto the TiO_2 catalyst, thereby consuming the catalyst surface. These metals may be removed in a post-treatment step to allow recycling of the catalyst, or the catalyst with heavy metals becomes a secondary waste requiring treatment and/or disposal.

2.5.3.3 Technology Status

There is a significant amount of research being performed by university, EPA, and DOE researchers into photocatalytic treatment of wastewaters. Most of this is at the laboratory or bench-scale level to evaluate the process parameters and characterize the destruction process. However, there is some effort to commercialize this process, and there have been several pilot- or field-scale tests performed.

UV Technologies, Inc. is developing a technology using a proprietary light source and a photocatalyst with H_2O_2 as the oxidant to treat waste streams containing 100 to 1,000 ppm organic contamination. Details regarding the system and detailed test results regarding process efficiency, secondary waste products, and process parameters are not available.

Matrix Photocatalytic, Inc. was accepted into the EPA's SITE Emerging Technology Program in May 1991 (Ref. 23). Tests performed on a variety of organics including polychlorinated biphenyls (PCB); phenols; benzene, toluene, ethylbenzene, and xylene (BTEX); and others demonstrated conversion to CO₂ and water. Destruction typically occurred in 30 seconds to 2 minutes; however, complete mineralization took longer. Inorganics such as cyanide, sulphite, and nitrite are also oxidized. This technology has treated wastewaters with contaminants as high as 1000 ppm with effluent qualities as low as 5 parts per trillion. Extended field trials on BTEX, trichloroethane, and methyl tertiary butyl ether demonstrated an average treatment time of 60 seconds at a direct operating cost of \$1 to \$2 per 1000 gallons. Modular systems have been developed for high flow rates with capacity increments of 5 gpm.

The State University of New York at Oswego (SUNY) is developing a photocatalytic system to treat sediments contaminated with PCBs and other chlorinated organics. This system was accepted into the SITE Emerging Technology Program in 1993, and it will be demonstrated at a state superfund site in 1994. They are currently building a pilot-scale reactor to treat 1000 pounds of sediment. The system consists of three chambers which contain water. Contaminated sediment is delivered to chamber A, where it is agitated to allow separation of the suspended and bottom fractions. Titanium dioxide is added to the slurry and, as agitation proceeds, the suspended fraction is irradiated at the slurry-air interface. The suspended fraction is slowly discharged to chamber B, exposing the bottom fraction in chamber A. Following continued treatment in chamber B, the suspended sediment fraction is discharged to chamber C for continued treatment and eventual discharge. Once the bottom fraction in chamber A is adequately treated, it is also removed for further treatment or disposal. Experiments with this process reduced PCBs in sediments by 62% and 68% after 4 and 6 hours of sunlight irradiation, respectively. Costs are estimated at < \$300 per ton of sediment (Ref. 26).

Laboratory and small field-scale tests have been performed by the National Renewable Energy Laboratory (NREL) using sunlight as the UV source (Ref. 27 and 28). Previous tests have demonstrated that the photodestruction reaction is more efficient at lower light intensities so that current tests have been with nonconcentrating solar collectors.

Three different solar systems designed to treat 100,000 gal/day at a constant flow rate of 70 gpm with 24 hr/day operation were tested at LLNL (Ref. 27). Pumping 24 hrs/day requires designing several days of retention time into the system to accommodate several days of poor weather. In these tests, the photocatalyst was supported on a small buoyant pellet about 1/8 inch in diameter, and the catalyst was recovered from the treated water and recycled to the photoreactor inlet.

A flat-plate solar collector was also tested on groundwater contaminated by jet fuel at Tyndall Air Force Base (AFB), Florida (Ref. 28). This system used powdered TiO_2 and 3% H_2O_2 and was generally tested on sunny days. The destruction levels of BTEX was typically 50% to 75% over 3 hours, and the addition of peroxide almost doubled the observed rate of destruction. However, total organic carbon was unchanged during this period, indicating that the parent compounds were destroyed, but complete mineralization did not occur. Catalyst reuse tests showed that the activity dropped rapidly after the first test due to large amounts of organic material on the catalyst surface. This material could block light from reaching the catalyst surface, capture the photogenerated OH radicals, or both, thereby preventing degradation of the BTEX compounds.

2.5.3.4 Destruction Efficiency

DREs depend on a variety of parameters, as previously defined, including the design of the photoreactor. Consequently, they have little absolute meaning and each case of waste stream and treatment system must be tested to determine applicability. DREs for specific systems and applications were provided in the previous section and the results of several tests are provided here.

In tests on the photodegradation of 40 ppm of 2,4-DCP, 60% degradation and 40% mineralization was achieved in 10 minutes using a UV lamp emitting in the 300-400 nm range (Ref. 21). The lamp was surrounded by a fiberglass sleeve coated with titanium dioxide (anatase), and the flow rate was 3 l/min in a recirculating mode. The destruction rate was 2.9 ppm/min. When ozone was added, the destruction rate was 40 ppm/min, destruction of 2,4-DCP was complete in 2.5 minutes, and mineralization was complete in 10 minutes.

Tests on TNT and RDX explosives (Ref. 29) indicated between 70% and 80% mineralization in about 300 minutes using a 100 Watt Hg lamp. Although the catalyst accelerated the mineralization of TNT and decreased concentrations of light absorbing reaction intermediates, other nonlight-absorbing intermediates were formed that were intractable to further degradation. However, if the reactor was purged with nitrogen during the photocatalytic reaction to produce anaerobic conditions, no light-absorbing or intractable intermediates were formed, and greater mineralization of TNT was achieved. Aerobic photocatalytic degradation of RDX was achieved with little byproduct formation.

In laboratory tests on photocatalytic treatment of water contaminated with heavy metals and organics (Ref. 23), it was found that only those metals with half-reaction standard reduction potentials more positive than 0.3 V (vs. normal hydrogen electrode) can be treated using TiO_2 as the photocatalyst. Upon exposure to UV light for 40 minutes with salicylic acid as the reductant, nearly 100% of the gold(III), silver(I), mercury(II), and platinum(IV) were reduced to the metallic state onto the photocatalyst; and approximately 84% of the chromium(VI) was reduced to chromium(III), 50% of which stayed in solution and the rest precipitated. The presence of oxygen inhibited the reduction of silver, mercury, and platinum. Other metals such as copper(II), cadmium(II), and nickel(II) experienced little or no reduction.

In these studies, the salicylic acid disappeared at different rates depending on the oxidant used, and it disappeared only for those metals that were reduced. In the absence of either metals or oxygen, the acid remains unreacted; however, it disappears rapidly in the presence of O_2 alone. In the absence of O_2 , oxidation of salicylic acid is controlled by the rate of reduction and stops when the dissolved metal has been depleted. Although dissolved oxygen generally slows the reduction of metals by competing for conduction-band electrons, dissolved oxygen may be necessary for the simultaneous treatment of organics and metals if the concentration of metals is insufficient for the total destruction of the organic. The organic species also appears to have a profound effect on the reduction rate and the reduction in TOC.

2.5.4 Technology Comparison

Although processes such as $\text{H}_2\text{O}_2/\text{UV}$, O_3/UV and $\text{H}_2\text{O}_2/\text{O}_3/\text{UV}$ have been shown to be effective for treatment of contaminated groundwater, and no chemicals are added that produce secondary waste requiring extensive treatment, these technologies do have their disadvantages. Though these systems have proven somewhat successful at contaminated groundwater sites, they have encountered problems in treating water containing perhalogenated organics (Ref. 28). This is due to the resistance of carbon-halogen bonds to $\text{OH}\cdot$ attack at low temperature, in contrast to easily broken carbon-hydrogen bonds.

All of the photochemical processes suffer from the same weakness (Ref. 30). At low temperature, photo-induced reactions are not energetic enough to build the complex chain reactions that can result in the efficient destruction of waste molecules and products resulting from the initial reactions. This problem is magnified in condensed phases (such as liquid water), where relatively slow diffusion rates limit the interaction of the waste molecules and short-lived reactive radicals.

As indicated previously, solubility of gaseous ozone in the aqueous phase becomes the limiting factor when the processes involve ozone. Although H_2O_2 can eliminate this mass transfer problem, the decomposition of H_2O_2 by UV light generated by inexpensive mercury lamps is inefficient. The waste stream must be low in turbidity and solids to allow penetration by the UV light. Finally, the UV penetration depth is difficult to match to the size of the reactor due to absorption of the light by the glass window and the water since the reaction rate is directly proportional to light intensity. Excessive light intensity could be wasted by heating the water and/or the window, which in turn could cause fouling of the surface in contact with the waste stream.

It is generally inappropriate to treat large-volume, dilute streams with the high temperature, high pressure, or acid-digestion processes designed for higher concentration organics. Photo-reactive technologies that completely destroy undesirable dilute organics in water are attractive because they produce no secondary waste stream other than reaction byproducts. However, total oxidation would require all hydrogen and carbon to be converted to water and carbon dioxide for this process to be seriously considered as an alternative to incineration. Although this technology works well with simple, known contaminants, its applicability to complex mixtures is unknown. Oxidation rates for some classes of organics, such as haloalkanes, are unacceptably low. However, lamps that provide direct photolysis and catalysts that produce hydrated electrons and reduce such compounds have been developed. Although some organic species are easily destroyed by this process, they are rarely converted completely to carbon dioxide and water (at least not in a reasonable period of time), and hazardous compounds can be produced as a result. In addition, contaminant destruction is often monitored with little attention to complete oxidation of undesirable intermediates and products. Thus, more emphasis must be given to determination of the endproducts and material balances. Consequently, TOC in solution should be taken as a measure of the extent of the reaction, rather than disappearance of the initial compound.

Limitations are imposed by the ability of UV light to penetrate and destroy pollutants. At the current state of development, most systems are only useful for treatment of aqueous streams contaminated with less than 10% organics. They are restricted to low loading rates, particularly in turbid or opaque solutions or soil. The catalyzed processes have experienced problems with high susceptibility of the catalyst to degradation. Also, some harmless organics that are generated can cause competing reactions.

For these technologies to be successful, a thorough knowledge of the waste to be treated is essential. Systems developed for specific waste streams that have unvarying species and

concentrations lack the operational flexibility to accommodate changing stream characteristics extant in many waste treatment facilities. The choice of a particular system, and the optimum oxidant concentration, flow rate, and wavelength, will depend on the specific waste or range of wastes to be treated. These oxidation technologies cannot be used as generic destruction techniques; each waste stream to be treated will need some development work to verify the applicability of these oxidation technologies. Finally, there is little experience with mixed waste, and the fate of RCRA metals and radionuclides needs investigation.

The advantages of these technologies includes:

- Use of ambient conditions and mild solutions
- Processes are easily controlled
- For the intended wastewater streams (containing a few percent organics), this technology should easily satisfy most regulatory requirements
- Systems are usually skid-mounted and portable, permitting on-site treatment
- Only innocuous chemicals are added, none which are solid-waste forming
- They are "clean" technologies with minimum air emissions, as compared to thermal technologies. However, an offgas system will be required to ensure VOCs are not emitted with the CO₂.

2.5.5 Cost of Technology or Equipment

UV/oxidation processes are reported to be cost-competitive with other alternative treatments such as carbon adsorption. Capital costs for the Ultrox system have been estimated to range between \$70,000 to approximately \$260,000 (Ref. 11). Operation and maintenance costs may be as low as \$0.25 per 1,000 gallons treated, considering only oxidant and electrical costs, or may exceed \$17 per 1,000 gallons treated if extensive pretreatment is required.

UV Technologies indicates a cost of \$3 per 1,000 gallons for wastewaters containing 100 ppm organics and at a flow rate of 100 gpm using a UV lamp source (Ref. 14). However, for excimer laser systems, the operating costs were about \$10K to \$20K per month due to the need to replace optics, the inner cavity, and other parts after about 10⁹ pulses (Ref. 31).

Cost estimates were obtained for Peroxidation Systems, Inc. UV/hydrogen peroxide system which is capable of treating 10 ppm to produce an effluent with a contamination level of 0.5 ppb (Ref. 32). A 30 kW lamp system designed for flow rates of 5 to 35 gpm would cost about \$70K; a 800 kW lamp designed for flow rates of 5,000 gpm would cost about \$750K. Total actual costs for a CAV-OX I system ranged from \$1.46 to \$2.08 per 1,000 gallons treated; this included operating cost and capital cost of \$21,000 to \$61,000 amortized over 5 years (Ref. 17).

Costs for the Purus system used to treat Trimsol at LLNL were estimated (Ref. 18) to be about \$0.20/gram of TOC destroyed, assuming a price for H₂O₂ of \$0.0015/gram (\$0.68/lb of pure H₂O₂). This cost does not include lamp replacement, neutralization, water evaporation, and miscellaneous costs that will approximately double the overall cost. A total operating cost of \$45 to \$68 million was estimated to completely mineralize 30,000 gallons of Trimsol waste over a period of 5 years. To achieve this rate of destruction, a capital cost of \$20 million was estimated.

Some operating costs for specific applications of Solarchem systems were provided in previous sections. Methods to estimate the capital and operating costs of a Solarchem system are described in References 6 and 33.

The direct operating cost for the Matrix Photocatalytic system was \$1 to \$2 per 1,000 gallons treated during mini pilot-scale trials for the SITE Program (Ref. 24). Operating costs for treating PCB contaminated soils using a photocatalytic process were estimated to be approximately \$300/ton (Ref. 26). Cost estimates for the solar photocatalytic systems tested at LLNL ranged between \$5.00 and \$6.00 per 1,000 gallons treated (Ref. 27). The estimate for the system tested at the Tyndall AFB site was \$70 to \$100 per 1,000 gallons. This is due to interference in the destruction process by nontarget organics in the waste stream and the need to replace TiO₂ after every use. It was estimated that the nontargeted compounds increased the cost by almost an order of magnitude (Ref. 28).

2.5.6 References

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2.6 ULTRASONIC DETOXIFICATION

2.6.1 Technology Description

This process uses ultrasonic energy (high-frequency sound) waves to produce an alternating adiabatic compression and rarefaction of the liquid media being irradiated. During the expansion cycle, a sound wave of sufficient intensity can generate cavities, which grow gradually with each cycle. Upon reaching a critical size, the final compression part of the wave violently collapses the cavities, creating extremely high-local temperatures of up to 5000°C and high-local pressures up to 500 bars. In this environment, water is decomposed into extremely reactive hydroxyl radicals and hydrogen atoms which propagate outward into the surrounding fluid to react with organic material. During the subsequent cooling phase, these can recombine to form hydrogen peroxide and molecular hydrogen. Organic vapors within the collapsing bubbles are destroyed by direct pyrolysis. Inorganic compounds can be either oxidized or reduced.

The use of ultrasonic energy has been studied for many years for the promotion of chemical reactions. The application of ultrasonic radiation to the treatment of hazardous chlorinated organic wastes started in the early 1980s (Ref. 1). A U.S. patent was granted in 1984 for a process by which PCBs were detoxified by ultrasonic energy. Results reported in this patent and in subsequent tests in which small batch reactors with PCB-contaminated oils and soil samples were used showed DREs between 60% to greater than 90%. Recent tests at Argonne National Laboratory (ANL) show rapid and almost complete destruction of CCl₄, TCE, and triethylamine in water and/or soil, and for destruction of PCBs in soils and sludges (Ref. 2).

Tests on destruction of CCl₄ in water show that the destruction was strongly affected by the intensity of the ultrasonic energy applied, with the destruction rate increasing proportionally to the intensity. However, solution temperature or initial pH, or the addition of an oxidant (i.e., H₂O₂) had little affect on the destruction rate of CCl₄. On the other hand, in tests with TCE the addition of Fenton's reagent to the solution had a significant effect on the destruction rate of TCE with or without ultrasonic radiation, although the addition of ultrasonic energy increased the destruction efficiency and rate (Ref. 2). Figure 2-15 is a conceptual design for a process to treat groundwater with ultrasonic detoxification and can be adapted to treat other aqueous wastes. This is a simple process in which the contaminated groundwater is

directed into the ultrasonic chamber, which is sized to provide an adequate residence time to obtain the desired destruction efficiency for the contaminants. After treatment, the cleaned water may be reinjected into the ground. If catalysts are required to increase the reaction rate, these catalysts may need to be removed prior to discharge.

Figure 2-15. Schematic of Ultrasonic Groundwater-Detoxification Process

Decontamination of soils is accomplished by the intense shearing action produced by cavitation which causes the adsorbed molecules on the soil particles to desorb from the surface. In addition, the repeated rarefaction/compression cycles enhance diffusion of the organic molecules from the surface of the particles thereby enhancing desorption rates. The desorbed organics are then destroyed by the mechanisms described above for groundwater contaminants.

Tests at ANL on soils contaminated with CCl_4 indicate excellent desorption and destruction of the contaminant; however, additional unit operations are required to process soils (Ref. 3). In these experiments, soil consisting of medium-fine and coarse sand with 19% silty clay, was contaminated with a known amount of CCl_4 . These experiments showed that most of the organic material (approximately 80%) adsorbed onto the surface of the clay-type soils which are too small to settle in water. On the other hand, the coarse sandy soil which will settle out of water adsorbs only a small amount (20%) of the organic material. The contaminant can be washed from the settled soil and the resulting wash water treated ultrasonically, and

only the small fraction of the silt/clay materials suspended in the water needs detoxification. Thus, an ultrasonic system for the treatment of contaminated soils would consist of soil preparation, soil-water slurring, sedimentation, washing, and dewatering as indicated in Figure 2-16.

Of the process parameters investigated, the energy intensity and the solids concentration had the greatest effect on the desorption and destruction of the contaminant in the soil samples. There appeared to be an optimal combination of these two parameters. Other process parameters, such as the operating temperature and pH of the slurries, had insignificant effects on the soil detoxification.

2.6.2 Input and Output Stream Characteristics

Ultrasonic detoxification is a process for treating aqueous streams containing low concentrations of chlorinated organics and other RCRA components in soil and groundwater. Inorganics and radionuclides may be oxidized or reduced so they may remain in solution or precipitate out depending on the species.

The output streams consist of CO₂ in the offgas, and treated water and soils which may contain RCRA metals and radionuclides. Since the process takes place at ambient temperature, little or no VOCs will be present in the offgas. At this time intermediate products of organic decomposition have not been determined; however, it is expected that the reaction will go to completion so that little or no intermediate organic material will remain in the effluent.

2.6.3 Technology Status

This is an emerging technology that has been demonstrated at the bench-scale. The technical feasibility of this process has been demonstrated in small bench-scale batch units at ANL for the destruction of CCl₄, TCE, and triethylamine in water and/or soil, and for destruction of PCBs in soils and sludges (Ref. 1, 2 and 3).

Work is also proceeding at the University of Akron where the efficacy of the ultrasonic process has been demonstrated for the destruction of aqueous chloromethanes, chloroethanes, chloroethylenes, benzene, and toluene (Ref. 4). Westinghouse Hanford has contracted with The University of Akron to perform proof-of-principle experiments on simulated Hanford waste

Figure 2-16. Ultrasonic Process for Detoxification of a Contaminated Soil

and wastewater. In addition, The University of Akron is investigating a commercial application consisting of using ultrasonics, heat and pressure to decompose used tires (Ref. 5). Once the rubber is fluid it can be formed into other products or mixed with new rubber. The current capacity is 5 pounds per hour which is to be increased to 100 pounds per hour by late 1994; enough capacity to treat small items such as gaskets. Recycling tires will require 5,000 pounds per hour and significantly more development.

Currently there is no commercial industry using ultrasonics for organic destruction of waste in wastewater or soils, and very little development work is being performed to move this technology from the laboratory to the field. However, this technology appears to have significant potential for treatment of hazardous and mixed wastes. In addition to *ex situ* treatment of wastewaters and soils, ANL has developed a concept for *in situ* treatment of groundwater as shown in Figure 2-17. However, this concept will require extensive development, testing and demonstration.

2.6.4 Destruction Efficiency

Early experiments used a 375 W ultrasonic generator at 20 kHz frequency on sludges from a hazardous waste site containing an average concentration of 2.6% Aroclor 1242 and 3.3% Aroclor 1260 indicated that about 98% of the former and 63% of the latter were destroyed. Other test results from soil samples spiked with PCB (1260) oils indicated a DRE of 99% had been achieved (Ref. 6).

The work at ANL used a small sonication cell with an ultrasonic probe capable of reaching 500 W/cm² power intensity and 20 kHz frequency to decontaminate CCl₄ spiked water (Ref. 1). Most of the tests were run at 25°C since increasing the temperature had little or no effect on the destruction efficiency or the reaction rate. The results of these tests show an exponential decrease in CCl₄ concentration with time. Greater than 99% removal efficiency of the CCl₄ was achieved in these experiments in times on the order of 10 minutes. For an initial CCl₄ concentration of 130 ppm, the residual concentration decreased to about 5 ppm after 5 minutes of irradiation (see Figure 2-18), while for an initial concentration of 1.6 ppm, the residual concentration decreased to about 0.05 ppm within the same irradiation period. At higher initial concentrations of CCl₄, and within the same sonication period, greater amounts of contaminant were destroyed; however, the DRE was about the same.

In general, destruction begins when the applied intensity is above a critical level, and any increase in intensity will increase the sonochemical effect. Thus, residual CCl₄ decreases with

Figure 2-17. Schematic Diagram of a Sonication Well

Figure 2-17. Schematic Diagram of a Sonication Well

Figure 2-18. Decrease in CCl_4 Concentration vs. Sonication Period at a CCl_4 Concentration of 130 ppm

increasing power density, and Figure 2-19 shows the effect of power density on destruction rate (Ref. 1). However, the intensity cannot be increased indefinitely because with increasing power density the cavities may grow so large during rarefaction that the time available for their collapse is insufficient for effective coupling of the ultrasonic energy to the system.

Tests at ANL on soils spiked with equilibrium concentrations of CCl_4 indicate significant decreases in residual contamination in periods on the order of 10 to 20 minutes (Ref. 3). Figure 2-20 shows that an initial amount of CCl_4 of 55 mg/l decreased to about 11 mg/l with 6 minutes of ultrasonic irradiation, and an extended sonication period of 25 minutes resulted in a

decrease of CCl_4 to 0.5 mg/l or 1 ppm by weight of soil. Two parameters are of primary importance in soil/water detoxification; these are the energy intensity or power density as described earlier, and the dilution factor expressed as grams of water/gram of soil. For a given energy intensity and specified treatment level, there appears to be an optimum dilution factor that minimizes the time required for destruction of the contaminant. However, at high-power levels and low-dilution factors, a point is reached where soils can be crushed by the ultrasonic energy producing very fine particles and changing the characteristics of the mixture into a high-viscosity slurry. In such a case, the mixing capability of the system is decreased, thereby decreasing the detoxification efficiency and causing problems in returning the soil to the site.

Figure 2-19. Dependence of CCl_4 Destruction Rate on Power Intensity

Figure 2-20. Residual CCl₄ Concentration in Soil versus Sonication Time

The experiments at ANL indicate that the addition of oxidizing agents or catalysts had little or no effect on the destruction of CCl₄. However, the irradiation time for a given degree of destruction of TCE can be reduced by the addition of a chemical oxidant such as Fenton's reagent (Ref. 7 and 8). Batch tests on TCE showed a removal efficiency of 31.5% in 15 minutes with sonication only, and a 94.4% removal efficiency with sonication plus Fenton's reagent (Ref. 7). A TCE reduction of 80% was achieved in 2 minutes with Fenton's reagent alone, and a reduction of over 90% was achieved in the same time period when ultrasonic radiation was simultaneously applied (Ref. 8). Results of some of these TCE tests are shown in Figure 2-21.

Other studies have demonstrated over 90% dechlorination of chlorobenzene and m-dichlorobenzene in 60 and 100 minutes, respectively (Ref. 9).

94-0320-TR-G-05

Figure 2-21. Detoxification of TCE-Contaminated Soil with the Addition of Additives

2.6.5 Required Development

Development of engineering data is needed for the design of a commercial-scale continuous-flow facility. Determination of the optimum operating conditions for various organic materials and mixtures is required, as well as determination of any toxic byproducts in the effluent. Mass balance of VOCs is needed to confirm destruction versus possible evaporation. This method of destruction also needs to be compared with alternatives in terms of efficiency of destruction, reliability, and cost to determine its applicability to mixed wastes.

2.6.6 Technology Comparison

This process takes place under ambient conditions, requires little or no pretreatment, and can be used to treat a wide variety of organics, including chlorinated compounds, due to the non-specific nature of the process. The process should be able to handle aqueous streams with

moderate amounts of suspended solids, and solutions with low-light transmissivity. Since this is a direct treatment, few byproducts or secondary wastes should be generated. However, this technology is a new and emerging technology, and will require extensive development and testing before it can be applied with confidence in the field. Work has not been done to determine the nature of the end-products of this process, and it is doubtful if the process would be applicable to the destruction of a variety of solid organic materials. However, initial small-scale demonstrations of this technology indicate it may be more reliable, will generate fewer secondary environmental emissions, and will be cost-effective when compared with conventional technologies such as incineration for treating soil.

2.6.7 Cost of Technology or Equipment

Preliminary cost estimates indicate processing costs of about \$300 to \$400 per ton of contaminated soil (Ref. 6). In addition, the technology may be more reliable and generate fewer secondary environmental emissions than competing technologies.

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27 ELECTRON BEAM OXIDATION

2.7.1 Technology Description

Electron-beam processing involves exposing material to high-speed electrons produced by electron accelerators. A single high-energy electron is capable of initiating several thousand reactions as it dissipates its energy. The process of irradiation in aqueous solutions produces sizable quantities of the reducing free radicals e_{aq}^- and $H\bullet$, the oxidizing radical $OH\bullet$ in approximately equal concentrations, and the more stable oxidant H_2O_2 . These highly reactive radicals react with organic contaminants to break the chemical bonds and produce CO_2 , H_2O , nonhazardous salts, and intermediate organic reaction products. In this process, the e_{aq}^- and $OH\bullet$ radicals account for over 90% of the reactive species. Most of the organic species investigated are primarily oxidized by the $OH\bullet$ radical; however, with some species the reaction is predominantly reduction with the e_{aq}^- radical. For example, reactions involving the e_{aq}^- radical may result in dechlorination of organohalogen compounds, and further reaction of the resulting organic radical may completely destroy the compound (Ref. 1).

High voltage (1.5-2.0 Mev) systems are being tested for application to aqueous waste streams at LANL, Florida International University (FIU) and the University of Miami, and High Voltage Environmental Applications, Inc. (HVEA).

The work at the Florida universities and at HVEA has been performed at the Miami Electron Beam Research Facility at the Miami-Dade wastewater treatment plant under a National Science Foundation Grant (Figure 2-22). This facility consists of an e-beam pilot plant capable of treating an aqueous hazardous waste stream at a flow rate of 120 gpm. This plant uses a 1.5 Mev, 50 milliamp, continuous duty profile accelerator to produce doses in water approaching 1 Mrad. Magnetic coils spread the electron beam into a rectangular pattern 4 feet wide by 5 inches tall. The beam passes through two 1-mil thick titanium windows and then into the water that cascades in a thin sheet over a weir. The thickness of the stream of water varies from 0.22 inches to 0.133 inches as it falls through the path of the beam. Since the maximum penetration in water is approximately 0.29 inches for 1.5 Mev electrons, some electrons pass through the stream so that all the beam energy is not transferred to the water. Thus, when the system is operating at 50 ma and 120 gpm, the waste stream is receiving approximately 650 kilorads. The beam current and wastewater flow rate can be altered to vary the dose (Ref. 2).

Side View

Figure 2-22. Electron Beam Research Facility, Miami, Florida

However, there is a potential for considerable loss of volatile organic contaminants (e.g., benzene, toluene and xylenes) in this configuration due to volatilization as the waste stream passes over the weir.

2.7.2 Input and Output Stream Characteristics

The high-voltage e-beam systems have been targeted at dilute organic liquids in an aqueous waste stream with concentrations in the hundreds of ppm range and less. However, experimentation is beginning on concentrations in the 1% organics range. The process will destroy liquid organics, such as solvents, from aqueous slurry and may destroy nitrates and nitrites (Ref. 3). Tests have been performed with up to 5 wt.% clay added to the waste stream with no effect on the contaminant removal rate. However, this process is not feasible for destruction of organic solids in any form, except possibly for biological materials (Ref. 3).

Natural waters often contain scavengers that lower the concentration of the reactive species and slow the reactions leading to destruction of organic contaminants. These scavenger species include carbonate, bicarbonate, nitrate ions, oxygen, and dissolved organic carbon contained in humus. Thus, pretreatment may be required to remove these scavengers or adjust the pH to remove alkalinity, the major $\text{OH}^\bullet$ radical scavenger (Ref. 4). However, nitrates in the water may improve the solute removal efficiency by scavenging e_{aq}^- radicals, thereby minimizing recombination and increasing the reactions with $\text{OH}^\bullet$ (Ref. 5).

Reaction byproducts for various compounds studied (TCE, PCE, chloroform, benzene, toluene, and phenol) are highly oxidized in nature (Ref. 6). For example, formaldehyde and formic acid, at micro-molar (μM) concentrations, were the only reaction byproducts identified from TCE, PCE, and chloroform destruction. The remainder of the parent compound was completely mineralized to CO_2 , H_2O , and HCl . The decomposition of benzene, toluene, and phenol proceeds through $\text{OH}^\bullet$ addition, producing phenolic compounds (i.e., phenol, catechol and resorcinol) at low doses. At high absorbed doses, these initial reaction byproducts were oxidized to low molecular weight aldehydes and carboxylic acids. The sum of these final reaction products account for less than 10% of the initial carbon mass, and it is assumed that the remainder of the parent compound was mineralized to CO_2 and H_2O .

Reaction byproducts during the destruction of BTEX compounds included phenols and various carbonyl compounds (Ref. 5). Phenol concentration in the effluent increased at low doses and then fell below the input concentration (or background) at high doses. The addition

of H_2O_2 in the influent resulted in a decrease in the phenol concentration in the effluent (i.e., more efficient destruction) at low doses and a substantial decrease in the phenol content of the effluent at high doses.

2.7.3 Technology Status

LANL has configured an existing electron accelerator for technology evaluation studies and demonstrated destruction of two hazardous organic compounds characteristic of priority mixed wastes. The test bed operates in a single-pulse mode (65-ns pulse width) and produces beam voltages of 1.5-2.0 Mev and doses in the range 4-7 Mrad. However, the short, single-pulse destruction is much less efficient than other dose profiles, such as continuous duty or repetitively pulsed profiles (Ref. 7).

Computer-based chemical kinetic models have been developed at LANL to understand the waste removal process, predict the expected removal efficiency, develop scale-up parameters, and compare standard electrostatic accelerators to pulsed accelerators in terms of free radical production (Ref. 7). The model has been modified to include radical scavengers normally occurring in potable and natural water (e.g., carbonates). Scavenger-included calculations produced excellent correlations with FIU experimental results, providing confidence in the models. Initial evaluations indicate that e-beam irradiation also holds promise for the treatment of nitrates in aqueous solution or sludges due to the production of large amounts of reductive as well as oxidative free radicals.

These models show that a continuously applied dose is more efficient in destroying waste than the same amount of pulsed dosage due to less radical-radical recombination, and a repetitively pulsed machine can produce similar radical concentrations to those of a dc machine when pulsed at high repetition rates (e.g., 10 kHz, 100 ns pulses). Recent technology developments have led to a new generation of pulsed linear induction accelerators driven by solid state electrical power conditioning elements. These new generation accelerators are considered less expensive per unit e-beam dose and physically smaller, modular, and more reliable than conventional electrostatic accelerators. Although the computer models predict that these repetitively pulsed accelerators will produce better chemical destruction, no data is available to confirm these calculations. LANL has been negotiating with an industrial partner to install a pulsed linear induction accelerator for testing on hazardous wastes (Ref. 7).

Three basic types of electron accelerators are currently available in the energy range of 1-5 Mev and power up to 100 kw, and are in widespread use in industry. The type of accelerator used by HVEA is the insulated core transformer (Ref. 1), which produces high voltage by a three-phase transformer with multiple secondary windings that are energized by insulated core segments in an iron core. In 1991, approximately 180 of these machines were in use by industry. Other types of dc accelerators used in industry include the Dynamitron and the Cockcroft-Walton machines. These machines require the direct generation of high electrical potentials to accelerate emitted electrons. Indirect methods of acceleration, such as the linear induction accelerator mentioned previously, may allow smaller and cheaper machines for applications where high power is required at high potentials.

HVEA has recently been accepted into the EPA SITE Program. They are building a mobile treatment plant that will be able to treat 50 gpm and were scheduled to demonstrate the system at the Savannah River Site in September 1994. The system consists of a 500-kilovolt accelerator that produces a continuously variable beam current from 0 to 50 millamperes. At full power, the system is rated at 25 kilowatts. The flow rate and beam current can be varied to obtain doses of up to 2,000 kilorads in a one-pass, flow-through mode (Ref. 8).

Studies by HVEA at the Miami Electron Beam Research Facility are continuing using influent streams of potable water, and raw and secondary wastewater with various contaminants. Rate constants have been defined for the reactive species both with scavenging species in natural waters and with various contaminants (Ref. 5 and 6). Removal efficiencies for a single pass through the system range from 85% to greater than 99% for most common solvents. These are ongoing studies with the goal of commercializing the e-beam technology for municipal wastewater and sewage sludge.

2.7.4 Destruction Efficiency

A measure of efficiency is the change in solute (or contaminant) concentration for a given absorbed dose (GD). Although the percentage removal rises with increasing dose, the efficiency decreases. This is because excess radicals recombine at high doses, thereby decreasing the number of reactive species that can react with the organic contaminant. Thus, it is more efficient to operate the system at a low dose (e.g., 100 krad) and flow the fluid past the e-beam several times to achieve an additive dose, rather than using a single pass at a high dose. The removal efficiency also increases with solute concentration due to decreased radical-radical recombination in the presence of contaminants. Thus, factors that affect removal efficiency

include water quality (i.e., the presence of radical scavengers), dose, and contaminant type and concentration. These factors also affect treatment cost because increasing efficiency (decreased dose requirements) results in a decrease in cost per 1,000 gallons processed due to increases in flow rate.

Although removal efficiency generally improves with increased contaminant concentration, the percent removal at low solute concentrations is found to be higher in all waters than for the high solute concentration. In general, removal efficiencies are best in potable water vs. raw or secondary wastewater; however, experiments in raw wastewater showed an increased removal efficiency relative to secondary wastewater for TCE and several other organic compounds. This may be due to increased organic carbon in the raw waste stream and associated decrease in radical-radical recombination, effectively increasing the concentration of the transient reactive species (Ref. 1). Tests have indicated that as the concentration of the organic solute increases, the dose required to remove 90% of the initial solute concentration increases for all compounds studied. Therefore, increased radiation doses are required as the concentration of the target chemicals increases (Ref. 5).

Tests have been performed with trihalomethanes (CHCl_3 , CHBrCl_2 , CHBr_2Cl , CHBr_3) and with mixtures of these compounds (Ref. 9). These tests demonstrated over 97% reduction with influent concentration between 76 to 86 $\mu\text{g/l}$ at 200-300 krad dose levels. These THMs are quantitatively decomposed to halogen acids with no formation of halogenated organic compounds as reaction byproducts. Other tests (Ref. 10) indicate nearly complete mineralization of TCE and PCE with no formation of halogenated organic byproducts. Reaction byproducts included formic acid, which accounted for approximately 5 to 10% of the carbon in TCE or PCE, and formaldehyde and acetaldehyde in concentrations an order of magnitude lower. Table 2-10 provides a summary of the average dose required to remove 99% of various contaminants.

Large-scale recirculation experiments were performed at high concentrations of phenol (90 mg/l) and a flow rate of 100 gpm (Ref. 11). The solution was recirculated through the e-beam and the dose was varied from 0 to 600 krad over a 2.5 hour experiment. After the third recirculation by volume, the phenol concentration was reduced to <1% of its initial concentration at low pH (pH=3.95). Phenol removal was less efficient at higher pH (7.75) with a reduction to <5% of its initial concentration. However, the total organic carbon did not significantly decrease at either pH, indicating the main removal pathway for phenol was not through mineralization, but more likely through a polymerization process to form higher

molecular weight polymers. The experimenters anticipate that continued recirculation of the waste stream would lead to the destruction of these polymeric intermediates.

Table 2-10. Summary of the Average Dose Required to Remove 99% of Organic Species from an Aqueous Solution (Ref. 6)

Compound	Initial Concentration (mg/l)	Average Dose (krad)
TCE	5.2 - 7.6	107
PCE	0.93 - 4.8	442
Chloroform	5.2 - 7.0	1004
Benzene	1.8 - 6.8	200
Toluene	3.7 - 6.1	169
Phenol	56.4 - 61.5	1110

A summary of the removal percentages for most organic compounds that have been investigated to date by HVEA is presented in Table 2-11 for a single pass through the e-beam (Ref. 12). Although experiments were run with compounds dissolved in waters of varying qualities (potable water, chlorinated secondary, and raw wastewater) and initial concentrations, doses of 50 to 800 kilorads effectively removed most of the compounds. Only insignificant quantities of reaction byproducts (e.g., submicro-Molar concentrations) have been identified when destruction of the parent compound is near completion. When complete destruction does occur the compounds are reduced to CO₂, H₂O and salts.

Although some removal efficiencies are less than desirable, these are based on a single pass through the system. Since this is a flowthrough system, there is essentially no retention time; once the electrons enter the water, treatment occurs in a fraction of a second. Therefore, it may be economical to recycle the waste stream two or three times to achieve the required removal efficiency.

2.7.5 Technology Comparison

Electron-beam technology appears more robust than UV photo-oxidation, and further along in development than ultrasonic destruction, for application to aqueous waste streams. Following is a summary of advantages and disadvantages of e-beam technology.

Table 2-11. Summary of Electron-Beam Removals of Various Organic Compounds (Ref. 12)

Compound	Percent Removal	Required Dose (krad)
Benzene	>99	49-650
Chloroform	83-99	586-650
Bromodichloromethane	>99	80
Dibromochloromethane	>99	80
Bromoform	>99	80
Carboon Tetrachloride	>99	80
Chlorobenzene	97	650
1,2-Dichlorobenzene	88	650
1,3-Dichlorobenzene	86	650
1,4-Dichlorobenzene	84	650
<i>trans</i> -1,2-Dichloroethylene	93	800
1,1-Dichloroethylene	>99	800
1,2-Dichloroethylene	60	800
Dieldrin	>99	800
Ethylbenzene	92	650
Hexachloroethane	>99	800
Methyl Chloride	77	800
Phenol (total)	88	37-800
Toluene	97	45-650
1,1,2,2-Tetrachloroethane	88	650
Tetrachloroethylene (PCE)	>99	241-500
1,1,1-Trichloroethane	89	650
Trichloroethylene (TCE)	>99	57-500
<i>m</i> -Xylene	91	650
<i>o</i> -Xylene	92	650

2.7.5.1 Advantages

- E-beam treatment is effective for destruction of a broad range of hazardous wastes, particularly chlorinated hydrocarbons. This technology is not sensitive to the treatability of the contaminant or the particular target species, and it treats waste streams of varied composition.

- The aqueous systems are closed loop with a short (fraction of a second) residence time. Recycling of the waste stream can provide the required destruction efficiency for compounds that are difficult to destroy.
- It is a low temperature process, so VOCs and volatile metals or metal compounds are not vented or produced during treatment of aqueous wastes. However, some off gasing of VOCs may occur as the aqueous waste flows over the weir of the HVEA system. Plugging, scaling, and corrosion issues characteristic of high temperature or chemical processing are avoided.
- High power e-beams can treat slurried waste directly (i.e., without chemical addition) and have been effective in treating wastes with up to 5% solid content.
- This technology has an established engineering base in that electron accelerators are an established technology. It is presently economically competitive with other destruction technologies, and it is expected to be less expensive and more effective when new, repetitively pulsed accelerator technology is implemented.
- The waste treatment unit stands off from the waste stream, preventing large-scale contamination and generation of secondary waste and making the system easy to maintain. This stand-off characteristic makes this technology applicable to mixed waste since only the plumbing will become contaminated with radionuclides.

2.7.5.2 Disadvantages

- The need for highly skilled operators and maintenance personnel for the accelerators.
- This process will not destroy solids.
- There is a potential need for post-processing to achieve the required destruction efficiency, depending on contaminants and local discharge requirements.
- Treatability studies are required to determine dose requirements to ensure hazardous byproducts are not produced in the effluent.

2.7.6 Cost of Technology or Equipment

One of the possible major drawbacks to the e-beam technology is the initial capital cost of the accelerator for a fixed, large-scale facility such as that at the Miami Electron Beam Research Facility. An accelerator capable of delivering 1,000 kilorads at 100 gpm will cost approximately \$1,700,000 (Ref. 13). Total treatment costs using this permanent large scale facility would be approximately 1.0 to 1.5 cents per gallon, assuming one pass through the beam is sufficient (Ref. 1).

Estimates for processing waste streams with e-beam accelerators is about \$2.50 per 1,000 gallons of treated water at a flow rate of about 120 gpm (Ref. 14). Sandia researchers have performed preliminary tests on the removal of organics from Hanford tank simulants and estimated processing costs of approximately \$10/gallon for this extremely complicated waste (Ref. 7). Thus, costs for processing waste streams with the e-beam may vary widely depending on the compounds in the waste stream and the flow rate.

The cost of treatment using e-beam technology depends on many factors, including the dose required to obtain the desired destruction; the volume of waste to be treated; the size of the treatment facility; the time utilization of the facility; and the manner in which capital recovery is handled. Several estimates were developed for different situations (Ref. 12), which are summarized below:

- *A site with TCE contamination of 10 mg/l with a treatment objective of 5 µg/l (i.e., 99% removal).* The groundwater contains no alkalinity and no dissolved organic carbon. To treat 500 to 1,000 gpm, the cost would be \$0.75 per 1,000 gallons. The facility and operators would increase the cost to approximately \$2.00 per 1000 gallons.
- *Contaminated leachate containing 1% dense nonaqueous phase liquid to be treated to the FO39 treatment objectives.* The quantity of leachate is estimated to be 30 billion gallons with over 100 compounds. For continuous treatment at 100 gpm the cost was estimated to be between \$0.30-\$0.40 per gallon.
- *Contaminated leachate containing small amounts of light nonaqueous phase liquid to be treated to FO39 treatment objectives.* The quantity is estimated to be 10 billion gallons to be treated at a rate of 5,000 gallons per day initially with the flow decreasing with time. For a 5-day-per-week, 8-hour-per-day operation the treatment system was estimated to cost between \$0.40-\$0.50 per gallon.

- *Removing 99% of 20 mg/l benzene and 20 mg/l of TCE from groundwater.* The cost was estimated to be \$1.95 per 1,000 gallons using a 75 kw e-beam system, assuming a life of 10 years and a flow rate of 250 gpm. This does not include the time value of money, cost of operators, supervision, overhead, or necessary pretreatment.

These cost estimates were based on using a continuous beam accelerator, which costs approximately \$1,700,000. Use of a smaller accelerator or pulsed LINAC, which may cost approximately \$500,000, would decrease the treatment costs due to decreased cost of capital and decreased maintenance requirements.

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SECTION 5 THERMAL DESORPTION

5.1 TECHNOLOGY DESCRIPTION

Thermal desorption is an established technology for the treatment of soils, sludges, sediments and filter cakes that are contaminated with organic compounds or volatile inorganics. This is an *ex situ* method to separate halogenated and nonhalogenated volatile and semivolatile organic compounds, fuels, and volatile metals from solid and sludge wastes. Although the temperatures, residence times, and carrier gases used in thermal desorption are designed to volatilize selected organic contaminants rather than destroy them, the higher temperatures in some systems will result in localized oxidation, pyrolysis, and/or destructive distillation.

Thermal desorption is essentially a drying process that uses modified drying technology to heat solid wastes to temperatures between 300°F and 1200°F, without oxygen, to volatilize water and organic compounds. Volatilized contaminants are transported to a gas treatment system by a carrier gas or vacuum system where particulates and organic material are removed from the gas stream before discharge. Organics in the offgas may be burned in an afterburner, condensed, recycled, disposed of, treated by other means, or captured by carbon adsorption beds. Emerging technologies for treating organic material in the vapor phase are discussed in Section 6.

Contaminant removal is highly dependent on the following parameters:

- Media temperature—modest increases in temperature greatly decrease residual concentrations or decrease the time required to reach a specified concentration.
- Residence time—a sufficient amount of time at temperature is required to bring the soil to the required temperature for volatilization of organics from the surface of the particles, and for the organic material to diffuse to the surface of the particles and be swept away in the offgas.
- Soil matrix—coarse particles such as sands will desorb contaminants easier than fine grained clays and silts.
- Contaminant—some contaminants will bind strongly to soils and others will not. In addition, the vapor pressure of the contaminant will determine the temperature required for desorption.

- Moisture content—increased moisture reduces the capacity of the contaminant to adsorb on soils; however, moisture absorbs heat and a significant portion of it must be driven off before the soil temperature can be increased above the vaporization temperature of the water. As the moisture is vaporized, it tends to steam strip some of the organics from the soil.

The basis of the process is physical removal of the contaminants from the medium by vaporization or, in some cases, pyrolysis or destructive distillation. At medium to high temperatures some organics will decompose to produce volatile breakdown products which are driven off. Thus, bed temperature directly determines which organics will be removed and the effectiveness of removal. The key physical property influencing the rate at which a contaminant is thermally desorbed is the vapor pressure of the compound. The optimum soil treatment temperature range is that at which a contaminant would exhibit a vapor pressure between 0.5 and 2.0 atmospheres in a closed system (Ref. 1). Figure 5-1 illustrates the temperature range required to achieve vapor pressures in this range for several common organic compounds, with higher molecular weight organics requiring higher soil treatment temperature for adequate removal.

Figure 5-1. Vaporization Temperature of Hydrocarbon Constituents

Researchers have found that, while 90% of a contaminant may be easily removed, the final 10% will require a much longer residence time, especially if the cleanup criteria is in the ppb range. This is due to the adsorptive properties of some soils that have a tendency to strongly attract monolayers of contaminant on the surface and in the pores of soil particles.

Tests on several pesticides (Ref. 2) indicate a lower temperature limit below which very little desorption takes place. In this case, the pesticides were dieldrin, aldrin, endrin and isodrin and the temperature limit was 340°F. At higher temperatures between 340°F and 542°F, desorption occurs relatively rapidly. Research indicates that the minimum soil temperature depends on the soil type, with higher temperatures required as the humic content of the soil increases due to the adsorption of the pesticides onto the organic material. Additional data indicate that both treatment time and time at temperature have significant effects on the overall pesticide removal efficiency. Various combinations of these two factors can produce the same residual concentrations of the target pesticides. In addition, care must be taken to ensure toxic residuals from the decomposition of complex organics at low treatment temperatures do not remain in the treated soil. For example, soils with high levels of DDT treated at 500°F were found to have 4 times the level of DDE than the untreated soil due to the dechlorination of DDT. At a treatment temperature of 700°F and 36 minutes residence time, the DDE was removed from the soil with >99% efficiency.

The soil processing rate, and consequently the operating cost, of a thermal desorption system is strongly influenced by the soil moisture content. Moisture can be a major heat sink affecting both the amount of energy required to heat the soil to the target temperature and the physical handling properties of fine-grained soils. A very high moisture content can result in low contaminant removal during the residence time in the desorber, thus requiring the soil to be recycled through the system and increasing treatment costs. Wet clays are sticky and can significantly reduce the soil feed handling capacity of thermal desorption systems, and can stick to the surfaces of the desorber. Thus, wet sludges and solids may require dewatering for optimal performance of thermal desorption and gas treatment systems.

A process flow for a typical desorber system is shown in Figure 5-2. The thermal desorber is the unit operation that heats the soil to volatilize organic contaminants into a purge gas. The purge gas may be air, nitrogen, a combustion gas, or other inert gas. Thermal desorbers typically operate at soil treatment temperatures in the range of 300°F to 600°F for petroleum contamination applications. However, systems are available that can operate at soil discharge temperatures as high as 1200°F (Ref. 1). The soil treatment temperature capabilities of various thermal desorption systems are shown in Figure 5-3.

Figure 5-2. Flow Diagram for Generalized Thermal Desorption System

Figure 5-3. Thermal Desorber Soil Discharge Temperature Range

There are two approaches to thermal desorption: stationary facilities to which the contaminated media is transported, and mobile systems that operate on-site. Both kinds of systems are available for treating petroleum-contaminated wastes; however, only mobile systems are available for treating Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) wastes (Ref. 3).

Different types of desorbers are used by various vendors. The dryer can be a directly or indirectly heated rotary kiln, indirectly heated screw auger or paddle dryer, a directly heated continuous belt conveyor dryer, or an indirectly heated vacuum dryer. Heat may be transferred directly to the matrix by hot exhaust gas from the burners, or indirectly by steam or hot oil circulating through the drum and/or augers. In some cases high temperatures (over 1000°F) are generated internally by electrical resistance heating or by using a molten salt heat-transfer medium.

An inert gas, such as nitrogen, may be injected as a sweep stream to prevent contaminant combustion and to vaporize and remove the contaminants. If hot combustion gases from the desorption burner are used, they must be oxygen-deficient (<4%) to prevent combustion and the possibility of an explosion in the desorber. If air is used, vapor organic concentrations within the desorber must be kept below 25% of the lower explosive limit (LEL) in the event excess oxygen is present.

An important design factor is the direction of flow of the sweep gas relative to the flow of the solid in the desorber. The flow configuration of the desorber (co-current or counter-current) will affect the size and arrangement of components used in the gas treatment system. In the co-current configuration, the gases exiting the desorber are relatively hot, typically about 50°F to 100°F hotter than the soil discharge temperature, or about 400°F to 1000°F. The larger entrained particles are removed by a cyclone, but the gases are too hot for smaller particles to be removed in a baghouse. Therefore, the most common design places the cyclone after the desorber, followed by an afterburner, a gas cooler or quench unit, a baghouse, an induction fan, and the stack. Since the afterburner is upstream of the baghouse, the particles collected should be relatively free of contaminants. Therefore, co-current rotary dryer systems can treat heavier petroleum products than can counter-current systems. A scrubber may be required for acid gas removal/neutralization, and carbon adsorption units can be used in place of the afterburner.

In the counter-current configuration, the gases leaving the desorber will generally be cool enough to flow directly from the cyclone to the baghouse. For example, the purge gas from a counter-current rotary dryer is typically limited to a temperature range of 350°F to 550°F by the

materials of construction of the bags in the baghouse. Thus, the arrangement of the gas treatment system is typically desorber, cyclone, baghouse, induced draft fan, afterburner, and stack. Since the purge gas can go directly to the baghouse without adding water or air for cooling, and the afterburner is at the end of the gas treatment train, the flow rates are lower than in the co-current configuration allowing smaller air pollution control equipment to be used. However, because of the cooler temperatures in the baghouse, heavier organics may condense in the baghouse posing a fire hazard or blinding the bags. In addition, the particles collected in the baghouse may not be fully decontaminated, or organics may condense on the particles. Course particles may be recycled back to the desorber; however, fine particles must be disposed since they will simply be re-entrained in the carrier gas.

Although typical baghouse materials limit the purge gas temperature and determine the arrangement of offgas treatment components, specialized high-temperature bag materials are available, but at a high cost. These baghouse materials include 3M Company Nextel ceramic weave that can operate up to 1500°F, and metallic weave material from Pall Corporation. Use of these materials in high-temperature baghouse operations may minimize organic condensation.

An additional consideration in selecting co-current vs. counter-current operation is that the driving force for heat transfer from one fluid to another is directly related to the mean temperature difference. A larger log mean temperature difference between the purge gas and the soil can be achieved with a counter-current flow configuration than with a co-current configuration. In order to achieve an equivalent driving force with a co-current system, significantly higher exhaust gas temperatures are required. This increases the size of the desorber or increases the velocity of the gas stream. With higher velocities, the size and quantity of fines carried over to the downstream equipment are increased. Thus, co-current systems are generally larger and more expensive than counter-current systems with an equivalent processing capacity. In addition to increased capital cost, higher maintenance can be expected due to additional fines carry-over and their impact on the afterburner and quench unit, required to decrease the temperature of the gas/particulate stream entering the baghouse (Ref. 4).

Rotary Dryer

Rotary dryer systems are available as both mobile and fixed-base systems and may be operated in the co-current or counter-current mode. Treatment capacities range from 5 to over 100 tons of contaminated soil per hour. A rotary dryer uses a cylindrical, rotating metal drum that is inclined slightly to the horizontal. In directly heated systems, the natural gas, propane, or fuel oil fired burner is located at one end of the dryer to provide heat to raise the temperature of the soil. A series of lifters inside the drum picks up the soil and drops it through the hot combustion gases from the burner. The intense mixing that occurs enhances heat transfer by

convection and allows soils to be heated very rapidly. Rotary dryers that treat petroleum contaminated soils are normally constructed of carbon steel and operate at soil temperatures of 300°F to 600°F (Ref. 1). Rotary dryers constructed of alloys are available that can heat contaminated soil up to 1200°F. The gas post-treatment system for a direct-fired desorber requires a larger capacity than the system used for indirectly heated desorbers because of the larger combustion gas volume.

Typical residence times of petroleum-contaminated soils, in direct-fired thermal desorbers, are usually less than 10 minutes. The residence time for semi-volatile organic compounds can be as long as 20 to 30 minutes (Ref. 3). When clay or silt-type soils are treated, particles may become entrained in the sweep gas and may not be fully decontaminated. Residence time is determined by the length and diameter of the desorber, and is controlled by varying the rotational speed, the angle of inclination, the lifter design, and the feed rate.

In indirectly heated systems the rotating shell is heated on the outside by combustion of natural gas or propane. A sweep gas is used to transfer the volatiles and water to the offgas treatment system. Co-current flow is normally used with lifters inside the rotating drum to enhance solid-gas contact (Ref. 3). Post-treatment does not normally involve destruction in the gas or vapor phase; rather, the recovery system uses condensation and refrigeration units to reduce the volume of wastes requiring treatment, and to recover the organic material in liquid form for subsequent treatment. In these systems, the nitrogen blanket reduces the necessity of maintaining the organic vapor concentration below the LEL by keeping the oxygen concentration below 4%. Since the majority of the nitrogen is recycled, only 5 to 10% of the carrier gas is vented to the atmosphere (Ref. 3). A typical range of retention times is 30 to 120 minutes in indirectly heated systems.

Thermal Screw

Thermal screw systems are generally trailer-mounted with a soil treatment capacity of 3 to 15 tons per hour. Excavated solids are screened or crushed to remove rocks and debris, and to decrease the particle size to 1 to 2 inches to prevent jamming the flights.

Most thermal screw systems circulate hot heat-transfer oil through the hollow flights of the auger and return the hot oil through the shaft to the heat-transfer fluid heating system. The heated oil also circulates through the jacketed trough in which the auger rotates. The maximum soil temperature that can be attained in a thermal screw system is limited by the maximum working temperature of the heat-transfer fluid. Heat-transfer oils can be heated to approximately 650°F and molten salt can be heated to approximately 1100°F. Thus, systems using hot oil can achieve soil temperatures of 500°F, and those using molten salt can heat soil to

900°F (Ref. 1). One system uses electrical heating elements to transfer heat through the augers and vessel jacket to achieve a material temperature of 1200°F (Ref. 5).

The retention time of the conveyor system is determined by the volumetric feed rate of the media and the systems conveying velocity. Throughput of screw conveyors can be varied with rotational speed, flight diameter, and flight pitch. Screw augers can be arranged in series to increase the solids retention time, or they can be configured in parallel to increase throughput capacity.

Since thermal screws are indirectly heated, the volume of purge gas is less than half the volume from a directly heated system with an equivalent soil processing capacity (Ref. 1). Thus, the offgas system is relatively small. Indirect heating with an inert purge gas also allows thermal screws to process materials with high organic content because the lower explosive concentration limit is no longer a concern.

Vaporized organics, water, and the inert purge gas exiting the desorber are drawn under induced draft through the offgas system. A particulate control device, such as a venturi scrubber or fabric filter, is commonly used directly downstream of the desorber. Most thermal screw systems use a condenser to remove organic vapors and water from the gas stream. A phase separator is used to remove the organics for subsequent treatment, and the water fraction is treated in an aqueous phase activated carbon adsorption unit and used to control dust from the treated soil. Non-condensable organics are normally removed from the gas exiting the desorber by a vapor-phase activated carbon adsorption system.

Conveyor Furnace

The conveyor furnace may be transportable with a typical capacity of 5 to 10 tons of soil per hour (Ref. 1). This system uses a flexible metal belt to convey the soil through a primary heating chamber. A 1-inch deep layer of soil is spread evenly over the belt, and as the belt moves through the system, soil agitators lift the belt and turn the soil over to enhance heat transfer. A series of burners fire into the chamber above the belt to heat the soil. The conveyor furnace can heat soils in the temperature range of 300°F to 800°F (Ref. 1). The retention time of belt conveyors is based on the bed depth because of volatilization limitations, and belt speed.

The following sections describe several representative commercial systems. This is not meant to be all-inclusive as there are many other thermal desorption systems available from various vendors.

5.1.1 IT Corporation's Thermal Desorption System

Process development efforts have been conducted in IT Corporation's bench-scale batch Rotary Thermal Apparatus (RTA) and pilot-scale thermal desorber. This custom-designed and fabricated system is used to develop thermal treatment data for hazardous and mixed waste solids, soils, and sludges. The thermal separation process utilizes an inclined rotating metal shell that is enclosed in a natural gas or fuel oil fired furnace. Contaminated materials flow through the inside of the shell and are heated in an inert atmosphere by indirect heat transfer. Organic materials are vaporized and are exhausted to a downstream device such as a secondary combustion chamber or a condensation system, leaving behind radionuclide contaminated solids suitable for further treatment prior to placing in a permanent repository.

5.1.2 Chemical Waste Management, Inc. X*TRAX™

The X*TRAX™ system shown in Figure 5-4 consists of an indirectly heated rotary kiln which is a sealed, rotating cylinder heated on the outside by propane burners, and an offgas handling system. An auger or pump is used to feed the contaminated solids or sludges into the dryer where they are heated from 400°F to 800°F. An inert nitrogen carrier gas flows co-current to the solids and transports the volatilized water and organics to the offgas handling system where the offgas is scrubbed to remove particulates and some of the volatilized organics, and cooled to condense the remaining organics and water. The recirculating scrubber water continuously passes through a phase separator to remove condensed light organics, and discharge a bottom sludge containing solids, water and organics.

Organics are removed from the liquid condensate by gravity separation, and the remaining condensed water is used to cool the treated solids exiting the desorber and minimize the generation of dust. The cooled carrier gas is reheated from 400°F to 700°F and recirculated into the dryer. A small portion of carrier gas passes through a filter and a carbon adsorption drum before being vented to the atmosphere. A 100-ton per day system releases 0.25 to 5 lbs/day of VOCs in the offgas after passing through the carbon adsorber which has demonstrated a removal efficiency of 89 to 98% (Ref. 6).

Indirect firing and recycle of the carrier gas allows the gas emissions to be a factor of 100 to 200 times less than an equivalent capacity incinerator, and the air pollution control system to be one tenth to one hundredth the size of an equivalent incinerator. The small volume of carrier gas discharged (5 to 10%) allows makeup nitrogen to be added to keep the oxygen

concentration low; typically between 0 and 1%. In addition, an indirect-fired process is classified as a separation process making it easier to permit than an incinerator.

Figure 5-4. X*TRAX™ Process Flow Diagram

Three X*TRAX™ systems are available from Rust Remedial Services (Ref. 7). Two laboratory scale systems are available for treatability studies on RCRA, TSCA, and mixed wastes at the Clemson Technical Center in South Carolina. These are small, continuous flow systems capable of treating 2 to 5 lbs/hr and simulating the pilot and full-scale systems. The pilot-scale system is a mobile unit, mounted on two trailers, with a 5-ton per day capacity for a feed containing 30% moisture (Ref. 8), and is available for larger scale treatability studies and demonstrations. The full-scale unit (Model 200) is transportable with a nominal capacity of 125-tons per day of contaminated soil at 20% moisture. To justify the cost of mobilizing of the full-scale system, a single location should have at least 5,000 yd³ of waste to process.

This system was designed to treat solids or pumpable sludges containing organics with boiling points less than about 800°F, less than 20% total organics, and less than 50% moisture,

although <25% moisture is preferable (Ref. 7). Retention time in the kiln can vary from 30 to 120 minutes; however, typical retention times are 60 to 90 minutes (Ref. 9). An economic evaluation is necessary before treatment of wastes with higher organic or moisture levels to determine the cost effectiveness. Solid feeds must be screened to less than 2 inches in size.

5.1.3 Chemical Waste Management, Inc. VAC*TRAX™

The VAC*TRAX™ system is a small mobile system that requires minimum mobilization and demobilization activities. This system uses a high vacuum (7 kPa or 1 psi absolute) to reduce the operating temperature and heating time required to vaporize contaminants (Ref. 10). It is a completely sealed, indirectly heated system that uses 650°F oil that passes through the dryer jacket and internal agitator to heat the solid to approximately 550°F. Nitrogen carrier gas is used to transport the vaporized gases to a gas treatment system, where they are cooled and condensed and the organic compounds are recovered as a liquid.

Since the unit operates at high vacuum, it must be a batch dryer that can be completely sealed (Ref. 10). The dryer can accept soils and sludges, and has been sized to accept solids of relatively large size such as assorted debris. The system is designed for a maximum organic concentration of 20% (Ref. 11), and a maximum moisture content of 50% with 25% moisture optimum.

After the waste is loaded and the dryer sealed, it is inerted with the nitrogen carrier gas. After the dryer is inerted, the waste is heated which requires from one to two hours. After the solids have reached the treatment temperature, they are held at full vacuum for 15 minutes to several hours, depending on the type and quantity of contaminants and the nature of the matrix. The vacuum is then released, the unit is opened, and the waste discharged from the bottom. The unit is then ready for another treatment cycle.

The desorbed vapors and nitrogen exit the dryer through the top of the vessel into a cupola equipped with a metal filter that removes entrained solids (dust) from the gas stream. These solids are retained in the dryer and discharged with the treated solids when the vessel is emptied.

This system is designed for sites with small quantities of waste in the 1000 ton range or a few hundred drums of waste (e.g., 200 to 5,000 m³), and can process about 40 to 60 tons per day (Ref. 12). The system operates in a batch mode and can process about 3 batches per day with a

4-hour cycle time. The vacuum extends the range of thermal desorbers to hard-to-remove chemicals, prevents melting of heat-sensitive materials (e.g., plastics), and increases the production rate. The process has been demonstrated on soils, rags, personal protective equipment (PPE), and shredded paint waste. Tests are planned for Rocky Flats waste consisting of combustibles such as Kimwipes™, plastics, PVC, metals, glass, and rubber gloves (Ref. 13). The objective will be to remove volatile organic compounds from these wastes without impacting the integrity of the waste. Thus, the melting temperature of the most susceptible matrix will define the maximum process temperature.

5.1.4 Canonie Environmental Services Corporation's Low-Temperature Thermal Aeration (LTTA)

The Canonie Environmental Services Corporation's Low-Temperature Thermal Aeration (LTTA) desorption technology is a direct-contact rotary dryer (Ref. 14). It removes organic contaminants from contaminated soils into a contained air stream, which is extensively treated to either collect the contaminants or to thermally destroy them. A direct-fired dryer is used to heat an air stream which, by direct contact, desorbs water and organic contaminants from the soil at temperatures up to 800°F. The processed soil is quenched to cool it and to mitigate dust problems. The treated soil, once verified to meet the treatment criteria, can be backfilled on-site without restrictions.

The hot air stream containing vaporized water and organics is treated by one of two air pollution control systems. One treatment system removes the organic contaminants from the air stream by adsorption on granular activated carbon (GAC) and includes the following units in a series: (1) cyclones and baghouse for particulate removal; (2) wet scrubber for acid gas and some organic vapor removal; and (3) GAC adsorption beds for organic removal. When the GAC beds are used for air pollution control, the spent GAC is regenerated or incinerated.

The second air stream treatment system is used when soils containing high concentrations of petroleum hydrocarbons are treated. It includes the following units in a series: (1) cyclones for particulate removal; (2) thermal oxidizer/afterburner for destruction of organics; (3) quench tower for cooling of air stream; (4) baghouse for additional particulate removal; and (5) wet scrubber for acid gas removal.

5.1.5 Remediation Technology, Inc. (ReTec) High-Temperature Thermal Processor

Remediation Technologies, Inc.'s (ReTec), high-temperature thermal processor is a thermal desorption system that can treat solids and sludges contaminated with organic constituents (Ref. 14). The system consists of material feed equipment, a thermal processor, a particulate removal system, an indirect condensing system, and activated carbon beds.

Waste from the feed hopper is fed to the thermal processor, which consists of a jacketed trough that houses two intermeshing, counter-rotational screw conveyors. The rotation of the screws moves material through the processor. A molten salt eutectic, consisting primarily of potassium nitrate, serves as the heat-transfer media. This salt melt has heat-transfer characteristics similar to those of oils and allows maximum processing temperatures of up to 850°F. The salt melt is noncombustible, it poses no risk of explosion, and its potential vapors are nontoxic. The heated transfer media continuously circulates through the hollow flights and shafts of each screw and also circulates through the jacketed trough. An electric or fuel oil/gas-fired heater is used to maintain the temperature of the transfer media. Treated product is cooled to less than 150°F for safe handling.

A particulate removal system (such as a cyclone or quench tower), an indirect condensing system, and activated carbon beds are used to control offgases. The processor operates under slight negative pressure to exhaust the volatilized constituents (moisture and organics) to the offgas control system. An inert atmosphere is maintained in the headspace of the processor through the use of air lock devices at the feed inlet and solids exit, and through the introduction of an inert carrier gas (such as nitrogen) to maintain an oxygen concentration of less than 3%. The oxygen and organic content of the offgas are continuously monitored as it exits the processor. Entrained particulate matter is collected and combined with the treated solids on a batch basis. The volatilized moisture and organics are subsequently condensed and decanted. A mist eliminator minimizes carryover of entrained moisture and contaminants after the condenser. Any remaining noncondensable gases are passed through activated carbon beds to control volatile organic compound emissions.

This system can treat soils, sediments, and sludges contaminated with volatile and semivolatile organics, including PCBs. Preliminary testing indicates the system has the potential to treat cyanide. With the exception of mercury, the process is not suitable for treating heavy metals. Wastes must be prescreened to a particle size of less than 1 inch before treatment.

5.1.6 Roy F. Weston, Inc. Low-Temperature Thermal Treatment (LT³) Technology

The LT³ system consists of three main treatment areas (Ref. 15): soil treatment, emissions control, and condensate treatment. The thermal processor consists of two jacketed troughs, one above the other. Each trough houses four intermeshed hollow-screw conveyors. The conveyors move soil across the upper trough of the thermal processor until the soil drops to the lower trough. The soil then travels across the processor and exits at the same end that it entered. Hot oil circulates through the hollow screws and trough jacket. The treated soil is discharged into a conditioner where it is sprayed with water to cool it and minimize fugitive dust emissions.

A burner heats the heat transfer oil to an operating temperature of 400°F to 650°F (about 100°F higher than the soil treatment temperature). Combustion gases released from the burner are used as a sweep gas in the thermal processor. The sweep gas is drawn through a fabric filter where dust is collected. Exhaust from the filter is drawn through a series of condensers to remove most of the water vapor and organics, and then through a vapor-phase activated carbon adsorption column to remove any remaining organics.

This system is best suited for soils with moisture content of less than 20%, and VOC concentrations of up to 1%. SVOCs with boiling points greater than 500°F may also be treated depending on the cleanup objectives. Wastes with moisture content between 20% and 50% can be treated at a reduced capacity. Wastes with moisture content greater than 50% must first be dewatered. Pretreatment screening or crushing of oversized materials (greater than 2 inches) or clay shredding may also be required.

5.1.7 ETG Environmental, Inc. Therm-O-Detox® System

The Therm-O-Detox® system consists of a feeding system, a low- or medium-temperature thermal desorber (LTTD or MTDD), offgas scrubbers and condensing unit, and a vapor-phase carbon adsorption unit (Ref. 16). The system is mobile with a throughput of 5 to 15 tons/hr depending on the feed characteristics and treatment requirements. The Base Catalyzed Decomposition (BCD) process, discussed in Section 4, has been used in conjunction with the Therm-O-Detox® system to dechlorinate chlorinated hydrocarbons condensed from the offgas.

The thermal desorber is an indirectly heated, twin-shaft, low-speed paddle dryer. The overlapping design of the paddles provides thorough mixing and de-balling action to improve exposure of the particles to the heat-transfer surfaces. The paddle configuration is reported to minimize caking or balling of the waste feed and promote homogeneous bed conditions to

reduce retention time. The desorber uses a combination of hot oil and electric current (or other indirect heating methods) as the heat sources. The units are designed to achieve waste material temperatures of up to 950°F.

5.2 INPUT AND OUTPUT STREAM CHARACTERISTICS

Chemical contaminants for which bench-scale through full-scale treatment data exist include petroleum-based hydrocarbons, VOCs, SVOCs, pesticides, and higher boiling point compounds such as PCBs. The technology is not effective in separating inorganics from the matrix; however, volatile metals such as mercury may be removed with high-temperature systems. A number of variables, such as the specific mix and distribution of contaminants, affect performance. The effectiveness of thermal desorption on general contaminant groups for various matrices is shown in Table 5-1 from Reference 17.

The physical properties of the soil matrix are important parameters in the selection and operation of a thermal desorption system. Large boulders and cobbles (>1 to 2 inches in diameter) will need to be crushed or removed because damage to the desorber or, in the case of screw conveyors or heated screw desorbers, jamming of the screws may occur. Additionally, the desorption unit size and configuration will limit the size of material that may be used as feed, limiting the application for contaminated debris.

Course-grained soils are generally free-flowing, have low moisture adsorption capacities and do not agglomerate into large particles, and have relatively good heat-transfer characteristics. Silts, clays, organic soils, and peat are fine-grained and adsorptive and may result in poor performance due to caking. Caking will also occur if the moisture content is above the plastic limit. Plasticity will determine whether the material is likely to stick to screening, sizing, conveying, or desorber equipment. Some matrix material may stick to itself and to dryer surfaces as it enters the dryer, some materials may pass through the sticky or plastic phase as they dry, and others may case-harden thus sealing in the moisture and contaminants and fusing the particles into a block. The problems associated with moist, sticky material may be alleviated by blending treated dry solids with the incoming material. In most systems the contaminated medium must contain at least 20% solids to facilitate loading of solids into the desorption equipment. Some systems specify a minimum of 30% solids (Ref. 17).

Table 5-1. Effectiveness of Thermal Desorption on General Contaminant Groups for Soil, Sludge, Sediments, and Filter Cakes

Contaminant Groups		Effectiveness			
		Soil	Sludge	Sediments	Filter Cakes
Organic	Halogenated volatiles	■	▼	▼	■
	Halogenated semivolatiles	■	▼	▼	■
	Nonhalogenated volatiles	■	▼	▼	■
	Nonhalogenated semivolatiles	■	▼	▼	■
	PCBs	■	▼	▼	▼
	Pesticides	■	▼	▼	▼
	Dioxins/Furans	■	▼	▼	▼
	Organic cyanides	▼	▼	▼	▼
	Organic corrosives	□	□	□	□
Inorganic	Volatile metals	■	▼	▼	▼
	Nonvolatile metals	□	□	□	□
	Asbestos	□	□	□	□
	Radioactive materials	□	□	□	□
	Inorganic corrosives	□	□	□	□
	Inorganic cyanides	□	□	□	□
Reactive	Oxidizers	□	□	□	□
	Reducers	□	□	□	□
■ Demonstrated Effectiveness: Successful treatability test at some scale completed ▼ Potential Effectiveness: Expert opinion that technology will work □ No Expected Effectiveness: Expert opinion that technology will not work					

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Soils with a high fraction of fine silt or clay will generate large dust loadings in the air pollution control system. Because the degree of particulate entrainment is directly related to particle size and gas flow rate, different types of desorbers will entrain varying quantities of solids. The treated medium will typically contain less than 1% moisture. Dust generated during the transfer of the treated medium from the desorption unit can be mitigated by water sprays.

Total organic loading is limited in some systems to 10% or less whereas others can accept up to 20% organics. In addition, vapor organic concentrations within the desorber must be kept below 25% of the lower explosive limit if the desorber is operated with excess oxygen. A waste medium exhibiting a very high pH (greater than 11) or very low pH (less than 5) may require pre-treatment to prevent corrosion of the system components (Ref. 17).

Heat sensitive materials, such as plastics and rubber, may melt and foul the heat-transfer surfaces. Vacuum systems operating at lower temperatures may eliminate this problem and allow treatment of such materials.

Up to seven process residual streams are generated by thermal desorption: treated medium, oversized medium rejects, condensed contaminants and water, particulate control system dust, offgas scrubber water (if used), clean offgas, and spent carbon (if used). Treated condensed water or scrubber purge water may be used as a dust suppressant for the treated media, sent to the site wastewater treatment facility, or disposed to the sewer. Dust collected from the particulate control system may be combined with the treated media, disposed of in a regulated facility or, if high in contaminant carryover, recycled through the desorber.

Offgas from desorption is processed to remove particulates. Volatiles in the offgas may be burned in an afterburner, collected on activated carbon, or recovered in condensation equipment. The selection of the offgas treatment system will depend on the mode of operation (co-current or counter-current), contaminants, contaminant concentration, cleanup standards, and economics.

In addition to the process streams, there is evidence that with some system configurations polymers may foul and/or plug heat-transfer surfaces. Tests of thermal desorption systems have documented the deposition of insoluble brown tars on internal system components (Ref. 17). Two EPA SITE demonstrations have produced evidence of dioxin/furan formation when solids contaminated with chlorinated aromatic organics were treated (Ref. 3). These dioxin/furans were found in the intermediate liquid and gaseous treatment residuals, and were rarely detected in the treated soils. Treatment of pesticides resulted in low concentrations of various thermal degradation products detected in the scrubber liquor, vapor-phase activated carbon beds, and the stack gas (Ref. 2).

5.3 TECHNOLOGY STATUS

Commercial scale units exist and are in operation. Most of the hardware components of thermal desorption are readily available off-the-shelf. There are more than 150 full-scale thermal desorbers available in the U.S. and in operation (Ref. 3). Although most of these units treat only petroleum-contaminated soils, the application to Superfund site remediation is increasing. As of February 1992, thermal desorption appeared in the Record of Decision (ROD) for 28 Superfund sites (Ref. 3). Thermal desorption was selected by EPA for evaluation as an alternative technology to incineration because of its demonstrated capability to remove volatile and semivolatile contaminants from soils and solids with treatment performance equivalent to incineration.

5.3.1 IT Corporation's Thermal Desorption System

Pilot-scale tests have been conducted on herbicide orange and dioxin contaminated soils and coral from two Department of Defense (DOD) facilities, PCB-contaminated soils from an electrical equipment salvage operation at the University of Minnesota Rosemount Research site, and soils contaminated with PCBs, heavy metals, and low-level mixed wastes from two DOE uranium enrichment facilities. Some sludges present a processing problem due to the formation of hard balls of dried sludge which could occlude trace levels of contaminants. The sludge was treated adequately at 550°C for 20 minutes at temperature in a unit designed to prevent balling. This equipment modification eliminates the need for back mixing the sludge with previously treated material to produce a feed that does not form into balls on processing.

5.3.2 Chemical Waste Management, Inc. X*TRAX™

As described previously, Chemical Waste Management has three X*TRAX™ systems operated by Rust Remedial Services at the Clemson Technical Center in South Carolina: a laboratory scale system, a mobile pilot-scale system, and a transportable full-scale production system.

The laboratory system has operated since 1988 and was used by Chem-Nuclear Systems in Barnwell, South Carolina, in 1989 to evaluate the process for treating mixed waste (Ref. 8). The laboratory system has also been tested on various Superfund soils, including those containing PCBs.

The pilot system has also been tested since 1988 on a variety of TSCA- and RCRA-regulated materials. In 1988 it was demonstrated at the Oak Ridge Gaseous Diffusion Plant on mixed waste. During 1989 and 1990, 10 different PCB-contaminated soils were processed under a TSCA research and development (R&D) permit, and three different wastes were tested under an EPA RCRA permit (Ref. 18).

The full-scale commercial system was accepted into the EPA SITE Program in 1989 at the Resolve, Inc. Superfund site in Massachusetts which contains approximately 35,000 tons of PCB-contaminated soil. A pilot demonstration took place over 10 days in 1992 during which the system processed 500 tons of soil at feed rates of 100 to 158 tons per day, and a system availability of over 85% (Ref. 18). An EPA SITE demonstration was also performed in which 215 tons of soil were treated at an average feed rate of 4.9 tons per hour, a residence time of 2 hours, and an average treated soil temperature of 732°F (Ref. 19).

5.3.3 Chemical Waste Management, Inc. VAC*TRAX™

The VAC*TRAX™ system is operated by Rust Remedial Services at the Clemson Technical Center in South Carolina (Ref. 12). This system is currently at the pilot stage. Tests with the pilot-scale system are scheduled by Geotech at Grand Junction, Colorado, for 15 different waste streams from DOE/Albuquerque sites. Pilot tests have been performed at Clemson Technical Center through the PRDA on Rocky Flats waste and on two mixed waste streams from the Grand Junction Project Office (GJPO) (Ref. 20). VAC*TRAX™ has also been endorsed by the Western Governor's Association/Develop On-Site Innovative Technologies (DOIT) Committee.

The existing pilot unit can accept up to 31 liters of material per charge. Under the DOE PRDA, pilot plant tests have been performed on surrogate wastes, RCRA waste, and mixed waste at the Clemson facility. The final phase of the PRDA is to construct a field-scale system scheduled for 1995 with a limited demonstration at a DOE site (Ref. 20). This commercial unit will be constructed on two trailers and will have a processing capacity of approximately 35 m³/day (Ref. 10).

5.3.4 Canonie Environmental Services Corporation's Low-Temperature Thermal Aeration

The LTTA technology was accepted into the SITE Demonstration Program in summer 1992 (Ref. 21). A demonstration was performed on soils contaminated with pesticides at the

Old Marsh Aviation site in Arizona during September 1992. Results will be published in an Applications Analysis Report and a Technology Evaluation Report which are under preparation. The full-scale LTTA system has remediated contaminated soils at six sites including three Superfund sites. More than 100,000 tons of soil have been treated by the full-scale LTTA system.

The LTTA is reported to remove VOCs, SVOCs, organochlorine pesticides (OCPs), organophosphorous pesticides (OPPs), and total petroleum hydrocarbons (TPH) from soils, sediments, and some sludges. LTTA has been used at full-scale to remove VOCs such as benzene, toluene, tetrachloroethylene (PCE), trichloroethylene (TCE), and dichloroethylene (DCE); SVOCs such as acenaphthene, chrysene, naphthalene, and pyrene; OCPs such as DDT and its metabolites, and toxaphene; OPPs such as ethyl parathion, methyl parathion, merphos, mevinphos; and TPHs.

5.3.5 Remediation Technology, Inc. (ReTec) High-Temperature Thermal Processor

ReTec has performed numerous tests on RCRA-listed petroleum refinery wastes including refinery vacuum filter cake, as well as creosote-contaminated clay and coal tar-contaminated soils. All tests were performed with ReTec's 100 lb/hour pilot-scale unit processing actual industrial waste (Ref. 17).

This technology was accepted into the SITE Demonstration Program in June 1991. The SITE demonstration was at the Niagara-Mohawk Power Company, a manufacturing gas plant site, in Harbour Point, New York, in summer 1992.

5.3.6 Roy F. Weston, Inc. Low-Temperature Thermal Treatment (LT³) Technology

This is an available, commercialized technology that has been applied to a variety of contaminated DOD, EPA, and commercial sites. The technology was accepted into the SITE Demonstration Program in September 1991 and was demonstrated at the Anderson Development Company Superfund site in Michigan. The system was tested on lagoon sludge contaminated with VOCs, SVOCs, and 4,4-methylene bis(2-chloroaniline) (MBOCA). Results have been published in Reference 15.

Bench-, pilot-, or full-scale systems have treated soil contaminated with coal tar, drill cuttings (oil-based mud), No. 2 diesel fuel, JP-4 jet fuel, leaded and unleaded gasoline,

petroleum hydrocarbons, halogenated and nonhalogenated solvents, VOCs, SVOCs, and PAHs (Ref. 15).

5.3.7 ETG Environmental, Inc. Therm-O-Detox® System

This system has been applied to several refineries to process API separator sludge (K051) and DAF unit wastes (K048) (Ref. 16). In late 1992, the MTTD/BCD technology was demonstrated at the Kopper's Superfund site in South Carolina under the EPA's SITE program.

5.4 REMOVAL EFFICIENCY

Several thermal desorption vendors have reported performance data for their systems ranging from laboratory studies to full-scale operations at designated Superfund sites. The quality of this information has not been evaluated and is provided as a general guideline to the performance of thermal desorption equipment. Thus, this data may not be directly applicable to a specific site. Good site characterization and treatability studies are essential to refine and screen any treatment technology.

Most thermal desorption systems offered by vendors include an offgas treatment system. The following summaries of performance data include only the removal efficiencies of the desorber and not the performance of the offgas treatment system as offgas treatment requirements and methods will vary.

5.4.1 IT Corporation's Thermal Desorption System

Thermal separation effectively separated PCBs from mixed waste to enable the treated soil to be managed as low-level radioactive waste at the DOE Oak Ridge Site. PCB contamination of 37.5 to 35 ppm was reduced to less than 2 ppm with a total residence time of 19 minutes at 1022°F. All identified semivolatile contaminants in the waste were effectively treated to below detection limits. Residual organic carbon in the treated soil indicated incomplete removal of all the carbonaceous materials due to nonvolatile pyrolysis products. At the same operating conditions, mercury contamination was reduced from 0.8 ppm to less than 0.1 ppm. The majority of the uranium and technetium in the waste feed remained in the treated soil; however, entrained particles in the exit gas produced a concentration of radionuclides in the cyclone.

Higher concentrations of PCBs in the cyclone-captured solids were also attributed to entrainment of untreated soil particles in the gas stream, or to condensation of PCBs on the particles. Furans were generated and captured in the cyclone solids and in the scrubber filter solids. The presence of benzene in the treated material may be due to the breakdown of other hydrocarbons present in the feed or by a reformation of benzene during the extended cool-down cycle. The concentration of flammable components within the offgas suggests that offgas treatment will be required to prevent discharge of toxic or flammable gas.

5.4.2 Chemical Waste Management, Inc. X*TRAX™

Chem-Nuclear performed treatability studies on two types of soils contaminated with mixed waste at the Oak Ridge Y-12 Plant beginning in late 1989 (Ref. 22). Type 1 soil was characterized as dewatered, mercury and uranium contaminated sewer sediment. Type 2 soil was PCB, organics and uranium contaminated oil landfarm soil. For the Type 1 soil the process achieved 98.2% mercury removal and 97.6% PCB removal with an initial feed of 1,000 to 1,300 mg/kg and 10 to 12.2 mg/kg, respectively. The feed contained 86 pCi/gm of gross alpha, and 250 pCi/gm of gross beta activity. The resulting condensate liquid contained less than 5 pCi/l of alpha and beta activity; however, the phase separator data indicated 140 to 160 pCi/l of alpha and beta activity, respectively. This high activity was assumed to be the result of the high particulate loading in the phase separator. Volatile mercury was condensed in the liquid phase and collected in the condensate sample. The Type 2 soil showed an average PCB removal of 97.4%. Treated soils showed ppb levels of organics such as phenol, 2,4-dimethylphenol, benzene, styrene, etc.

Pilot tests were performed at CWM's Kettleman Hills facility in California. Twenty tons of PCB- and organic-contaminated soils were processed through the 5 ton per day pilot system. The results of PCB separation from soil is presented in Table 5-2 (Ref. 17). Results of various laboratory and pilot-scale studies on the X*TRAX™ system are provided in References 6, 8 and 18. In most cases, volatile organics are reduced to below 1 ppm, semivolatile organics to below 10 ppm and often below 1 ppm. Soils containing 120 to 6,000 ppm PCBs have been reduced to 2 to 25 ppm, and removal efficiencies of 96% to over 99% have been demonstrated for soils contaminated with pesticides. Mercury has been reduced from 5,100 ppm to 1.3 ppm (Ref. 23).

Table 5-2. X*TRAX™ System Removal of PCB from Contaminated Soil (Ref. 17)

Matrix	Feed (ppm)	Product (ppm)	Removal (%)
Clay	5,000	24	99.3
Silty Clay	2,800	19	99.5
Clay	1,600	4.8	99.7
Sandy	1,480	8.7	99.1
Clay	630	17	97.3

The Resolve Superfund site contained contaminated soil with PCB concentrations in the range from 181 to 515 mg/kg. The pilot demonstration resulted in PCB concentrations in the treated soil consistently less than 2 ppm (Ref. 18). For the SITE demonstration at the same site, PCB concentrations in treated soil samples were less than 1.0 mg/kg and the average concentration was 0.25 mg/kg. PCDDs and PCDFs were not formed, and concentrations of TCE, oil and grease were below detectable limits in treated soil (Ref. 19).

5.4.3 Chemical Waste Management, Inc. VAC*TRAX™

Tests have been performed on the pilot system with spiked material, RCRA waste and mixed waste including a variety of volatile and semivolatile contaminants. Results of these tests are summarized in Table 5-3 (Ref. 10). PCP had a much lower removal, indicating a possible limitation for certain semivolatile compounds (Ref. 20). In some cases, low temperatures (100°C) were required to prevent melting of assorted plastic items. These cases resulted in reduction of volatiles to below the regulatory level but required a longer time at temperature.

This process also demonstrated containment of radioactive components within the solids matrix. In the case of mixed waste containing Radium-226, the condensate recovered from the process, after simple filtering, had a radioactivity level <0.57 pCi/l. In a test soil spiked with molybdenum trioxide as a surrogate for uranium oxide, all the molybdenum was accounted for in the treated product.

A pair of surrogate tests were conducted on a RCRA waste from the RFP (Ref. 20). This waste stream is called "combustible shop waste" and consists of cloth, plastics and similar trash type components that are contaminated with solvents and industrial lubricants and oils. The VAC*TRAX™ unit was operated at an oil temperature below the melting point or degradation point of the waste material (i.e., 124°C or 255°F). The final product temperature was about 102°C, and the total heating time was 4 and 6 hours. Results are shown in Table 5-4.

Table 5-3. Results of the VAC*TRAX™ Process on Various Waste Streams (Ref. 10)

Contaminant	Solids Matrix	Final Solids Temp (°C)	Time at Temp (min.)	Starting Conc. (ppm)	Ending Conc. (ppm)	Removal (%)
<u>Volatiles</u>						
Acetone ¹	Soil/Clay	239	45	1,644	5.98	99.6
Acetone	Debris/PPE	101	240	7.51	BQL(0.4)	>94.5
Carbon Tetrachloride ¹	Soil/Clay	239	45	105	BQL(0.2)	>99.8
2-hexanone	Debris/PPE	101	240	5.93	0.20	96.6
Toluene	Debris/PPE	104	360	6.7	0.055	99.2
Tetrachloroethylene ¹	Soil/Clay	239	45	118	BQL(0.2)	>99.8
Tetrachloroethylene ²	Soil/Lint	257	360	1,000	J(0.003)	>99.9999
Ethylbenzene ¹	Soil/Clay	239	45	630	BQL(0.2)	>99.97
Ethylbenzene	Debris/PPE	104	360	20	0.075	99.6
MIBK	Debris/PPE	104	360	15	0.14	96.8
Xylene ¹	Soil/Clay	239	45	2,672	BQL(0.2)	>99.993
Xylene	Debris/PPE	104	360	110	0.092	99.92
Styrene ¹	Soil/Clay	239	45	461	BQL(0.2)	>99.96
Styrene	Debris/PPE	104	360	230	0.14	99.94
<u>Semivolatiles</u>						
Bis(2-ethylhexyl) phthalate ¹	Soil/Clay	239	45	577	1.05	99.8
Pentachlorophenol ¹	Soil/Clay	247	90	581	126	83.2
<u>Metals</u>						
Molybdenum Trioxide	Soil/Clay	239	45	211	209	0.9

Notes: 1. Tests performed on spiked sample.
2. Tests performed on mixed waste.
BQL(A) = Below Quantitation Limit; quantitation limit = A
J(A) = Estimated value of A, below quantitation limit
PPE = Personal Protection Equipment

Table 5-4. VAC*TRAX™ Results for the RFP RCRA Combustible Waste Tests (Ref. 20)

Component	4-Hour Run Time		6-Hour Run Time	
	Feed Conc. (ppm)	Avg. Product Conc. (ppm)	Feed Conc. (ppm)	Avg. Product Conc. (ppm)
Acetone	7.51	<0.41	1.0	0.07
MIBK	18.7	1.1	15	0.48
Toluene	3.54	<0.20	6.7	0.06
2-Hexanone	5.93	0.22	—	—
Ethylbenzene	9.59	0.24	20	0.10
Xylene	50.1	1.35	110	0.09
Styrene	90.7	2.73	230	0.14

One of the GJPO waste streams consisted of dry cleaner's lint trap waste combined with uranium mill-tailings (Ref. 20). The waste consisted of approximately 70% soil and 30% lint contaminated with TCE. The second waste stream consisted of soil and rock with a small amount of lint contaminated with TCE. Final treated product temperature was 251°C to 258°C, the total processing time was about 6 hours, and the time at temperature was typically over 3 hours. In total, 29 batches were tested with feed concentrations ranging from 6.5 to 1,160 ppm of TCE. All batches were treated to below 0.005 ppm except for 5 batches that required re-treatment because they contained up to 0.017 ppm after the first treatment cycle. These tests also demonstrated the ability to retain radionuclides in the dryer, preventing the condensate from being radioactive.

5.4.4 Canonie Environmental Services Corporation Low-Temperature Thermal Aeration

Canonie Environmental has extensive performance data for its Low-Temperature Thermal Aeration (LTTASM) system at full-scale operation (15 to 20 cu. yds. per hour). This system has been applied at several Superfund and privately funded sites. Table 5-5 presents a summary of some of the available data (Ref. 17).

Table 5-5. Summary Results of the LTTASM Full-scale Clean-up Tests

Site	Processed	Contaminant	Soil (ppm)	Treated (ppm)	Removal (%)
S. Kearney	16,000 tons	VOCs	177 (avg)	0.87 (avg)	99.5 (avg)
		PAHs	35.31 (avg)	10.1 (avg)	71.4 (avg)
McKin	>9,500 cu yds	VOCs	ND to 3310	ND to 0.04	>99.9
	2,000 cu yds	PAHs		<10	
Ottati & Goss	4,500 cu yds	VOCs	1,500 (avg)	<0.2 (avg)	>99.9 (avg)

ND = Nondetectable

The LTTA system used at the EPA Superfund site in Arizona treated approximately 52,000 tons of soil contaminated with toxaphene, DDT, DDD, DDE, and other OCL pesticides (Ref. 2). Average total concentrations of OCL pesticides were in the range of 200 to 500 mg/kg; however, hot spots were identified with concentrations as high as 2,500 mg/kg. The soil was

treated at a feed rate of 34 to 38 tons per hour with a soil discharge temperature of 730°F. Pesticide removal efficiencies in percent are as follows:

4,4'-DDT	99.97	Dieldrin	99.27
4,4'-DDD	>99.97	Toxaphene	>99.83
4,4'-DDE	90.26	Endosulfan I	99.98
Endrin	>99.85	Endosulfan II	99.34
Endrin aldehyde	97.43		

In this case, no dioxins were detected in the stack gas, the treated soil, the liquid condensate, or the activated carbon. However, low concentrations of thermal degradation products were found including acetone, acrylonitrile, dihydrofuranone, phenol, and others.

5.4.5 Remediation Technology, Inc. (ReTec) High-Temperature Thermal Processor

Tests using ReTec's 100 lb/hr pilot-scale system on industrial wastes, with treatment temperatures of 450°F to 500°F, demonstrated removal efficiencies greater than 97% for most compounds. Removal efficiencies were somewhat lower when treating coal tar contaminated soils, ranging between 90 to 99%, depending on the organic compound.

5.4.6 Roy F. Weston, Inc. Low-Temperature Thermal Treatment (LT³) Technology

Table 5-6 presents a summary of performance data on the Weston LT³ system for full-scale treatment of soil contaminated with No. 2 fuel oil and gasoline at a site in Illinois (Ref. 17).

Table 5-6. Full-scale Performance Results for the LT³ System

Contaminant	Soil Range (ppb)	Treated Range (ppb)	Removal (%)
Benzene	1,000	5.2	99.5
Toluene	24,000	5.2	99.9
Xylene	110,000	<1.0	>99.9
Ethyl Benzene	20,000	4.8	99.9
Naphthalene	4,900	<330	>99.3
Carcinogenic Priority PNAs	<6,000	<330-590	<90.2-94.5
Non-Carcinogenic Priority PNAs	890-6,000	<330-450	<62.9-94.5

The contaminated lagoon sludge at the Anderson Development Company SITE demonstration was heated to above 500°F for a residence time of 90 minutes. A total of 80 tons of sludge was treated at a processing rate of 2.1 tons/hr. Key results of these tests are as follows (Ref. 15):

- VOC concentrations in untreated sludge varied from 35 to 25,000 µg/kg and were removed to less than detection limits (60 µg/kg for most compounds). For example, toluene was present in the untreated feed at levels of 1,000 to 25,000 µg/kg and PCE was present at concentrations from 690 to 1,900 µg/kg. Both compounds were treated to a concentration below 30 µg/kg.
- MBOCA concentration in the untreated sludge ranged from 43.6 to 860 mg/kg and was removed with efficiencies ranging from 79.8 to 99.3% leaving 3 to 9.6 mg/kg in the treated sludge. MBOCA was not completely removed during treatment, and higher concentrations were observed on the fabric filter dust than in the treated sludge, most likely due to the high tendency of MBOCA to adsorb onto clay particles. The decrease in MBOCA concentration was accompanied by an increase in the concentration of AC-MBOCA, a metabolite of MBOCA. Thus, the removal of MBOCA was likely due to desorption as well as conversion to AC-MBOCA.
- The concentration of all SVOCs initially present in the sludge were decreased with removal efficiencies of 57 to 97.4% except for phenol, which increased in concentration due to chemical transformations during heating.
- Dioxins and furans were formed during heating and distributed in the treated sludge, fabric filter dust, exhaust gas, and liquid condensate. The formation of these compounds is encouraged by the sludge treatment conditions such as elevated temperature (> 500°F), the presence of chemical precursors, alkaline pH from lime being added to the sludge, and a high concentration of free chlorine from adding ferric chloride to the sludge as a conditioning agent before dewatering.

5.4.7 ETG Environmental, Inc. Therm-O-Detox® System

The MTTD unit was applied to an Ohio refinery that generated belt press cake from API separator waste (K051) containing approximately 40% water and 60% oil and solids. The waste material was processed at 950°F and reduced the VOC content of the soil to below detection

limits, and SVOC content to less than 2 mg/kg which was below BDAT standards for landfill disposal.

Tests were performed at the Kopper's Superfund site on soils containing PCP in excess of 8,000 ppm with a MTTD/BCD system, capable of handling 0.25 to 0.5 tons/hr (Ref. 16). PCDDs/PCDFs were treated from several thousand $\mu\text{g}/\text{kg}$ in untreated soil to below detection limits of less than 20 $\mu\text{g}/\text{kg}$ in the treated soil. PCDDs/PCDFs in the condensed oil were treated with the BCD process from several hundred to several thousand $\mu\text{g}/\text{kg}$ to below 1 $\mu\text{g}/\text{kg}$.

5.5 TECHNOLOGY COMPARISON

Applicability of thermal desorption and the optimum type of desorber, and appropriate operating conditions is highly site specific. Whether thermal desorption is a viable alternative, in terms of cost and performance, depends on site location, soil characteristics, and the contaminant to be removed as discussed in previous sections. For mixed waste, thermal desorbers that minimize the generation of radioactively contaminated dust and fine particulates would be preferable. Thus, indirectly heated systems are preferred for dust containment.

Thermal desorption itself is a non-oxidation process and as such may avoid the stigma associated with incineration. However, the U.S. EPA regulation on treatment of debris notes that a thermal desorber is regulated under the RCRA "either as an incinerator (if the device is direct-fired or if the offgas is burned in an afterburner) under Subpart O of Part 264 or 265, or as a thermal treatment unit under Subpart X, Part 264 or Subpart P, Part 265" (Ref. 24). Use of condensers and vapor-phase activated carbon adsorption columns transfer the problem to another medium requiring on- or off-site disposal or treatment. Thus, one of the vapor-phase destruction technologies discussed in Section 6 may be useful.

High localized temperatures may cause pyrolysis and "coking," producing carbonized deposits on the soil that are difficult to remove. In addition, some materials, such as tars, may foul and/or plug heat-transfer surfaces. Some fine grained soils, such as wet clay or sediments, may be difficult to treat and may form balls with a hard crust entrapping moisture and contaminants inside, or may stick to and foul heat-transfer surfaces. If this occurs, the desorber will require manual cleaning.

Typically large objects must be rejected from the feed stream limiting the application of thermal desorption to treatment of contaminated debris. Low melting point materials, such as plastics, cannot be treated in most desorbers because they will foul the heat-transfer surfaces.

However, this limitation may be overcome with a vacuum dryer allowing operation at a lower temperature. A vacuum dryer may also prevent the coking problem associated with some materials.

Use of lime to decrease the pH to prevent corrosion, and the use of ferric chloride to enhance dewatering can provide conditions favorable to the formation of dioxins and furans in the desorber.

In the LT³ Superfund demonstration (Ref. 15), metal concentrations in the fabric filter dust were greater than the concentration in either the treated or untreated sludge. This may be due to the potential for volatile metal species to form in the presence of chlorine and subsequently condense on particles or condense homogeneously to form small particulates (Ref. 3).

5.6 COST OF TECHNOLOGY OR EQUIPMENT

Published processing costs for thermal desorption vary depending on the author and the time when the estimate was made, as well as other technical factors. These cost estimates are highly variable due to the base year of the estimate, quantity of waste to be processed, terms of the remediation contract, moisture content of the waste, organic contaminants, characteristics of the contaminated medium, and cleanup standards. Site specific features affecting cost include site area, accessibility, availability of utilities, and geographic location. Costs estimates should include work plan preparation, sampling and analysis, permitting, excavation, processing, quality assurance/quality control (QA/QC) verification of treatment performance, disposal/treatment of secondary waste, and reporting. Some cost estimates may include some or all of these factors, and some may not. The factors included in these cost estimates are not identified in most cases. However, the final determination of the lowest cost alternative will be more site-specific than process equipment dominated (Ref. 17).

Processing costs documented by several vendors are summarized in an EPA Bulletin (Ref. 17). These costs range from \$80 to \$350 per ton processed. Costs summarized in Reference 3 are identified as being scale dependent, ranging from \$90 to \$130 per ton for a 1,000-ton site to \$40 to \$70 per ton for a 10,000-ton site for mobile system treating petroleum-contaminated soils. A mobile system treating a CERCLA site is reported to range in cost from \$300 to \$600 per ton for a 1,000-ton site to \$150 to \$200 per ton for a 10,000-ton site.

According to J. J. Cudahy (Ref. 1), mobile thermal treatment units start to compete with fixed facilities, on a treatment cost basis, at site sizes in the range of 3,000 to 4,000 tons. Thermal desorption costs can range from about \$35 to approximately \$125 per ton, depending on the site size, desorber capacity, and the soil moisture content. A large fixed-base system can treat low-moisture contaminated soils for approximately \$35 to \$60 per ton.

Cost estimates by Roy F. Weston (Ref. 15) for the LT³ system indicate treatment costs per ton of \$373, \$537, and \$725 for soils containing 20, 45, and 75% moisture, respectively. Costs for the X*TRAXTM system are quoted at \$150 to \$250 per ton for remediations >5,000 yd³ (Ref. 8).

5.7 REFERENCES

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SECTION 6

GAS-PHASE DESTRUCTION PROCESSES

The technologies described in this section are used to destroy organic contaminants in gas or vapor phase. They may be used for on-site destruction of organics volatilized by soil vapor extraction techniques, air or steam stripping of organics from groundwater, or by thermal desorption systems. Some of these technologies may also be used for offgas treatment for upstream thermal destruction technologies. Afterburners, or secondary combustion chambers, and catalytic oxidation devices are commonly used devices to destroy organics in the vapor or gaseous phase. There is a significant amount of literature and vendor information available for these systems, so they are not discussed in this report. Rather, this section is devoted to less common or emerging technologies that do not use combustion processes and may be more acceptable to the public.

The technologies discussed in this section include the following:

- Thermal Gas-Phase Reduction Process
- Gas-Phase Electron Beam Oxidation
- Nonthermal Plasma Processes
- Vapor-Phase Photolytic Oxidation
- Packed-Bed Reactor (Thermatrix Process)

Note that in the following sections the abbreviation "PICs" (products of incomplete combustion) is used rather loosely to refer to reaction byproducts even though the reactions do not involve combustion.

6.2 GAS-PHASE ELECTRON BEAM OXIDATION

6.2.1 Technology Description

The high-voltage electron-beam systems discussed in Section 2.7 have been targeted at dilute organic liquids in an aqueous waste stream. This high-energy electron-beam (in the 2 Mev range) processing involves irradiating aqueous solutions to produce sizable quantities of the free radicals e_{aq}^- , H^+ , $OH^\bullet$ that react with the organic contaminants to break the chemical bonds and produce CO_2 , H_2O , and salts. However, for vapor-phase destruction, medium-energy electron beams (in the 200 kev range) are adequate. Even lower energy electrons (in the 10 ev range) are used in cold electric discharge plasmas to destroy vapor-phase organics. These low-energy devices will be discussed in the next section. In these systems the energetic electrons may directly break the chemical bonds of the organic compounds or produce free radicals from oxygen in the carrier gas which, through oxidation reactions, also destroy the organic contaminants.

Initial tests performed at a LLNL Superfund site, at which vacuum extraction wells were used to remove subsurface air enriched with trichloroethylene (TCE) vapor, used a hardware arrangement shown in Figure 6-3 (Ref. 1). The cylindrical exposure plenum (5) was fabricated from sheet steel and placed in the ground. The plenum was 213 cm in diameter, and 610 cm long; the length is approximately the range of 2 Mev electrons through atmospheric air. The electron accelerator (1) was placed at the ground surface with the beam (2) pointing downward, entering the plenum through a foil window. A small shielded structure of cement blocks was placed around the accelerator to minimize radiation to personnel. The TCE vapor was pumped through the inlet pipes (3) and deposited at the chamber floor at atmospheric pressure and moved upward toward the two exhaust pipes (4) at the top of the plenum. The vapor was exposed to the electron beam as it passed through the plenum.

The maximum electron beam power for these tests was 400 watts, and the vapor was pumped through the system at a fixed rate of 270 cfm. Vapor travel time through the plenum was approximately 2 minutes, and the maximum dose at 400 watts was 90 krad.

There are currently two known medium-energy systems being developed or commercialized: a 200 kW system developed by Zapit Technology, Incorporated; and a Tunable Hybrid Plasma system, being developed by PNL in coordination with Massachusetts Institute of Technology (MIT), that currently operates at a laboratory scale of 50 W.

Figure 6-3. Schematic of Field Hardware for Electron Beam Destruction of TCE Vapor at the LLNL Superfund Site (Ref. 1)

6.2.1.1 Zapit Technology, Inc.

Zapit Technology, Incorporated has developed a low-power (200 kW), skid-mounted, portable e-beam system for application to organic vapors (Ref. 2). This technology is currently being marketed and commercialized for on-site groundwater treatment and air pollution control applications. The system consists of a self-contained portable unit weighing 2,500 pounds, and the size of a large desk. The unit has a single power source and electron beam head and can treat up to 1,000 cfm with contaminant concentrations of up to 250 ppm in a one cubic foot reaction chamber. Different combinations of flow and concentration can be accommodated, such as 500 cfm and 500 ppm. More heavily contaminated vapor streams can be treated by adding a second power source and e-beam head.

The Zapit system uses a simple 160 to 220 kV, dc power supply to provide up to 200 kW of beam power with up to 80% efficiency. It can be designed and tuned for the appropriate power, dose levels, and throughput for specific applications and contaminants.

6.2.1.2 Tunable Hybrid Plasma

In this system a 100 to 300 kev electron beam is directed into a flow of air containing organic contaminants to produce a plasma. The electron beam is created by accelerating electrons from a heated tungsten filament in a vacuum toward a thin titanium window which forms the vacuum seal and allows the electrons to enter the flowing air stream. The electron beam produces a plasma with electron densities in the range of 10^9 - $10^{10}/\text{cm}^3$ and creates reactive radicals such as OH, O, and O_3 (Ref. 3). The electron density of the plasma, and thus the chemical reaction rates, can be controlled by the electron-beam current, and the electron temperature can be controlled by a superimposed electric field. The combination of the electron beam and electric field gave rise to the term tunable hybrid plasma (THP) reactor.

Laboratory tests (Ref. 4, 5 and 6) indicate the mechanism for the plasma-induced decomposition of organics is dissociative electron attachment. The electrons produced by the electron beam lose their energy in the waste gas/air stream primarily by creating secondary electrons and producing a room temperature plasma. These low-energy electrons selectively interact with the organic compounds depending on the electron temperature. At low-electron energies or temperatures the attachment reaction rate constant for carbon tetrachloride (CCl_4), which is equal to the dissociative attachment rate constant, is very high and decreases with increasing electron energy. Thus, increasing a superimposed electric field tends to slightly decrease the decomposition rate of CCl_4 in dry air. However, for compounds such as CHCl_3 , CH_2Cl , and other VOCs, the electron attachment rate constant increases with increasing electron energy. Tests demonstrate that with an increasing superimposed electric field, the decomposition rate of these compounds increases in dry air.

The primary variable that governs the destruction level for any set of inlet conditions is the absorbed dose. The system parameters that contribute to the absorbed dose include the beam acceleration voltage, the beam current, and the mass flow rate of the contaminated air stream. For a specific inlet concentration of organic material, destruction improves with increased absorbed dose. However, for a specified dose, destruction also improves with decreasing inlet concentration. Thus, if the inlet concentration decreases, the specific power deposition may be reduced and still maintain a specified fractional removal of the contaminant. For example, for a 90% removal of CCl_4 , the required specific power deposition could be reduced by a factor of 10 as the intake concentration was reduced by a factor of 25 (from 663 ppm to 26 ppm) (Ref. 7).

6.2.2 Input and Output Stream Characteristics

VOCs can be removed from soils by thermal desorption or soil vapor extraction, and from aqueous wastes by air or steam stripping, thereby producing a gas or vapor phase capable of being treated by this technology. At this time the only known limitations on the input concentration of organics is the dose available to destroy the organic compounds, which is determined by the flow rate (or residence time in the beam) and beam power.

Tests at the LLNL Superfund site (Ref. 1) resulted in very low concentrations of reaction products from the destruction of TCE. These included chloromethane (0.008 ppm), dichloromethane (0.02 ppm), and chloroform which increased from an initial concentration of 0.01 ppm to 0.1 ppm. Trimethylbenzene was found at a concentration of 0.1 ppm, most likely due to trace amounts of diesel fuel in the TCE stream. Concentrations less than 0.1 ppm of acetone were also produced and then partially destroyed.

Tests at the same LLNL Superfund site were performed by Zapit Technology, Incorporated (Ref. 2). Most waste streams tested had over 99% relative humidity; however, the destruction efficiency for TCE was the same in the presence and absence of water. Therefore, it is unclear whether water is required for chemical bond destruction. It should be no problem with adding water vapor to the waste stream if water is required. Most of the reactions are exothermic, so the process must be controlled to hold the temperature below 400°C to prevent the formation of undesirable recombination products in the exit stream.

In the Zapit site demonstration at LLNL, no evidence of sulfur or nitrogen oxides were found in the treated waste stream, and no carbon monoxide was found in the treated waste for other tests at McClellan AFB.

The THP can be applied to a wide variation of chlorinated VOC concentrations (from 10 to 2,000 ppm) in dry air. It has been demonstrated to destroy carbon tetrachloride, chloroform, and trichloroethylene. Laboratory tests are planned to apply the technology to other VOC contaminants. The importance of the presence of O₂ in the THP system (possibly to form CO₂) was demonstrated by the fact that significantly lower CCl₄ fractional removal was obtained when dry nitrogen was used as the carrier gas (Ref. 4). With dry argon as the carrier gas very little decomposition was observed.

Tests with the THP system indicated a definite decrease in destruction efficiency in humid air. Because electron densities were found to be significantly less in humid air than in dry air (Ref. 5), and since attachment of electrons is the major mechanism for decomposition of

the materials tested (CCl_4 and CHCl_3), this decreased electron density is the most likely reason for decreased destruction efficiency in wet air. Approximately twice as much electron-beam specific power (kW/kg/sec) is generally required to achieve the same fractional removal in humid air as in dry air. Thus, the field system design includes an air dryer prior to admitting the air to the destruction chamber.

The main byproducts from CCl_4 decomposition with the THP are CO_2 , CO , Cl_2 and HCl with trace amounts of phosgene (Ref. 8). Passing the gas stream through a basic scrubbing solution will convert the chlorine compounds to NaCl . The byproducts from the decomposition of TCE were dissolved in an aqueous solution of sodium hydroxide to produce sodium acetate; the byproducts in the offgas were not determined.

6.2.3 Technology Status

The Zapit system has been tested at a TCE ground-contaminated site at LLNL, and at McClellan Air Force Base at a site containing a complex mixture of organic contaminants. A prototype unit is being installed at the University of Tennessee Space Institute to test various compounds and mixtures, perform basic research to understand the destruction mechanisms, to debug the system design, and develop reliability data. Current applications are for waste streams containing up to 500 ppm of contaminants and flowing at 2,000 cfm. In the future, the Zapit system is expected to be applicable to waste streams containing up to 3,000 ppm and flowing at 10,000 cfm (Ref. 2).

The THP system has been demonstrated at the MIT laboratory on CCl_4 and several other chlorinated VOCs, and is being supported by the DOE's Office of Technology Development, VOC in Arid Soils Integrated Demonstration. The electron-beam unit for the field demonstration at the Hanford site has been delivered to MIT (Ref. 9). The field test unit has been successfully tested in the laboratory and installed in a 45-foot truck trailer. The unit is to be installed at the DOE Hanford site in late 1994. This field test unit is a small-scale pilot plant which has the same technology that will be used for the full-scale system.

The field-test unit is capable of processing $0.3\text{--}0.6 \text{ m}^3/\text{min}$ of contaminated air. Based on this rate, the full-scale units will be capable of processing $50 \text{ m}^3/\text{min}$. The goal is to have this technology available for commercial use by the end of 1995.

6.2.4 Destruction Efficiency

The TCE concentration in the unirradiated vapor at the LLNL Superfund site was 60 ppmv. The TCE concentration was reduced to less than 1 ppmv when the electron beam was operating at maximum power of 400 watts which is equivalent to 90 krad at the flow rate of 270 cfm (Ref. 1). The net concentration of organic reaction products was much less than the initial TCE concentration. An analysis of inorganic compounds in the irradiated vapor found no oxides of nitrogen or ozone.

Zapit reports reduction of TCE to non-detectable levels, and other toxic contaminants by 99.99% or more in some applications. Tests performed in 1991 at LLNL successfully reduced TCE concentrations by several orders of magnitude (Ref. 10). Tests performed at McClellan Air Force Base involved waste samples containing 17 major hazardous compounds (including TCE, TCA, vinyl chloride, DCE, freon, benzene, and xylene) with total VOC concentrations up to 9,000 ppmv (Ref. 2 and 10). Laboratory analysis indicated that most of the hazardous organics were reduced to non-detectable levels at a dose of approximately 60 kilograys (6,000 krad) using instruments capable of detecting down to 1 ppmv (Ref. 10). The use of a promoter (considered proprietary) enhances the oxidation process significantly to provide overall destruction efficiencies of 99% for the more resistant compounds (Ref. 2). Treatability tests on a variety of organics, including PCBs, halogenated aromatics, and other halogenated hydrocarbons indicate complete destruction with the production of CO_2 , H_2O , and HCl .

The THP field test unit at MIT demonstrated the reduction of CCl_4 from 1,100 ppm to less than 1 ppm, with a 99.97% removal efficiency (Ref. 9). The destruction of TCE required less than 10% of the energy needed to destroy CCl_4 .

6.2.5 Technology Comparison

This technology destroys organic material rather than concentrating it in carbon adsorption beds which must undergo further treatment, or incinerating it in a combustion chamber. The technology is claimed to achieve the same DRE as combustion in an afterburner, but at a much lower temperature. Thus, the amount of gas produced is significantly reduced by eliminating the fuel and associated combustion air. Low temperature operation may also mitigate the formation of recombination products such as dioxins and furans. Finally, the beam electrons have much higher energy than ultraviolet light, so that more reactions are possible and more resistant bonds can be broken.

6.2.5.1 Advantages

- E-beam treatment is effective for a broad range of wastes. This technology is not sensitive to the treatability of the contaminant or the particular target species, and can treat waste streams of varied composition.
- As with the aqueous systems, the gas/vapor stream may be closed loop with a short residence time. Recycling of the waste stream could provide the required destruction efficiency for compounds difficult to destroy.
- Developers report that, because this is a low-temperature process, recombination products are not formed. However, no test data was available confirming the composition of the offgas streams. Plugging, scaling and corrosion issues characteristic of high temperature or chemical processing should be avoided.
- The high-energy electron beams are effective in destroying hazardous organic waste, particularly chlorinated hydrocarbons.
- The principal components of these systems are standard items that have been manufactured for industrial use for several years. Electron accelerators are an established technology that is presently economically competitive with other destruction technologies.
- The waste treatment unit stands away from the waste stream preventing large-scale contamination and generation of secondary waste, and making the system easy to maintain.
- The technology is portable and could be ready for field implementation in about one year.

6.2.5.2 Disadvantages

- There is a potential need for post-processing to achieve the required destruction efficiency depending on contaminants, reaction byproducts, and local discharge requirements. The technology also requires post-processing such as acid gas scrubbers.

- The Zapit system has been limited to a concentration of 500 ppm of VOCs but is expected to be able to treat up to 3,000 ppm, while the THP system appears to be limited to concentrations of about 2,000 ppm.

6.2.6 Cost of Technology or Equipment

Capital costs for the Zapit system are approximately a factor of 5 to 10 less than the cost of high-energy accelerators. A one-time system cost is approximately \$100,000; however, with multiple purchases the cost is expected to decrease (Ref. 10). The Zapit system, using a dc power supply, has daily power costs of \$10 to \$15 (Ref. 2), and the treatment costs are estimated to be \$6 to \$10 per pound of VOC treated (Ref. 11).

A full-scale tunable hybrid plasma system (175 kW electron beam) is projected to cost about \$1 million including the accelerator and support equipment. The system is projected to treat about ten pounds of CCl_4 per hour and operate 90% of the time. Therefore, the system should be able to treat 78,000 pounds of CCl_4 per year. The estimated cost of destroying CCl_4 for a full-scale system is between \$3 and \$4 per pound; the cost for TCE is less than \$0.40 per pound (Ref. 9).

6.2.7 References

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6.4 VAPOR-PHASE PHOTOLYTIC OXIDATION

Vapor-phase photochemical detoxification has been tested at near-room temperature to treat VOCs in the offgas from vapor-phase extraction systems (Ref. 1 and 2), at elevated temperatures to treat offgas from thermal desorbers (Ref. 3 and 4), and to treat PICs and other combustion byproducts using solar radiation (Ref. 5).

Unlike photolysis in an aqueous medium where UV light is primarily used to produce oxidizing radicals from hydrogen peroxide or ozone, in the gas or vapor phase the initial destruction is due to direct photolysis of the organic molecule. Depending on the contaminant and mixture of species, direct photolysis may be the only method of destruction, or it may produce active radicals (e.g., organic radicals and $\text{Cl}\cdot$) that initiate a chain reaction and reproduce $\text{Cl}\cdot$ to rapidly and more efficiently destroy additional contaminant molecules. Since destruction occurs by direct interaction of the photons with the molecule, there must be an overlap between the absorption spectrum of the reacting species and the emission spectrum of the light source. For efficient destruction, the absorbing species must have a high absorptance, or extinction coefficient, at the wavelength of the source having the highest intensity.

Typical UV sources include low- and medium-pressure mercury lamps having a peak output at 254 nm, with a smaller (<15%) emission at 185 nm. The balance of the energy is emitted in the visible and infrared regions, which are not useful for organic photolysis. Because most VOCs absorb in the sub-250 nm region as shown in Figure 6-8 (Ref. 1), mercury UV lamps rely on the production of hydroxyl radicals from hydrogen peroxide or ozone in an aqueous solution to attack organics. Purus, Inc. has applied xenon plasma-pulsed flashlamps to produce relatively high-intensity emissions in the deep UV region (<250 nm) as compared to mercury lamps. Figure 6-9 compares a 6-inch Purus 3675-W xenon flashlamp with a 7,500-W medium-pressure mercury lamp used in a Peroxidation system discussed in Section 2.

The overlap between the xenon emission spectrum and VOC absorption spectra is shown in Figure 6-8 where the lamp spectrum is given on a linear scale and the absorption spectra are on a logarithmic scale. The halomethanes and TCA are weak absorbers, whereas TCE and other chloro-olefins absorb strongly in the deep UV region. The VOCs all absorb strongly below 200 nm. A shift in peak output from 250 to 230 nm is significant because it corresponds to a 1 to 2 order of magnitude increase in absorptivity of many VOCs, thereby enhancing the rates of photolysis (Ref. 1).

Figure 6-8. VOC Absorbance Spectra Compared to Xenon Flashlamp Spectrum

Figure 6-9. Emission Spectrum for a Mercury Lamp vs. a Xenon Flashlamp
(All lamps corrected to 3,675 W input)

In combustion processes the molecules in the ground state (curve S_0 in Figure 6-10) must acquire sufficient thermal energy to overcome the activation energy barrier (E_a) to initiate decomposition reactions. However, an organic molecule exposed to UV radiation of an appropriate wavelength can be raised to an excited energy state as shown by the curve S_1 in Figure 6-10. In this excited state, the electronic configuration is modified from that of the ground state, tending to weaken the molecular bonds and reducing the activation energy required to induce chemical reactions. Thus, molecules in S_1 should react more rapidly than those in the ground state, and shorter wavelengths will produce higher energy states decreasing the activation energy further. With sufficiently energetic UV radiation (i.e., shorter wavelengths) the molecules may be dissociated, requiring no additional thermal energy for reactions to occur.

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Figure 6-10. General Energy Versus Reaction Coordinate Diagrams for Photochemical (Top), and Photothermal (Bottom) Decomposition

The lifetime of these excited states can be very short, often on the order of nanoseconds (Ref. 4). Thus, destruction reactions compete with deexcitation and only very fast reactions can occur from these states. These competing processes include radiative relaxation (i.e., emission from the excited singlet state, or fluorescence, and emission from the excited triplet state, or phosphorescence), and non-radiative processes such as internal conversion to thermal energy or electronic-spin inversion (Ref. 6). An important parameter defining the efficiency of a photochemical process is the quantum yield, defined as the ratio of the number of molecules of material undergoing the reaction process to the number of light quanta absorbed (Ref. 6).

Thus, although relatively small energy barriers exist for molecules in the excited state, allowing some hazardous species to react photochemically, at ambient temperatures the reaction rates are slow and often do not result in complete mineralization of the contaminant. However, at higher temperatures (>200°C) the small activation energy barriers are overcome more rapidly resulting in higher reaction rates, and the organic waste absorbs UV radiation more efficiently at lower energy (longer wavelength). Figure 6-10 illustrates that at high temperatures, higher energy vibrational levels in the ground state become populated, reducing the energy gap between the ground and excited states, and allowing photons of lower energy to excite the molecule. This is the theoretical basis of the photothermal detoxification process (Ref. 4).

Organic destruction in the gas phase is a function of the total dose and wavelength of radiation to which the organics are exposed, the molar extinction coefficient of the contaminant, and the temperature. The dose is defined as:

$$\text{Dose} = \text{Residence time} \times \text{Radiation intensity}$$

where the residence time is directly related to the flow rate. For the Purus flashlamps, the radiation intensity is given by flash frequency x number of lamps x energy/flash.

6.4.1 Low-Temperature Photolysis

6.4.1.1 Technology Description

Direct photolysis of organic contaminants in an air stream requires a light source emitting in the deep UV region. Purus, Inc. has applied a xenon plasma flashlamp that emits significant light intensity at wavelengths <250 nm. The spectral properties of the plasma produced in a pulsed inert-gas lamp approach those of an ideal black-body radiator, with a peak emission

wavelength defined by its characteristic temperature. Increasing energy discharged into the plasma increases the temperature, which lowers the wavelength of the peak emission, and increases the number of photons. Shortening of lamp life places an upper limit on the plasma temperature used.

The xenon flashlamp has a maximum at 230 nm as shown in Figure 6-9, and significant output at wavelengths as low as 200 nm, whereas mercury lamps have most of their output at wavelengths above 250 nm. The peak power to the lamp determines the UV content of the spectral emission, and the frequency of the pulses determines the average power. Flashlamp intensities of several hundred to 1,000 watts per inch are possible compared to a few hundred watts per inch for medium-pressure mercury lamps. Lamp life for both lamps is on the order of 1,000 hours.

The Purus flashlamp is 6-inches long and can be pulsed at a rate from 1 Hz to 30 Hz. Laboratory, pilot-scale, and field tests have been performed. Field tests at the LLNL Superfund site, where a vapor extraction system removed TCE from contaminated soil, used two types of reactors. One configuration (designated Air-2) was a steel cylinder 4-feet in diameter by 8-feet long (Figure 6-11). Four flashlamps were distributed around the center of the cylinder pointing inward, and the process stream flowed from one end of the cylinder to the other. The other test configuration (designated Air-3) is a Purus-patented reactor consisting of four disc-shaped stainless steel chambers (Figure 6-12). Each chamber is 42 inches in diameter by 6.1-inches high with a volume of 4.1 ft³ exposed to the light source. The lamps are positioned in the center of each chamber. The process flow enters the bottom of each chamber, around a deflection plate, in toward the lamp, and out the top (Ref. 2).

6.4.1.2 Input and Output Stream Characteristics

Very rapid destruction has been observed for chloro-olefins such as TCE, PCE, and DCE, which has been attributed to chlorine-atom chain reactions (Ref. 2). For these compounds as well as chloroform, methylene chloride, and possibly 1,2-dichloroethane, Cl• is photogenerated under UV light and subsequently takes part in chain reactions to remove the compound from the waste stream. However, with the current Purus lamps, only the rate constants for the chloro-olefins are high enough for a commercially viable process (Ref. 7). Despite the high quantum yields for CH₂Cl₂ and CHCl₃, their absorption cross-sections are too low to cause enough production of Cl• to initiate a chain reaction. Although the chloro-olefins rapidly photogenerate Cl•, they are also efficient scavengers of the Cl• and therefore do not sensitize

Figure 6-12. Schematic of Air-3 Photochemical Reactor

the photooxidation of CH_2Cl_2 or CHCl_3 (Ref. 7). Other compounds having a much longer rate constant cannot propagate a chain reaction and are destroyed only by direct photolysis.

Co-contaminants can cause both sensitization and inhibition of photolysis. The photolysis rate of TCE decreases by a factor of 75 when mixed with a high concentration of $\text{Cl}\cdot$ scavenger, such as ethene which contains no chlorine and cannot propagate a $\text{Cl}\cdot$ chain (Ref. 1). However, when TCE is mixed with 1,1-DCE the rate of TCE loss is slightly reduced but the rate of 1,1-DCE loss is significantly enhanced. This is interpreted to be the result of photo-initiation by TCE which is a strong absorber, with chain propagation by 1,1-DCE which reacts with chlorine atoms more rapidly. Details of the chain reactions and the data that provide back-up to the proposed reaction pathways are contained in References 1 and 2.

The products of chloroolefin photolysis include chloroacetyl chlorides and phosgene, which require further treatment (Ref. 2). For example, the main product (>85%) from the photolysis of TCE is DCAC, which upon further photolysis is converted to about 20% dichlorocarbonyl (phosgene or DCC), both of which are acutely toxic. Compared to TCE, about 100 times more light exposure is required to reduce the DCAC concentration by 90%. Thus, although chloro-olefins are eliminated rapidly by chain reactions with $\text{Cl}\cdot$, the overall result of photolysis is limited by the rate of destruction of the reaction byproducts which occurs on a timescale similar to that for compounds that do not enter into chain reactions.

Because the toxicity of DCAC is 40 times greater than that of TCE, the most DCAC that can be emitted is 0.025% of the initial TCE concentration to achieve the goal of 99% reduction in initial toxicity (Ref. 2). Similarly, the concentration of DCC would need to be less than 0.45% of the initial TCE concentration. Therefore, taking advantage of the rapid chain reactions depends on the ability to detoxify the initial products by methods other than photolysis. DCC can be removed with a water scrubber where it rapidly hydrolyzes to CO_2 and HCl . However, DCAC will hydrolyze to dichloroacetic acid (DCAA) and HCl , and DCAA is equal in toxicity to DCAC. Thus, depending on the water flow, DCAA concentration may be above the proposed drinking water limits of 2 ppb (Ref. 2).

6.4.1.3 Technology Status

This technology is being tested and commercialized by Purus, Inc. LLNL has used this system, or modifications thereto, to perform tests and evaluations of the technology on aqueous waste streams of interest to DOE.

The technology was accepted into EPA's SITE Emerging Technology Program in March 1991, and field testing of a full-scale prototype began in October 1991 (Ref. 8). The test was conducted at the LLNL Superfund site which contains soil zones contaminated with TCE. A vacuum extraction system delivered contaminated air to the Purus system at flow rates of up to 500 cfm, and initial TCE concentrations in air of 250 ppmv.

6.4.1.4 Destruction Efficiency

Tests have been performed on a variety of VOCs using the Purus xenon flashlamp. Results of several laboratory tests are shown in Figures 6-13 and 6-14 (Ref. 1). As indicated previously, co-contaminants may enhance or hinder the destruction rate of the primary contaminant of interest. Moreover, as TCE is destroyed the rate constant decreases with time until at very long times (TCE <1ppmv) the chain propagation becomes inefficient and the observed reactions are predominantly direct photolysis (Ref. 1).

Figure 6-13. Purus System Photolysis Plots for Individual VOCs

In the field experiments at the LLNL Superfund site (Ref. 2), the Purus systems were operated at flash frequencies of 1 to 30 Hz, temperatures of 33°C to 60°C, flows up to 300 scfm (260 ppmv TCE), and concentrations up to 10,600 ppmv (100 scfm). Residence time ranged from 5 to 75 seconds. In all cases, except at the lowest flash frequency, greater than 99% removal of

TCE was observed. Under the highest exposure and optimal conditions, conversions of 99.9996% were demonstrated. However, it is clear that this technology does not achieve these destruction efficiencies for organics in general and reaction byproducts remain in the effluent. A summary of the field test results is provided in Table 6-2 (Ref. 8).

Figure 6-14. Purus System Photolysis Plots for Chloro-olefins

Table 6-2. TCE Photolysis Field Test Results for the Purus System (Ref. 8)

Freq. (Hz)	No. of chambers	Flow (cfm)	Res. time (sec)	TCE input (ppmv)	TCE output (ppmv)	TCE dest. (%)	DCC yield (ppmv)	DCAC yield (ppmv)
30	4	103	9.6	78.4	dl*	≥99.99	nd	20.2
30	4	97	10.1	108.5	dl	≥99.99	21.3	26.5
30	4	95	10.4	98.3	dl	≥99.99	25.6	34
30	2	106	4.6	91.7	0.07	99.92	15.9	49.2
15	4	97	10.1	106.8	dl	≥99.99	22.8	nd
15	2	103	4.8	101.3	dl	≥99.99	12.6	65.3
5	4	95	10.4	104.9	dl	≥99.99	8.7	75.7
5	2	103	4.8	101.4	dl	≥99.9	9.4	76.3
1	4	106	9.3	101.7	0.85	99.16	12.5	83.2
1	2	103	4.8	98.5	13.23	86.57	6.8	84.9

*Detection Limited

no published cost data.

Technology Description

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Name: High-Energy Corona

Owner: Pacific Northwest Laboratory

Status: A&A

Technology Image: Available

Technology Description:

Components-

Most Department of Energy (DOE) sites have been contaminated with volatile organic compounds (VOCs). Techniques for retrieving these VOCs from soils are being developed and demonstrated at various sites. These techniques generally remove VOCs as vapors (off-gas) from contaminated soil. These vapors must, in most cases, be treated prior to release to the environment. The High Energy Corona (HEC) technology is one of many approaches toward decontaminating soil off-gases prior to atmospheric release. The objective of the HEC technology is to provide a stand-alone, field-portable means of treating soil off-gases produced during soil treatment operations. Contaminants that can be treated include most or all volatile and semivolatile organic compounds. The potential also exists for treating inorganic compounds such as oxides of nitrogen and oxides of sulfur.

The HEC process uses high-voltage electricity to destroy VOCs at room temperature. As shown in the figure below, the equipment consists of the following: an HEC reactor in which the VOCs are destroyed; inlet and outlet piping containing process instrumentation to measure humidity, temperature, pressure, contaminant concentration, and mass flow rate; means for controlling inlet flowrates and inlet humidity; and a secondary scrubber.

Low-Temperature Plasma Reactor

The HEC reactor is a glass tube filled with glass beads through which the prefiltered contaminated off-gas is passed. Each reactor is 2-in. in diameter, 4 ft long, and weighs less than

20 lb. A high voltage electrode is placed along the centerline of the reactor, and a grounded metal screen is attached to the outer glass surface of the reactor. A high-voltage power supply is connected across the electrodes to provide 0 to 50 mA of 60-Hz electricity at 30 kV. The electrode current and power depend upon the type and concentration of contaminant.

The technology is packaged in a self-contained mobile office that includes gas handling equipment and on-line analytical capabilities. Site power is not absolutely required.

Installation consists of connecting inlet and outlet hoses to the HEC process trailer. Training in the use of the equipment can usually be accomplished well within one hour. Failure control is provided by a combination of automated and manually activated means, addressing electrical failure, loss of flow, and loss of VOC containment caused by breakage of the glass reactor vessel. The HEC process can be operated with little, if any, maintenance required. Neither catastrophic failure nor any diminishing in levels of performance have been observed through months of periodic operation in the laboratory. The on-line gas chromatograph and process instruments do require periodic recalibration to ensure data quality.

Procedures/Reliability-

General Applications and Limitations-

Support/Infrastructure Requirements-

Program Integration Issues and Compatibility with
Other Technologies-

Operator Staffing/Skill/Training/Physical Requirements-

Acceptability:

Environmental and Aesthetic Impacts-

Natural Resource Usage-

Land Use Impacts-

Other Socioeconomic Impacts-

Compliance with the Occupational Safety and Health
Administration regulations is required for hazardous waste
operations and protection of occupational workers from
high-voltage electricity.

Status:

Maturity-

Discussions with manufacturers/licensees have been initiated
with the belief that HEC is now ready for commercial
availability. The 105-scfm field prototype is available now
for commercial testing and evaluation. Pacific Northwest
Laboratory (PNL) is continuing R&D to improve and scale the
technology. Scaleup to 50 scfm per reactor seems feasible
for extremely large applications.

Future Development-

Continued research & development (R&D) is planned to
accomplish the following: fully characterize the reactor
emissions to complete mass balances; adapt the HEC process
to complete real-time control; better understand the
physical and chemical phenomena that make the HEC process
work; develop larger reactors; and optimize the hardware and
packaging associated with the technology for specific, as
well as modular or generic, treatment applications.
Since this technology is applicable to treating process
off-gases and liquid contaminants in government or
industrial settings, the potential commercial applications
are very broad. Any remediation or manufacturing process
that produces off-gases and/or liquid contaminants that
contain organic compounds could possibly be treated with
this technology.

Previous Applications (refs.)-

Patents-

Pacific Northwest Laboratory has applied for a patent.

Industrial Partnerships-

None at present.

Competing Technologies:

The most ubiquitous baseline technology is carbon sorption,
in which off-gas contaminants are absorbed onto
containerized activated carbon. Once "spent," the carbon is
shipped off site and incinerated, which partially
reactivates the carbon for reuse. In many or most cases, the

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spent carbon must be treated as Mixed Waste because of radon contamination, even if the soil being cleaned has not been contaminated with radioactive wastes. This further increases the cost of baseline carbon sorption use. Some other baseline technologies involve thermal treatment, such as incineration and high-temperature catalysis. Ionizing radiation sources, such as X-rays and electron beams, are also used.

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Effectiveness:

The HEC technology appears to destroy more than 99.9% trichloroethylene (TCE). The technology destroys tetrachloroethylene (PCE) to a level of 90 to 95%. In preliminary tests with heptane, destruction levels appear to be extremely high, but have not been quantified. When chlorinated VOCs are treated, water containing either sodium hydroxide or baking soda is recirculated in a scrubber to remove acid gases from the reactor effluent (hydrochloric acid and bleach.) It should also be noted that further contaminant destruction appears likely in this wet scrubber. This is presumably because of strong gaseous oxidants that exit the HEC reactor. Typical outlet properties would be nondetectable concentrations of TCE, ozone, hydrochloric acid, phosgene, and chlorine, with up to 1 ppmv NOx (below regulatory limits.) Air exits the HEC process at temperatures of 1000 C or lower or slightly above ambient temperature if a wet scrubber is used. A scrub solution (containing less than 10-wt% table salt in water) is produced when chlorinated VOCs are treated. One reactor processes up to 5 scfm of soil off gas. The HEC field-scale process that will be demonstrated early in 1993 at Savannah River uses 21 HEC reactors in parallel to treat up to 105 scfm of contaminated soil off-gas. A typical application will involve an inlet stream containing 1800 ppmv of TCE in humid air at 10 to 200 C. Power input is typically 50 to 150 W/scfm being processed. For dry inlet streams, deionized water is added as steam to produce an inlet humidity (hr) of 60 to 80%. Less than 20 mL/min of water is required to humidify a bone-dry stream at a flow of 105 scfm. For water-saturated inlet streams, the stream is preheated (using electric heaters) to lower the inlet humidity (hr) from 100% to 80%. In many cases, the vapor-extraction blower associated with retrieving the VOCs from soil will sufficiently preheat the soil off gas to 80% hr or lower so that no further preheating is required. Continued research & development (R&D) is planned to accomplish the following: fully characterize the reactor emissions to complete mass balances; adapt the HEC process to complete real-time control; better understand the physical and chemical phenomena that make the HEC process work; develop larger reactors; and optimize the hardware and packaging associated with the technology for specific, as well as modular or generic, treatment applications.

Cost:

Start-up-

O&M-

Initial outlay for a 105 scfm process, the prototype field treatment system, is \$50K. As with any other technology, large-scale production and customization would significantly reduce costs, perhaps to as little as \$20K. Labor requirements are projected as ~0.25 fulltime equivalent (FTE). Energy requirements are \$27/day, or roughly \$0.35/lb of contaminant. Total cost is roughly \$10.00/lb contaminant, including a 25% contingency to account for any unknown additional costs. Although maintenance costs are minimal,

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Low Temperature Plasma Reactor

SECTION 8 SOIL WASHING

Soil washing is the extraction of contaminants from excavated soil by mixing the soil with water, solvents, surfactants, or chelating agents (Ref. 1). Soil washing is a combination of physical and chemical treatments performed on soil in an aqueous solution. It is often used as a size segregation technique with washing of fines from coarse soil. The process removes contaminants that reside in specific grain-size domains, separates the waste stream into "cuts," and focuses on treatment appropriate to the contaminant/grain-size relationship. Usually, heavily contaminated soils are treated several times in a multistage counter-current system. The contaminated water or solution is then treated for removal of contaminants.

Early development and implementation of soil washing technology was based primarily on the use of water as the extracting solvent (Ref. 2). This process is most applicable to the remediation of soils containing highly water-soluble constituents, or soils containing very low concentrations of silt and/or clay particles (usually <15% smaller than 50 μm). The EPA Superfund Innovative Technology Evaluation (SITE) Program now includes soil washing processes using extraction media ranging from alkaline mixtures of ionic and nonionic surfactants and bioremediating agents which act as biosurfactants (Ref. 3) to acid extractions for removing heavy metals from contaminated soils and solids (Ref. 4). These processes represent a significant extension of existing soil washing techniques presently being used on a wide scale in Germany and the Netherlands.

Early soil washing applications have been for top soils rather than for buried and otherwise stored waste, although some buried waste and contaminants would be amenable to this approach. For example, if the contaminant is soluble and the contaminated surfaces are accessible (removed from bags and containers), it may be possible to decontaminate the bulk of such buried waste by washing/leaching/extraction. Additionally, soil washing may provide added benefit for debris treatment by enabling the application of the debris rule (Section 8.1.7).

EPA (Ref. 5) has the following insights on soil washing:

- "Soil washing is basically a volume-reduction technology that uses wash water to separate contaminated soil into two fractions: a large fraction of relatively clean, coarse soil, and a smaller fraction of fine soil/sludge containing the concentrated contaminants."

- "Hydrophobic contaminants can be difficult to separate from soil particles into the aqueous washing fluid."
- "Complex mixtures of contaminants in the soil, such as a mixture of metals, nonvolatile organics, semivolatile organics, etc., make it difficult to formulate a single, suitable, washing fluid that will remove all the different types of contaminants from the soil."
- "A high percentage of clay and silt (e.g., >30–50%) in the soil usually indicates that soil washing will be unfavorable due to the amount of time and money required to treat this volume of contaminated soil."
- "Chelating agents, surfactants, solvents, and other additives are often difficult and expensive to recover from the spent washing fluid and then recycle in the soil washing process."
- Identification of the contaminants is important. Volatile organics may require removal in a pretreatment step with treatment of air emissions. Solubilities of contaminants is important in deciding whether wash solution additives are needed. Metal speciation is important in metal solubility.
- Particle size distribution of the soil and chemical analysis of the contaminants are important characterization data for soil washing.

8.1 TECHNOLOGY DESCRIPTION

Soil washing technology is commercially available through numerous vendors. A search of EPA's Vendor Information Systems for Innovative Treatment Technologies (VISITT) database version 3 (Ref. 6), identified nineteen soil washing vendors with processes in various stages of development from laboratory bench-scale to full commercial scale. The stage of development as reported by the vendors is as follows: 3 bench-scale, 2 pilot-scale, and 14 full-scale. Additionally, numerous soil washing demonstrations (including solvent extraction and debris washing) have been conducted as part of the EPA SITE Program (Ref. 7).

Soil washing is primarily an *ex situ* process that incorporates size classification and vigorous scrubbing of soil particles with an aqueous-based solvent to remove heavy metals or organic contaminants. Soil washing can be, and has been, used as a single-stage or multi-stage, standalone technology where applicable, or coupled with other on-site remediation

technologies to achieve the final contaminant levels. In some cases, water soluble surfactants, chelating agents, acids, or bases may be used to facilitate contaminant removal. Soil washing is based on the observations that: 1) contaminants tend to concentrate in the fine and organic fractions of the soil (e.g., silt, clay, humic matter) due to physical and/or chemical adsorption, and 2) contaminants associated with the coarse soil fraction (e.g., sand, gravel) are often present as a thin surface coating that can be removed by vigorous scrubbing and attrition of the soil particle surfaces (Ref. 6). Many soil contaminants, both organic and inorganic, tend to chemically or physically attach to the silt and clay fractions of the soil as shown in Figure 8-1 (Ref. 8). The silt and clay, in turn, tend to attach to coarse sand and gravel particles. The various processes used in soil washing break the silt and clay away from the coarser fractions and scrub the coarser fractions, resulting in cleaner sand.

Figure 8-1. Typical Soil Distributions (Source: Brierley and Hultman 1994)

Thus, the objectives of the technology are to reduce the volume of soil that requires further treatment or disposal by concentrating the contaminants in a smaller volume of material, to transfer the contaminants to a more easily treated aqueous phase, and to produce a washed soil product that meets clean-up criteria.

A "basic" soil washing treatment plant shown in Figure 8-2 includes four major subsystems: 1) screening (soil sizing), 2) washing, 3) soil and water separation, and 4) wastewater and sludge treatment and management (Ref. 6, 9 and 10). Screening is employed to

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Figure 8-2. "Basic" Soil Washing Treatment Process

remove the oversized soil fraction. The initial process is done by vibrating screens and then by attrition scrubbers after water is added. More water is added and the resulting slurry is separated into coarse-grained sands and fine-grained materials, typically by use of hydrocyclones. Underflow from the hydrocyclones contain the coarse-grained sands requiring treatment, typically by air froth flotation. Surfactants may be added to the sand to aid in reducing the surface tension binding the contaminant to the particles. This allows the contaminants to "float," be removed by air froth flotation, and forwarded onto sludge management. Overflow from the hydrocyclones contains the fine-grained material containing the contaminant. This fraction can then be either processed by an alternative technology, or dewatered and disposed of off-site. The small volume of contaminated residuals are subsequently treated by appropriate destructive or immobilizing processes such as thermal desorption, chemical extraction, biodegradation, solidification, or vitrification. Sludge management typically requires additional treatment such as polymer addition, thickening, and dewatering. Cleaned soil may be either redeposited on-site or otherwise beneficially used as backfill or industrial sand. Low-level mixed waste may be cleaned to the point where it is no longer considered mixed waste and thus may be disposed of at appropriate facilities (e.g., the Nevada Test Site). Process water is cleaned of contaminants and recycled for further use in the system.

Other variations of soil washing technology include debris washing, solvent extraction, solvent washing and *in situ* soil flushing. General descriptions of debris washing and solvent extraction are presented in Sections 8.1.7 and 8.1.8, respectively (following soil washing descriptions). Solvent degreasing was used successfully at the Oak Ridge K-25 Site, but its use was stopped to avoid exposing the workers and the environment to the hazardous solvents. *In situ* soil flushing has been demonstrated and consists of water, or an aqueous solution, injected into, or sprayed onto, the area of contamination, and the contaminated elutriate collected and pumped to the surface for removal, recirculation, or on-site treatment and reinjection (Ref. 1). During elutriation, the flushing solution mobilizes the sorbed contaminants by dissolution or emulsification. Handling and treatment of the elutriate are required, and delivery and recovery systems are needed. Medium-solubility organics and soluble salts are the most likely contaminants to be treated.

Each soil washing vendor uses a slightly varied process train and/or reagents for removal of contaminants. For example, addition of catalytic ozone oxidation to the wash water destroys organic compounds (Ref. 7). Brief descriptions of selected processes (i.e., vendors), the removal efficiency, and costs are presented in this section and were based on available information obtained largely from the VISITT database (Ref. 6) and SITE Profile version 6

(Ref. 7). Thus, the processes discussed in this section should not be considered a comprehensive listing. Furthermore, bench-scale studies identify the basic mechanisms by which radionuclide, heavy metal, or organic contaminants can be removed from soil. Bench-scale studies do not provide engineering process information about the best methods to make liquid/solid separations or to handle a variety of soil components (rocks, clays, plant roots, etc.). Before full-scale soil washing plants are designed, pilot-scale studies need to be conducted addressing a variety of process engineering variables so that the full-scale facility can be designed to operate safely, effectively, and under the most economical conditions.

British Nuclear Fuels CACITOX™ Soil Treatment Process

Description CACITOX™ is a proprietary leaching process that uses a mild, environmentally friendly reagent system to selectively leach contaminants from soil as soluble chemical complexes. The reagent is a three component mixture consisting of carbonate, oxidizing agent, and a complexant such as carboxylic acid. The process is designed to treat soils with significant clay and silt content, for which conventional soil washing techniques are not cost effective, without damaging the soil matrix. The contaminants are leached from the soil using multi-stage contacting equipment; the leached soil is separated with hydrocyclones or mixer settlers, and washed; the contaminants are removed from the leachate and wash water by ion exchange and precipitation and the leachate and wash water recycled. Test results on soil containing 46% clay/silt include reduction of Cr from 1500 mg/kg to 55 mg/kg, Cd from 1000 mg/kg to 15 mg/kg, Pb from 14,000 mg/kg to 150 mg/kg, and removal of 98% of the organics. Tests on high clay content soils with single contact demonstrated the following removal percentages 52% Pu, 70% U, 76% Am, 70% Sr, and 2.2% Cs. (Brierly, K.W., and C.W. Swede Hultman, "British Nuclear Fuels' CACITOX™ Soil Treatment Process," Poster Session, Waste Management '94, Tucson, AZ, February 27 - March 3, 1994.)

Waste Treated The primary applications are soils, debris, and process residues contaminated with hazardous (heavy metals and organics), radioactive (TRU and actinides), and mixed wastes.

Residue Contaminated ion exchange resin, metal and radionuclide precipitates and/or filter cake, spent solvent and wash water.

State of Development Tests have been performed at the bench-scale on spiked soil samples and on soil from a contaminated nuclear site. This process is being commercialized by British Nuclear Fuels plc (BNFL) and is available with the EXCEL*CR™ transportable treatment plant.

Cost Data Not available at this time.

Issues None identified at this time.

GHEA Associates Process

Description This process applies surfactants and additives to soil washing and wastewater treatment to make organic and metal contaminants soluble. In soil washing the wash and rinse liquids are combined and treated to separate surfactants and contaminants from the water. Next, contaminants are separated from the surfactants by desorption, which regenerates the surfactants for reuse, and the contaminants are isolated as a concentrate. The liquid treatment consists of a sequence of operations involving phase separation, ultrafiltration, and air flotation. The treated water meets the NPDES discharge criteria. For wastewater treatment, surfactants are added to the water to adsorb contaminants, and the resulting liquid is treated in the same manner as for soil washing liquid. (EPA SITE Technology Profiles, 6th Edition, November 1993)

Waste Treated Applicable to soil, sludges, sediments, slurries, groundwater, surface water, industrial effluents, and in situ soil flushing. Contaminants include organics and heavy metals including non-volatile and volatile compounds.

Residue Highly concentrated fraction containing the contaminants, and spent surfactant.

State of Development This process is being developed by the New Jersey Institute of technology. Treatability tests have been performed on various matrices as part of the EPA SITE Program, and a 25-gallon pilot-plant has been tested. The removal efficiency for most organics from soil was >99%, and >96% of chromium was removed from soil.

Cost Data Costs for treatment range from \$50 to \$80 per ton.

Issues None at this time.

**RISK REDUCTION ENGINEERING LABORATORY
AND IT CORPORATION**
(Debris Washing System)

TECHNOLOGY DESCRIPTION:

This technology was developed by EPA's Risk Reduction Engineering Laboratory (RREL) and IT Corporation (IT) for on-site decontamination of metallic and masonry debris at Comprehensive Environmental Response, Compensation and Liability Act sites. The full-scale debris washing system (DWS) consists of dual 4,000-gallon spray-wash chambers that are connected to a detergent solution holding tank and rinse water holding tank. Debris is placed into one of two 1,200-pound baskets, which in turn is placed into one of the spray-wash chambers using a 5-ton crane integral to the DWS. If debris pieces are large enough, the crane places the debris directly into one of the two chambers. Process water is heated to 160 degrees Fahrenheit using a diesel-fired, 2,000,000-British-thermal-unit-

per-hour (Btu/hr) water heater and is continuously reconditioned using particulate filters, an oil/water separator, and other devices such as charcoal columns or ion exchange columns. About 8,000 to 10,000 gallons of water is required for the decontamination process. The system is controlled by an operator stationed in a trailer-mounted control room. The entire system is mounted on three 48-foot flatbed semi-trailers and can be readily transported from site to site.

WASTE APPLICABILITY:

The DWS can be applied on site to various types of debris (scrap metal, masonry, or other solid debris such as stones) contaminated with hazardous chemicals such as pesticides, dioxins, polychlorinated biphenyls (PCB), or hazardous metals.

Pilot-Scale Debris Washing System

STATUS:

The first pilot-scale tests were performed in September 1988 at the Carter Industrial Superfund site in Detroit, Michigan. PCB reductions averaged 58 percent in batch 1 and 81 percent in batch 2. Design changes based on these tests were made to the DWS before additional field testing.

An upgraded pilot-scale DWS was tested at a PCB-contaminated Superfund site in Hopkinsville, Kentucky, in December 1989. PCB levels on the surfaces of metallic transformer casings were reduced to less than or equal to 10 micrograms PCB per 100 square centimeters ($\mu\text{g}/\text{cm}^2$). All 75 contaminated transformer casings on site were decontaminated to EPA cleanup criteria and sold to a scrap metal dealer.

The DWS was also field tested in August 1990 at the Shaver's Farm Superfund site in Walker County, Georgia. The contaminants of concern were benzonitrile and Dicamba. After being cut into sections, 55-gallon drums were decontaminated in the DWS. Benzonitrile and Dicamba levels on the drum surfaces were reduced from the average pretreatment concentrations of 4,556 and 23 $\mu\text{g}/100 \text{ cm}^2$ to average concentrations of 10 and 1 $\mu\text{g}/100 \text{ cm}^2$, respectively.

Results have been published in a Technology Evaluation Report (EPA/540/5-91/006a), entitled "Design and Development of a Pilot-Scale Debris Decontamination System."

A manual version of the full-scale DWS was used to treat PCB-contaminated scrap metal at the Summit Scrap Yard in Akron, Ohio.

During the 4-month site remediation, 3,000 tons of PCB-contaminated scrap metal (motors, cast iron blocks) were cleaned on site. The target level of $7.7 \mu\text{g}/100 \text{ cm}^2$ or less was met, in most cases, after a single treatment with the DWS. The cleaned scrap was purchased by a scrap smelter for \$52/ton. The net costs for the on-site debris decontamination ranged from \$50 to \$75 per ton.

The automated, trailer-mounted DWS is scheduled for deployment to a hazardous waste site in The Netherlands for an initial demonstration of the new system. RREL and IT estimate that the system can decontaminate 50 to 120 tons of typical debris per day.

FOR FURTHER INFORMATION:

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EM Problem: Decommissioning

K-25 Site Problem: Enrichment process building, process support building, electrical and electrical switch gear, pumping stations, laboratory facilities, special development facilities, administrative facilities, and cooling towers.

Problem Area/Constituents: Concrete, structural steel, tile, epoxy, metal equipment (exterior), Ni-lined steel equipment (interior)—after disassembly, monel, copper, aluminum, sheet metal, steel pipe, aluminum pipe. These media may be treated by the subject technology for removal of all the listed contaminants.

Reference Requirements:

- Federal Facility Compliance Agreement for Oak Ridge Site
- Federal Facility Compliance Agreement for PCBs
- Clean Air Act
- Clean Water Act
- Toxic Substance Control Act
- DOE orders

Refer to Volume 1, Chapter 10, for potentially applicable proposed and promulgated environmental laws, signed and pending agreements for the Oak Ridge Reservation, radiation protection standards, DOE orders, and nonregulatory guidance. As site- and waste-specific characteristics are provided for each technology, specific regulatory requirements will be specified.

Subelement: Decontamination**Alternatives:** Surface Cleaning (transferable contamination)

Technology: High-Pressure Water (5,000–20,000 psig)—Blasting of surfaces with high pressure water will remove difficult deposits that are tightly adherent to substrate materials. Water pressure at the nozzle of commercially available high-pressure blasting systems is typically 5,000 to 20,000 psig. Flow rates vary from 4 to >100 gpm. When used with chemical additives, this technique can be effective for decontaminating piping trays, overhead surfaces, upper regions of walls, gratings, pumps, and similar items. However, splashing from blast operations can be extensive and result in recontamination if precautions are not taken. In the use of this decontamination technology, the high-pressure-water cleaning head may be manually moved about on the surfaces being decontaminated. Because the decontamination efficiency depends on the applicator translation speed, as well as on other operating parameters, remote operation of the high-pressure-water cleaning head would be desirable. Also, in some applications (such as decontamination of hot cells), remote operation will be required. Consequently, the adaptation of the equipment to a robotics control system would be necessary.

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Status: Accepted—High-pressure-water blasting has been used very successfully to decontaminate various large and complex surfaces at nuclear power plants. These include coolant pump impellers and cavities, fuel storage racks and handling equipment, floor drains and sumps, reactor cavity walls, pipes, and valves. When used as a preliminary step to wiping or scrubbing activities, DFs in the range of 50 are commonly achieved for loosely deposited and loosely adherent contamination. Experience has demonstrated that blasting effectiveness becomes negligible when the cleaning nozzle tip is more than 10–12 in. away from the surface being cleaned. However, before acceptance at K-25 and other DOE sites, the issues of wastewater treatment and prevention of spread of contamination must be addressed. The waste generated is the contaminated water from the cleaning operation. The waste production rate is essentially the same as the water rate in the cleaning step, which can range from 4 to >100 gpm.

Science/Technology Needs: To minimize waste generation, a water treatment system is needed for decontamination of the wastewater so that the water can be recycled and reused in the high-pressure-water cleaning operation. Remote operation will necessitate the adaptation of the mobile high-pressure-water and vacuum collection systems to a robotics control system.

Implementation Needs: Development costs—For development and demonstration of a water recycle system, in combination with high-pressure-water decontamination, an estimate of funding requirements is \$1.2M. Personnel requirements are estimated to be \$1.7M (approximately 50% engineer and 50% technician time) and 4.1 FTEs (approximately 10% P&E, 45% engineer, and 45% technician time) for FY 93 and FY 94, respectively. The cost of a robotics control system is estimated at \$250K. This is based on the cost of a system that is available from the Remotek Company. Estimated cost of a glove box is <\$50K and of a work room, >\$250K. Operating cost would be \$.06–\$2/ft².

Deployment costs—The capital cost of a high-pressure-water cleaning unit will be in the \$50K–\$75K range. Operating costs for a high-pressure-water cleaning unit would primarily involve labor costs. Assuming a minimum two-person operation (at a labor rate of \$40K/year/person) during the day shift, operating costs would be approximately \$350/day. Personnel training for operation of a high-pressure-water unit and a water treatment and recycle system would be required.

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References: MMES staff members

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