

Naval Surface Warfare Center Carderock Division

West Bethesda, MD 20817-5700

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September 2000

Survivability, Structures, and Materials Directorate

Technical Report

Survey of Technologies to Treat the Shipboard Incidental Liquid Wastes Identified During the Process to Set Uniform National Discharge Standards

By

Harold H. Singerman and Dean Putnam

Native American Consultants, Incorporated

Prepared for:

Mary Wenzel

Ships Environmental Support Office

Carderock Division, Naval Surface Warfare Center

Ships Environmental Support Office
Naval Environmental Protection Support Service



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ABSTRACT

The Navy will have to comply with Uniform National Discharge Standards (UNDS) requirements, which were recently established by amendments to the Clean Water Act, that control the overboard discharge of incidental wastewaters from ships of the Armed Forces in the contiguous zone of the United States. The Environmental Protection Agency and the Department of Defense are requiring the use of marine pollution control devices (MPCDs) to control 25 discharges which were identified in the Federal Register Volume 64, No. 89, Monday May 10, 1999. The MPCD performance standards and promulgating regulations regarding the design of the devices are being established. Commercial shipboard systems may not be able to treat the incidental wastewaters to those standards and meet the Navy's requirements in terms of size, weight, the interaction with other ship systems, and reliability.

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ADMINISTRATIVE INFORMATION

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The Ships Environmental Support Office is one of four specialty offices which comprise the Naval Environmental Protection Support Service (NEPSS). The NEPSS Specialty Offices Program Manager is S. Trembly, Naval Facilities Engineering Command (NAVFAC ENV); the Executive Manager is G. Gasperino, Naval Facilities Engineering Service Center (NFESC 42). The Program Manager of the Ships Environmental Support Office is M. Wenzel, Carderock Division, Naval Surface Warfare Center (CDNSWC 632).

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EXECUTIVE SUMMARY

The Navy will have to comply with recent amendments to the Clean Water Act that controls overboard discharge of various incidental wastewaters from ships of the Armed Forces in the contiguous zone of the United States. These are the Uniform National Discharge Standards (UNDS). The Environmental Protection Agency and the Department of Defense are requiring the use of marine pollution control devices (MPCDs) to control 25 discharges identified in the Federal Register Volume 64, No. 89, Monday May 10, 1999. The MPCD performance standards and promulgating regulations regarding the design of the devices are being established. Commercial shipboard systems may not be able to treat the incidental wastewaters to those standards and meet the Navy's requirements in terms of size, weight, the interaction with other ship systems, and reliability,

This report presents the results of a survey to identify and gather information on technologies that could lead to systems, operations and processes, and improved management practices to control the quality of the incidental wastewaters. Most of the technologies that were considered had demonstrated (or had reasonable potential for) a minimum 99% removal efficiency for contaminants when used alone or combined with another. None was judged for its cost or operational feasibility in a shipboard milieu.

Innovative technologies to treat liquid wastes are being developed through the Navy's Basic Research, Applied Research, Advanced Technology, and Advanced Developmental Programs; the Strategic Environmental Research and Development Program; the Environmental Protection Agency's (EPA's) Research Program; and the EPA's Superfund Innovative Technology Evaluation Program. The Department of Energy (DOE) has several active major programs to uncover and apply innovative thermal and nonthermal options to separate and destroy liquid wastes at contaminated sites around the country and is driven by legislation that requires them to develop plans to comply with all Resource Conservation and Recovery Act requirements. The products of the Navy, EPA, DOE, and other programs are presented and discussed. Options include membrane filtration, sorption, advanced photochemical oxidation processes, steam reforming, high-energy electron and X-ray irradiation, electrochemical oxidation, electro-field reactions, catalyzed chemical oxidation, supercritical water oxidation, wet chemical oxidation, and several proprietary processes. In addition, there are innovative elements and improvements to existing processes and systems that warrant consideration; viz., design modifications to the compensated-fuel ballast system.

While this report presents an array of interesting and innovative technologies; the application of any new system to a warship must first address its impact on the operation of that ship in terms of its weight, power and space requirements; affect on other ship systems, life cycle cost, and safety; and the mission of the ship.

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INTRODUCTION

The Navy must control and manage wastewater discharges from its ships. One of the goals established by the Chief of Naval Operations is the environmentally sound ship of the 21st century that will be able to enter all global waters and harbors without being constrained by environmental regulations. Provisions of the Clean Water Act control the overboard discharge of untreated blackwater, graywater, and oily wastewater within the contiguous zone of the United States. The implementation of Annex IV of the International Maritime Convention for the Prevention of Pollution from Ships (MARPOL) Protocol will regulate the discharge of blackwater and eventually graywater from all ocean-going ships. Navy ships that visit or operate in coastal waters throughout the United States encounter difficulties because they have to comply with varying local discharge requirements peculiar to the port or state. Clearly, uniform national requirements and standards would be preferable for the Navy.

Section 325 of the Fiscal Year 1996 Defense Authorization Act (10 February 1996) entitled "Discharge from Vessels of the Armed Forces" contains an amendment (Section 312) to the Federal Water Pollution Control Act that requires the Secretary of Defense and the Administrator of the United States Environmental Protection Agency (EPA) to develop Uniform National Discharge Standards (UNDS) to control certain discharges from vessels of the Armed Forces. Congress established requirements for the development of Uniform National Discharge Standards to (1) enhance the operational flexibility of vessels of the Armed Forces domestically and internationally, (2) stimulate the development of innovative vessel pollution control technology, and (3) advance the development of the U.S. Navy's environmentally sound ship. UNDS applies to vessels of the Armed Forces and liquid discharges (other than sewage) incidental to their operation and is applicable to discharges in the navigable waters of the United States and the contiguous zone. It requires the EPA and the Department of Defense (DoD) to develop regulations and performance standards to control discharges incidental to the normal operation of Armed Forces vessels where EPA and DoD determine that it is reasonable and practicable to require use of a marine pollution control device to mitigate adverse impacts on the marine environment. EPA will negotiate with a state if the state determines that the protection of the quality of some of its waters requires greater environmental protection.

DoD and EPA are required to (1) determine by 10 February 1998 those wastewater discharges from vessels of the Armed Forces that require Marine Pollution Control Devices (MPCD); (2) establish performance standards by 10 February 2000 for those discharges that require the devices; and (3) promulgate standards by 10 February 2001 for design, installation, construction and use; and repeat the process every 5 years. A marine pollution control device is a control technology or a management practice that can reasonably and practicably be installed or otherwise used on a vessel of the Armed Forces to receive, retain, treat, control or discharge a waste incidental to the normal operation of the vessel. The DoD and EPA considered seven factors to determine whether a discharge requires an MPCD: the nature of the discharge, the environmental effects of the discharge, the practicability of using the MPCD, the effect the MPCD has on the operation or the operational capability of the vessel, applicable United States law, applicable international standards, and the economic costs to install and use the MPCD.

The initial phase of UNDS identified and characterized discharges incidental to the normal operation of a vessel. The Navy and EPA identified 39 incidental discharges through consultation with personnel who had system expertise and through an extensive review of shipboard systems and operations. They identified the constituents of each discharge and evaluated the potential for the discharge to cause an adverse effect on the marine environment. The EPA and DoD classified the discharges into one of two categories, those that require control by an MPCD and those that do not. They determined that it is reasonable and practicable to require the use of an MPCD to control 25 discharges from vessels of the Armed Forces (*Federal Register*, Vol. 64, No. 89, Monday May 10, 1999, "Uniform

National Discharge Standards for Vessels of the Armed Forces Final Rule"). Table 1 lists the 39 discharges.

Table 1. Wastewater Discharges of Interest

Discharges Requiring Control	Discharges Not Requiring Control
Aqueous film-forming foam	Boiler blowdown
Catapult water brake tank and post-launch retraction exhaust	Catapult wet accumulator discharge
Chain locker effluent	Cathodic protection
Clean ballast	Freshwater lay-up
Compensated fuel ballast	Mine countermeasures equipment lubrication
Controllable pitch propeller hydraulic fluid	Portable damage control drain pump discharge
Deck runoff	Portable damage control drain pump wet exhaust
Dirty ballast	Refrigeration/Air conditioning condensate
Distillation and reverse osmosis brine	Rudder bearing lubrication
Elevator pit effluent	Steam condensate
Firemain systems	Stern tube seals and underwater bearing lubrication
Gas turbine water wash	Submarine acoustic countermeasures launcher discharge
Graywater	Submarine emergency diesel engine wet exhaust
Hull coating leachate	Submarine outboard equipment grease and external hydraulics
Motor gasoline compensating discharge	
Non-oily machinery wastewater	
Photographic laboratory drains	
Seawater cooling overboard discharge	
Seawater piping biofouling prevention	
Small boat engine wet exhaust	
Sonar dome discharge	
Submarine bilgewater	
Surface vessel bilgewater/oil-water separator discharge	
Underwater ship husbandry	
Welldeck discharge	

Description of the Twenty-Five Discharges and Basis for the Need of an MPCD

The 25 liquid discharges incidental to the normal operation of ships of the Armed Forces for which the EPA and DoD decided that it was reasonable and practicable to require the use of an MPCD are described below, along with the characteristics of each discharge that formed the basis of the decision. The list, the description, and the basis for the decisions was drawn from the "Technical Document for Phase I Uniform National Discharge Standards for Vessels of the Armed Services," EPA-821-99-001.

Aqueous Film-Forming Foam is the primary fire-fighting agent used for flammable liquid fires on vessels of the Armed Forces. It is a concentrated liquid that is mixed with seawater to form a 3% to 6% solution that is discharged during planned maintenance, testing, system inspections, and flight deck certifications. The Navy uses certain management practices to control these discharges that includes a self-imposed prohibition on discharges in coastal waters. These management practices to control discharges of AFFF demonstrate the availability of an MPCD to mitigate the potential adverse impacts that could result from the discharge of AFFF. The EPA and DoD determined that it is reasonable and practicable to require use of an MPCD for this discharge. AFFF discharges occur infrequently beyond 3 nm, but within 12 nm, from shore and in relatively small volumes; and the diluted (3-6%) AFFF solution is not believed to exhibit significant toxic effects. Furthermore, discharges that do occur take place while the vessel is underway and will be dispersed in the turbulence of the vessel wake.

Catapult Water Brake Tank and Post-Launch Retraction Exhaust discharges are from the water brake and retracting catapults on aircraft carriers during aircraft launching operations and testing. Lubricating oil that is applied to the catapult cylinder collects in the water brake tank during these operations and is eventually discharged overboard. In addition, expended steam and residual oil are released overboard when the catapult is retracted between launchings and tests. The Navy has imposed operational controls that limit the amount of oil applied to the catapult cylinder during the launch stroke, which directly affects the amount of oil that is subsequently discharged from the water brake tank or during the post-launch retraction exhaust. The Navy has also established requirements dictating when catapult testing is required within 12 nm of shore. These operational constraints minimize discharges of oil from the water brake tank and post-launch retraction exhaust in coastal waters. These existing management practices demonstrate the availability of controls for this discharge.

Chain Locker Effluent is seawater and debris that collects in the anchor chain storage locker as a result of anchor chain washdowns, retrievals, and heavy weather. The liquid collects in a sump and is removed by a drainage eductor powered by the shipboard firemain. The Navy and other Armed Forces already have management practices in place for most vessels. Those practices require that anchors and anchor chains be washed down with seawater while they are retrieved. In addition, the DoD has chosen as a matter of policy to continue prohibiting the discharge of chain locker effluent within 12 nm of shore. This prohibition, while not considered necessary to mitigate an existing or potential adverse impact, will eliminate the possibility of discharging into coastal waters any metals, other contaminants, or nonindigenous aquatic species that may have accumulated in the chain locker sump.

Clean Ballast is either seawater or freshwater that is transferred into and out of dedicated tanks to adjust a surface ship's draft and to improve stability under various operating conditions. In submarines, seawater is taken aboard into the main ballast system to control buoyancy and into the variable ballast system to control trim, list, and to adjust buoyancy. The discharge is generated when the ballast is no longer required and the tanks are partially or completely emptied. The Navy, MSC, and the Coast Guard either currently implement or are in the process of approving a ballast water management policy that requires open-ocean ballast water exchange. The policy is based on guidelines established by the International Maritime Organization (Guidelines for Preventing the Introduction of Unwanted Aquatic Organisms and Pathogens from Ships' Ballast Water and Sediment Discharge, 10 May 1995). These management practices demonstrate the availability of controls to mitigate the potential adverse environmental impact from this discharge.

Compensated Fuel Ballast is seawater that is introduced into fuel tanks to maintain the stability of a vessel by compensating for the weight of the consumed fuel. This seawater is displaced overboard while the ship is being refueled. The Navy has instituted operational guidelines to reduce the probability of overfilling tanks or discharging excessive amounts of fuel entrained in the displaced compensating water. These guidelines limit the amount of fuel that can be taken on in port (i.e., to prevent "topping off" the fuel tanks) and establish maximum allowable rates for taking on fuel in port. Additionally, submarines transfer all compensated fuel ballast water to shore facilities when refueling diesel fuel oil tanks. These surface ship and submarine operational controls demonstrate the availability of MPCDs to mitigate potential adverse environmental impacts.

Controllable Pitch Propeller Hydraulic Fluid is hydraulic fluid that is released from controllable pitch propeller (CPP) systems under three conditions: leakage through CPP seals, releases during underwater repair and maintenance of the CPP, or releases from equipment used to replace the blades. The EPA and DoD have determined that pollution controls are necessary to mitigate the potential adverse environmental impacts that could result from releases of hydraulic oil during underwater maintenance on controllable pitch propellers. The existing repair procedures and the staging of containment booms and oil skimming equipment to capture released oil demonstrate the availability of MPCDs (i.e., best management practices) for this discharge.

Deck Runoff is water that runs off from precipitation, freshwater or seawater washdowns, and seawater that falls on the exposed decks of a vessel such as a weather deck or flight deck. The water can wash off residues from the deck and topside equipment and become contaminated with materials from deck activities and be discharged overboard to receiving waters. Armed Forces vessels already institute certain management practices intended to reduce the amount of pollutants discharged in deck runoff. The management practices include keeping weather decks cleared of debris, immediately mopping up and cleaning spills and residues, and engaging in spill prevention practices. These practices demonstrate the availability of controls to mitigate adverse impacts from deck runoff.

Dirty Ballast is seawater that is occasionally pumped into empty fuel tanks to improve ship stability. Fuel in the tank to be ballasted is transferred to another fuel tank or holding tank before seawater is taken on. Dirty ballast is comprised of residual fuel mixed with seawater. The discharge is generated when the ballast is no longer required and the tanks are partially or completely emptied. Uncontrolled discharges of dirty ballast would be expected to exceed acute Federal or state water quality criteria for oil, benzene, phenol, copper, nickel, silver, and zinc. Concentrations of organic nitrogen would be expected to exceed the most stringent state water quality criteria. The use of oil content monitors, and oil-water separators to reduce the concentration of oil (and associated constituents) demonstrates the availability of MPCDs to control this discharge.

Distillation and Reverse Osmosis Brine is the seawater concentrate or "brine" that is left over by water purification systems that generate freshwater from seawater for a variety of shipboard applications including potable water for drinking. This brine is discharged overboard. Review of existing practices indicate that certain operational controls that limit the use of distillation plants and reverse osmosis units can reduce the potential for this discharge to cause adverse environmental impacts in some instances. Additionally, it appears that, for some vessels, reverse osmosis units may present an acceptable alternative to the use of distillation plants. Reverse osmosis units have nonmetallic membranes and operate at ambient temperatures and hence suffer from less system corrosion. Consequently, they discharge brines that are expected to contain lower concentrations of copper, lead, selenium, nickel, iron and zinc. Furthermore, the brine from the reverse osmosis units should not contain organic additives or dilute citric acid that is used to reduce the formation of scale on distillers. Further analysis is necessary to determine if reverse osmosis units should replace distillation plants. Nevertheless, existing operational practices for distillation and reverse osmosis plants and the availability of reverse osmosis units to replace distillation units on some vessels demonstrate that MPCDs are available to reduce the effects of this discharge.

Elevator Pit Effluent is liquid from deck runoff and from elevator equipment maintenance activities that collects in the bottom of elevator shafts. The effluent could contain grease, lubricating oil, hydraulic fluid, dirt, paint chips, aqueous film forming foam, glycol and sodium metasilicate. The liquid waste is directed overboard, collected for shore-side disposal, or processed along with bilgewater. These existing practices demonstrate the availability of controls to reduce the potential of this discharge to cause adverse environmental impacts to the environment.

Firemain Systems contain the seawater that is distributed for fire fighting and other services aboard ships. Discharges of firemain water from normal operations occur during firemain tests, maintenance and training activities, anchor chain washdown, and while cooling auxiliary machinery. Firemain systems on Armed Forces vessels are either wet or dry. With the exception of small craft, all Navy surface ships and some MSC vessels use wet firemain systems. Submarines and all Army and Coast vessels use dry firemain systems. Pollutants detected in the discharge of wet firemain systems include copper, iron, lead, zinc and bis (2-ethylhexylphosphate), a constituent of AFFF. The EPA and DoD believe that dry firemain systems may offer one means for reducing the total mass of pollutants discharged from firemain systems. The use of dry firemain systems for Coast Guard vessels demonstrates that, for at least some types of vessels, this option may be an available control mechanism. Another possible MPOD option for achieving pollutant reductions is the use of alternative material or metallurgy that would provide piping that would be less susceptible to corrosion and erosion. Dry firemain systems and the potential offered by alternative piping systems demonstrates the availability of controls that would mitigate potential adverse impacts on the environment.

Gas Turbine Water Wash is the water discharged when the internal and external propulsion and auxiliary gas turbine components are cleaned. Most vessels direct the discharge to a dedicated holding tank while they wash the turbine in coastal areas. This feature demonstrates the availability of controls for this discharge.

Graywater is the wastewater from showers, galleys, laundries, deck drains, lavatories, interior deck drains, water fountains, miscellaneous shop sinks, and similar sources. While most Armed Services vessels collect graywater and transfer it ashore while pierside, some do not have that capability and discharge it directly overboard. This accounts for less than half of the graywater discharged within 12 nm of shore. The rest is discharged within the 12-nm zone while ships transit it. The graywater can contain copper, lead, zinc, mercury, silver, nickel, and conventional and nonconventional pollutants such as total suspended solids, biochemical oxygen demand, grease, oil, ammonia, and phosphates. The EPA and DoD have determined that it is reasonable and practicable to require the use of an MPOD for graywater because containment systems can be used to transfer graywater to shore treatment facilities, which would relieve the impact on the environment.

Hull Coating Leachate is the agent that leaches, dissolves, ablates, or erodes into surrounding waters from hull coatings. Leachate is designed to prevent corrosion and to inhibit biological growth on the hull surface. The hull coatings on most vessels of the Armed Forces are either copper or tributyl tin (TBT)-based, with copper-based ablative coatings being the most predominant coating system. The DoD and EPA estimated that the leachate from the coating systems has the potential to cause an adverse environmental effect. The annual release of TBT is decreasing because TBT coatings are being phased out and research is being directed toward easy release coatings that resist biofouling when the vessel is underway. The phasing out of TBT-based paints and the encouraging progress in research programs to develop easy-release nonleaching coatings demonstrate the availability of controls to mitigate potential environmental effects from hull coatings. These controls may be needed because limits may be imposed on the amount of copper that may be released from copper-based systems.

Motor Gasoline Compensating Discharge is the seawater used to compensate for expended motor gasoline (MOGAS) used to operate equipment stored on some Navy vessels. MOGAS is stored in a compensating tank system to which seawater is added as fuel is consumed. This discharge occurs when

the ship is refueled and the displaced water is discharged overboard. Seawater in the MOGAS compensating system is in contact with the gasoline for long periods of time. MOGAS discharges are expected to contain benzene, ethylbenzene, toluene, phenols, and naphthalenes at concentrations that exceed acute water quality criteria. Specific operating procedures are followed to reduce the potential for discharging gasoline while the tanks are refueled with MOGAS. These procedures require MOGAS tanks to be filled slowly up to only 80 percent of the total tank capacity. Containment is placed around hose connections to contain any releases of gasoline, and containment booms are deployed in the water around the vessel being refueled. Diffusers are used within the tanks to prevent entraining fuel into the discharged compensating water. These management practices demonstrate the availability of controls to mitigate potential adverse impacts to the environment.

Nonoily Machinery Wastewater is generated from the operation of distilling plants, water chillers, low-and high-pressure air compressors, and propulsion engine jacket coolers. The discharge is captured in a dedicated system of drip pans, funnels, and deck drains to segregate the water from bilgewater, and drained directly overboard or into dedicated collection tanks before it is discharged overboard. The analysis of samples of this discharge showed copper, nickel, silver, and bis (2-ethylhexyl) phthalate present in concentrations that exceeded acute Federal or state water quality criteria, and nitrogen (in the form of ammonia, nitrates and nitrites, and total Kjeldahl nitrogen) and total phosphorus in concentrations that exceeded the most stringent state water quality criteria. The mass loadings for this discharge could not be determined because there were significant variations in sampling and flow rate data. System design changes to control the types and numbers of contributing systems and equipment, and implementation of management practices to reduce the generation of nonoily machinery wastewater are potential options to reduce the potential impact of this discharge on the environment.

Photographic Laboratory Drains waste consists of photographic lab wastes from the processing of color and black-and-white film. Typical wastes include spent film processing chemical developers, fixer-bath solutions, and film rinse water. The existing data are insufficient to determine whether drainage from shipboard photographic laboratories will cause adverse environmental effects. The Navy issued guidance to control photographic laboratory drains. It directs that all photographic processing wastes generated within 12 nm of shore be containerized for disposal ashore. The Navy is installing digital photographic systems that do not require chemicals. The current handling practices and the availability of digital photographic systems demonstrates that MPCDs are available to mitigate potential adverse effects, if any, from photographic laboratory drains.

Seawater Cooling Overboard Discharge is seawater used to cool heat exchangers, propulsion plants, and mechanical auxiliary systems. The heated seawater is discharge overboard directly. The demand for seawater cooling is continuous and occurs both within and beyond 12 nm from shore. Seawater cooling overboard discharge contains trace materials from seawater cooling system pipes, valves, seachests, pumps, and heat exchangers. Pollutants detected in seawater cooling overboard discharges include copper, zinc, nickel, arsenic, chromium, lead, and nitrogen (in the form of ammonia, nitrates and nitrites, and total Kjeldahl nitrogen). Copper, nickel, and silver were detected in concentrations exceeding both the chronic Federal and state water quality criteria. Nitrogen was detected in concentrations exceeding the most stringent state water quality criteria. These concentrations contribute to a significant total mass released by this discharge because of the large volume of cooling water. In addition, thermal effects modeling indicate that some vessels may exceed some state thermal mixing zone requirements. A potential MPCD option for achieving pollutant reductions is the use of alternative piping systems (i.e., different metallurgy) that would reduce the rate of pipe wall corrosion and erosion. The potential substitution of materials demonstrates the availability of controls to mitigate potential adverse impacts on the environment.

Seawater Piping Biofouling Prevention are anti-fouling compounds such as sodium hypochlorite that are introduced into seawater cooling systems to inhibit the growth of fouling organisms on interior piping and component surfaces. This discharge contains the chemicals used to prevent the

growth and attachment of biofouling organisms in seawater cooling systems on selected vessels, and the reaction byproducts. Some vessels use active biofouling control systems to control biological fouling when the piping does not have inherent antifouling properties. The most common systems use chlorination, chemical dosing, or an anode that releases metal ions into the piping system. Seawater discharged from systems with active biofouling control systems is likely to contain residuals from the fouling control agent (chlorine, alcohol-based chemical additives, or copper), in addition to constituents normally found in seawater cooling water. Modeling led the EPA and DoD to determine that receiving water concentrations of residual chlorine could exceed chronic Federal and state water quality criteria. The resulting mass loading of chlorine released to the environment is considered significant because of the large volume of seawater discharged from these systems. Existing operational controls that limit the residual chlorine discharged to the environment demonstrate the availability of an MPCD to mitigate the potential for adverse impacts from this discharge.

Small Boat Engine Wet Exhaust is seawater that is injected into the exhaust of small boat engines for cooling and to quiet operation. Exhaust gas constituents are entrained in the injected seawater and discharged overboard as wet exhaust. Small boats that operate within 12 nm from shore generate the discharge. Wet exhaust from outboard two-stroke engines that use a mixture of gasoline and oil as fuel contains several constituents (benzene, toluene, ethylbenzene, and naphthalene) that can exceed acute Federal or state water quality criteria. Wet exhaust from inboard (diesel) engines can contain benzene, ethylbenzene, BETX, and total polycyclic aromatic hydrocarbons (PAHs) that can exceed state water quality criteria. Mass loadings of these wet exhaust constituents are considered large. Potential MPCD options include replacement of existing outboard engines with new reduced-emission outboard engines, and the installation of inboard engines with dry exhaust systems on all new boats and craft.

Sonar Dome Discharge is generated by the leachate of antifouling materials from the sonar dome material into the surrounding seawater, and when water from inside the dome is pumped overboard before maintenance or repairs are performed on the dome. Some domes that house detection, navigation, and ranging equipment are filled with freshwater and/or seawater to maintain their shape and pressure. The domes are composed of rubber impregnated with TBT, rubber without an antifoulant, steel, or glass reinforced plastic (GRP). TBT is designed to leach continuously from the exterior surface of the dome when it is waterborne. The discharge can contain the butyl tins, copper, nickel, zinc, and tin. While the concentrations of TBT, copper, nickel, and zinc can exceed acute Federal or state water quality criteria, fleetwide mass loadings of these constituents are not considered large. The Navy has instituted a program to install new sonar domes that do not have TBT-impregnated internal surfaces as existing domes require replacement. This practice demonstrates the availability of a control to mitigate potential adverse environmental impacts, if any, from sonar dome discharges.

Submarine Bilgewater sources include seawater accumulation, normal leakage from machinery, and fresh water washdowns that collect in the bilge. All submarines generate this type of waste. Most submarines can segregate oily wastewater from nonoily wastewater. The non-oily waste is discharged directly overboard and the oily wastewater is collected in a tank that allows gravity separation of the oil and water. The separated water phase is discharged overboard, as needed, and the oil phase held until it can be transferred to shore facilities for disposal. Approximately 60 of the submarines (the SSN 688 class) discharge the separated water phase from the bilgewater collection tanks within and beyond 12 nm from shore. The rest of the submarines generally hold all bilgewater onboard until they are beyond 50 nm from shore. The bilgewater contains concentrations of cadmium, chlorine, copper, cyanide, heptachlor, heptachlor epoxide, mercury, oil, phenol, silver, and zinc that exceeded acute Federal or state water quality criteria. While submarines use gravity separation to reduce the concentration of oil in bilgewater before the water phase is discharged, this method does not consistently produce a discharge that meets water quality criteria. (The adequacy of existing gravity separation treatment to provide effective environmental protection will be addressed during the Phase II rulemaking.) The discharge could adversely impact the environment if it is not treated. The EPA and DoD have determined that it is

reasonable and practicable to require the use of an MPCD for submarine bilgewater because there are pollution controls available to reduce the oil content of the discharge.

Surface Vessel Bilgewater/Oil-Water Separator Discharge includes condensate from steam systems, boiler blowdown on some vessels, water fountains, and machinery space sinks that drain to the bilge. All vessels of the Armed Forces produce bilgewater and most of the larger vessels have oil water separator (OWS) systems. Small craft bilgewater is collected and transferred to shore facilities while pierside. On larger vessels, bilgewater is either held for shore-side disposal or treated in an OWS to remove the oil before it is discharged overboard. Oil collected during the OWS separation process is held in a waste oil tank until it is transferred to shore facilities for disposal. Under current policy, bilgewater treated by an OWS can be discharged as needed within 12 nm, while untreated bilgewater is held for transfer to a shore facility for treatment. The concentration of oil in the treated stream must be less than 15 mg/l. The treated stream may contain oil and concentrations of copper, iron, mercury, nickel, and zinc that exceed acute Federal or state water quality criteria. Sampling data also show concentrations of nitrogen and phosphorus that exceed the most stringent State water quality criteria. The estimated mass loading for oil is large. The data indicate that untreated bilgewater would likely cause adverse environmental impacts. The existing policies that prohibit the discharge of untreated bilgewater and the extensive use of oil-water separators and oil content monitors demonstrate the availability of pollution controls for bilgewater.

Underwater Ship Husbandry is the liquid discharge that develops when hulls and hull appendages are groomed, maintained, and repaired while a vessel is waterborne. Underwater ship husbandry is usually performed at the pier. It includes hull cleaning, fiberglass repair, welding, sonar dome repair, nondestructive testing, masker belt repairs, and painting operations. The process releases a significant mass loading of copper and zinc in quantities that exceed acute Federal and State water quality. The Navy has established policies to minimize the number of hull cleanings and has established procedures to use the least abrasive cleaning equipment necessary to reduce the mass of copper and zinc in the discharge. These practices represent available controls to mitigate adverse impacts from underwater ship husbandry operations.

Welldeck Discharge is the water that accumulates from the seawater flooding of the docking wells (welldeck) of a vessel used to transport, load, and unload amphibious vessels, and from the maintenance or washing off the welldeck and equipment/vessels stored in the welldeck with potable water. The discharge can include water and residuals from precipitation, equipment and vehicle washdowns, gas turbine engine washes, graywater from stored landing craft, and general washdowns of the welldeck and vehicle storage areas. Consequently, welldeck discharges can contain a variety of residual constituents, which include oil and grease, ethylene glycol, chlorine, detergents/cleaners, metals, solvents, and sea-salt residues. Existing practices for containment and cleanup of welldeck spills demonstrate the availability of controls to reduce contamination of welldeck discharges and the potential to cause adverse environmental impacts (e.g., oil sheens).

Defining the Problem

The foregoing indicates that the wastewaters could contain fats, oils and grease; detergents; fuel; volatile and nonvolatile organics (icing inhibitor additives such as ethylene glycol monomethyl ether and diethylene glycol monomethyl ether, urea, sulfamic acid, citric acid, and tributyltin); nonindigenous species; inorganics (calcium magnesium acetate and potassium acetate deicing agents); suspended and dissolved inorganic solids; metals; BETX and PAH; general metal-bearing corrosion products in cooling water and in the bilge fluids; trace amounts of chlorine and bromine; hull leachate, debris, and metals (copper compounds) from hull husbandry; antifouling paint leachates; biochemical oxygen demand; chemical oxygen demand; small amounts of coliform bacteria from the graywater stream; and aqueous film-forming foam. Because these contaminants could adversely affect the environment, many wastewaters could require control technology or management practices to mitigate contaminant effects.

Objective of the Study

The purpose of this report is to present the results of a survey conducted to gather information on the best available practicable unit operations and control technologies. New and innovative treatment technologies in the research, developmental or demonstration stages that could lead to systems, operations, and processes to treat the incidental discharges that require an MPCD were also examined. All the technologies considered that yielded a liquid waste stream must have demonstrated (or shown that they had a reasonable potential for) a minimum destruction and removal efficiency for organics or selected metals of at least 99% when used alone or when combined with another. While this survey is part of a program to uncover technologies and systems that ultimately can be used on a ship, no technology was judged for its overall cost and its operational feasibility in a shipboard milieu.

PROVEN TECHNOLOGIES THAT MAY BE RELEVANT TO THE CHALLENGE

Table 2 lists proven technologies that have been used to treat aqueous waste streams. The information was drawn from Version 5.0 of EPA's National Risk Management Research Laboratory's (NRMRL) Treatability DataBase (EPA 600/C-93/003a) and its September 1, 1998 update, which is available on the INTERNET (<http://www.epa.gov/tdbnrmrl/>), and information from the trade literature, peer-reviewed literature, Chapter 8 of *"Development Document For Proposed Effluent Limitations Guidelines and Standards For the Centralized Waste Treatment Industry,"* EPA Report EPA 821-R-98-020, (December 1998), and published Navy studies. Version 5.0 is described in a USEPA NRMRL Office of Research and Development (Glenn M. Schaul) letter dated December 11, 1998. The database gives performance data on numerous technologies. It reviews the removal/destruction of chemicals in various media and lists technical references. For each entry, the database includes the following:

- Physical /chemical properties
- Aqueous and solid treatability data. The data includes treatment technologies, the type of waste/wastewater treated, the size of the study/plant, and the treatment efficiency
- Other information such as Freundlich isotherm data
- Treatment performance data summarized in tables, separated according to influent concentrations, with citations to references. Quality control codes are included to give a sense of data quality.

Often, one simple or standard treatment process cannot remove all of the contaminants, and there is a need to provide more than one process or a process train where a series of processes forms a unique treatment system. The serial treatments in Table 2 are from the Treatability DataBase and Navy reports. See Tompkins, K.T., L.P. Murphy, B.L. Owsenek, R.P. Pignataro, A.T. Rodriguez, "Ultrafiltration Membrane Polishing System for Shipboard Treatment of Oily Wastewater," in *Proceedings of the ASNE Environmental Symposium, Environmental Stewardship: Ships and Shorelines*, November 1997 and Nickens, A.D. and J.F. Pizzino, "Protecting the Next Century's Environment-The Navy's New Shipboard Oily Waste Membrane Polishing System," *Deckplate Magazine*, Summer 1997. Those papers described a shipboard system that uses ceramic dense pack ultrafiltration modules to remove trace amounts of oil from the effluent of parallel plate oily/water separators that treat ship's bilge fluid before it is discharged.

One should note an important difference between the combination of technologies used with another (powdered activated carbon in a biological system) and the technologies used serially (a biological system followed by activated carbon) in a process train. The latter infers that the complete system is a chain of independent elements in series. The series structure is one in which all of the elements must operate to provide a path from the input to the output. The laws of probability are immutable; the probability of operating correctly over a specific length of time under specific conditions (the reliability) is the product of the probability of successful operation of each of the elements. For example, if a system uses two technologies in series to treat bilgewater, and the reliability of the first is

95% and the reliability of the second is also 95%, the overall reliability will be 90%, which is less than the individual elements. The Navy recognizes that problem and always subjects systems to rigorous reliability studies before they are accepted for use aboard a ship.

Table 2. Aqueous Treatment Technologies

Activated Alumina Sorption
 Activated Sludge
 Activated Sludge and Filtration
 Adsorption on Filter Media
 Aerobic Fixed Film
 Aerobic Suspended Growth
 Air Stripping
 Alkaline Hydrolysis
 Anaerobic Fixed Film
 Anaerobic Fixed Film and Activated (Granular) Carbon
 API Oil/Water Separator
 API Oil/Water Separator and Dissolved Air Flotation
 Biological Treatment: In-Situ and Ex-Situ
 Biological Granular Activated Carbon
 Bioremediation
 Chemically Assisted Clarification
 Chemical Oxidation by Chlorine
 Chemical Oxidation by Chlorine Dioxide
 Chemical Oxidation by Ozone
 Chemical Oxidation by Ultraviolet with Peroxide
 Chemical Oxidation by Ultraviolet with Ozone
 Chemical Oxidation by Ultraviolet with Ozone and Peroxide
 Chemical Oxidation/Precipitation
 Chemical Precipitation
 Chemical Precipitation Followed by Filtration
 Chemical Precipitation and Chemically Assisted Clarification
 Chemical Precipitation with Chemical Oxidation
 Chemical Reduction
 Continuous Stirred Aerobic Suspended Growth Reactor Followed by Microfiltration, the Separate Stage Membrane Bioreactor
 Continuous Stirred Aerobic Suspended Growth Reactor that Incorporates a Submerged Microfiltration Membrane, the Submerged Membrane Bioreactor¹
 Crossflow Microfiltration and Ultrafiltration
 Dechlorination Using an Alkoxide
 Dissolved Air Flotation
 Electrodialysis
 Emulsion Breaking/Gravity Separation and Ultrafiltration
 Emulsion Breaking/Gravity Separation and Dissolved Air Flotation
 Evaporation
 Filtration
 Filtration and Activated Carbon
 Fenton's Reagent

¹ This technology is included because the Navy has a research program to determine if it can be used to process a stream that contains both black water and graywater generated by a ship.

Table 2 (Continued)

Flocculation
Granular Activated Carbon
Hydrocyclone
Ion Exchange
Mechanical Centrifuge for Oil/Water Separation
Parallel Plate Gravity Coalescence Oil/Water Separator
Parallel Plate Gravity Coalescence Oil/Water Separator Followed by Ultrafiltration
Parallel Plate Oil/Water Separator Followed by Adsorption
Photochemical Oxidation
Plasma Arc Pyrolysis
Powdered Activated Carbon
Powdered Activated Carbon Addition to Activated Sludge
Powdered Activated Carbon and Filtration
Rotating Biological Contactor
Sequential Batch Reactor
Sequential Batch Reactor with Activated Carbon
Supercritical Water Oxidation
Sedimentation
Sedimentation with Activated Sludge
Semi-Permeable Membranes: Nanofiltration, Ultrafiltration, Microfiltration, and Reverse Osmosis
Solvent Extraction
Steam Reforming
Steam Stripping
Steam Stripping and Activated Carbon
Trickling Filter
Vacuum Extraction
Wet Air Oxidation

RELEVANT PAPERS IN THE RECENT LITERATURE

Scott and Ollis [Scott, J.P., and D.F. Ollis, "Integration of Chemical and Biological Oxidation Processes for Water Treatment: Review and Recommendations," *Environ. Progress*, Vol. 14, No. 2, pp. 88-103 (May 1995)] reviewed the prior literature. They examined the results of 58 studies that used a combination of chemical and biological degradation (usually oxidative) of organic contaminants in water and found that beneficial effects of such two-step treatments are commonly reported. They concluded that a combination of chemical and biological processes leads to greater and more thorough destruction of many organic compounds, with some exceptions. Nine cases reported a dramatic increase and all others reported some increase for at least one pollutant. These results, primarily from laboratory studies, suggest potential advantages for waste treatment via process integration rather than through single technology processing.

Scott and Ollis identified four wastewater contaminant types that can benefit from combined processes: 1) recalcitrant compounds, 2) biodegradable wastes with small amounts of recalcitrant compounds, 3) inhibitory compounds and 4) intermediate dead-end products. The first two are of special interest. Large macromolecules may not be easily biodegradable due to their size. Chemical oxidation can break these compounds into smaller biodegradable fragments. Ultraviolet photolysis, ozone, photocatalysts, and ozone followed by hydrogen peroxide have been used for that purpose. They cited a study that showed that polyethylene glycol needed to be broken down to a molecular weight of 300 before

a bioculture could utilize it. They pointed out that a combination of biological followed by a chemical process might prove useful to treat domestic waste that contains large amounts of biodegradable organics in addition to small amounts of recalcitrant compounds. The primary step reduces the number and concentration of compounds that may compete for the chemical oxidant. Similarly, pretreatment by a biological system can favorably affect the subsequent chemical oxidation by removing biogenic compounds that would otherwise compete for the chemical oxidant. The design key for such two-step systems lies in choosing processes that complement each other and lead to a synergistic effect. Predicting this performance outcome requires knowledge of the physical, chemical, and biological properties of the major reaction intermediates and their susceptibility to degradation by each process.

Another report [Gallup, D.L., E.G. Isacoff and D. N. Smith, III, "Use of Ambersorb Carbonaceous Adsorbent for Removal of BTEX Compounds from Oil-Field Produced Water," *Environ. Progress*, Vol. 15, No. 3, pp. 197-203 (Fall, 1996)] reported of studies on the removal of high concentrations of BTEX compounds (benzene, toluene, ethylbenzene and xylenes) from oil-field produced waters using a carbonaceous adsorbent. The primary objectives of the field studies were to evaluate the efficiency of oil removal processes to protect the adsorbent from fouling, to determine the BTEX removal efficiency of a carbonaceous adsorbent at a high flow rate, and to demonstrate regeneration of the adsorbent. Oil can physically coat the outer surface of all sorbents, and that includes granular carbon, carbonaceous adsorbents, and polymeric adsorbents. (The need to protect the sorbent from emulsified oil is of special interest if one contemplates a two-stage system consisting of the parallel plate separator followed by a polisher on Navy vessels.) Fouling was mitigated by a 5-micron filter followed by a mechanical coalescer for heavier crude and emulsion breaking for lighter crude. Adsorbent extenders and filters did not control fouling in the presence of exceedingly emulsified crude oil.

Karamanev and Nikolov [Karamanev, D.G. and L.N. Nikolov, "Application of Inverse Fluidization in Wastewater Treatment: From Laboratory to Full-Scale Bioreactors," *Environ. Progress*, Vol. 15, No. 3, pp. 194-196 (Fall, 1996)] found that the inverse fluidized bed bioreactor (IFBBR) is an effective device to treat wastewaters that have low concentrations of pollutants. Fluidized bed bioreactors can be used for processes in which the particles are used as an inert support for a biofilm. Inverse fluidization is a new (1980) multiphase gas-liquid or gas-liquid-solid system. It differs from the classic fluidization in that the solid particle density in the inverse fluidizing bed is less than the density of the continuous fluid and therefore the bed is fluidized by a downflow of the fluid. The IFBBR was designed to provide a solid support for an approximately 100- μ thick biofilm that the authors claim is the optimal biofilm thickness for the diffusion of O_2 and/or the organic substrate to the deeper layers of the biofilm. The plant was an IFBBR consisting of eight similar vessels in series. The reactor was built at a municipal wastewater plant and inoculated with activated sludge from the plant. BOD was used as the measure of effectiveness. The biofilm formed during a two-week period when the water retention time was 7.5 hours. The retention time was 1.8 hours once a stable biofilm was formed, and only three of the eight sections were required to complete the treatment. Most of the BOD was removed in the first three sections when the retention time was reduced to 0.8 hours.

Abe and Kondo [Abe, M. and Y. Kondo, "Filtering Organic Solutes From Water," *CHEMTECH*, pp. 33-36 (March 1999)] investigated a technique based upon surfactant vesicle-enhanced ultrafiltration to remove organic solutes from water. Micellar-enhanced ultrafiltration (MEUF) is a separation process in which a micellar solution that contains organic solutes is passed through a membrane with pore sizes smaller than the micellar diameter, and the micelles and solubilized solutes are removed from aqueous streams. Vesicles are much larger in diameter than micelles; substituting vesicles for micelles should improve MEUF because the ultrafiltration membrane pore size could be increased, thus resulting in large fluxes. It would also reduce the concentration of surfactant in the permeate. The experimental work used the solubilization of aromatic compounds by vesicles formed by a double-chain surfactant that uses equilibrium dialysis as a prerequisite step to remove organics from water. Their research provided some insight on the solubilization mechanism and the difference between the solubilization ability of vesicles

and other surfactant micelles. They found that vesicles have greater solubilizing ability than conventional surfactant micelles.

Cansell, Beslin, and Berdeu [Cansell, F., P. Beslin, and B. Berdeu, "Hydrothermal Oxidation of Model Molecules and Industrial Wastes," *Environ. Progress*, Vol. 17, No. 4, pp. 240-245 (Winter, 1998)] noted that the evolution of environmental regulations has led to new concepts for the destruction of waste. Supercritical water oxidation is being investigated as one of them. Reaction pathways do not yield toxic gaseous products, and residence times are less than one minute in comparison with wet oxidation where the residence time can be one hour. They used a pilot plant to study the effect of pressure, temperature and time on the oxidation of methanol and glucose (oxidation model compounds), paper mill sludge, wastewater from the car industry, and cutting oils. The reactor was constructed of 6-m long 2.7-mm inside diameter Inconel tubing. The oxidant was H_2O_2 . The cutting oils were included to study the effect of high chloride concentration on reactor corrosion and metal concentration in the liquid effluent. Results for that study showed COD reduction was not complete (88%) and that there was a very small amount of metal in the effluent. The metals were not in the cutting fluid and corresponded to the reactor corrosion. Ninety eight percent of the chlorine was recovered. The authors concluded that hydrothermal oxidation can be a competitive process for the treatment of aqueous industrial wastes in comparison with other processes such as incineration.

Brown and his associates [Brown, S.H., E.B. White, T.L. Chaney and R. Garman, "Shipboard Integrated Liquid Discharge System Concept," in Proceedings of the *International Conference on Incineration and Thermal Treatment Technologies*, Salt Lake City, UT, pp. 675-679 (1998)] discussed the status of a Navy program that addresses action taken to accommodate national and international regulations that restrict the overboard discharge of ship-generated liquid waste. Future discharges of untreated sewage, graywater, and oily wastes will probably be further restricted in littoral areas throughout the world. Consequently, the Navy has begun a research and development program to provide Navy ships the means to destroy liquid wastes aboard the ship, and thus maximize shore independence and minimize waste off-load costs in foreign and domestic ports. The Carderock Division of the Naval Surface Warfare Center has developed a conceptual model, the integrated liquid discharge system (ILDS), that is the guiding principal of the Environmentally Sound Ship of the 21st century and features a thermal destruction device as its central processing unit. The ILDS contains three distinct elements: the concentration of nonoily liquid wastes, the concentration of oily waste, and thermal destruction of the concentrates. The fundamental principle of the ILDS concept is the minimization of the volume of the waste streams so that a shipboard thermal destruction device can process the volume of waste in a practicable manner. Ultrafiltration and other techniques will be used to concentrate/minimize the volume of pollutants in nonoily and oily liquid waste streams. The thermal destruction device must be able to destroy all the resulting concentrated liquid wastes and waste oil. Vortex incinerators have been shown to successfully process blackwater aboard two classes of U.S. Navy ships that use reduced-flow vacuum collection toilets. A Navy R&D program has developed and will evaluate a prototype modified vortex incinerator to destroy the sewage from reduced flow toilets together with the concentrated black, gray, oily wastes, and waste oil. Data from the prototype will be used to develop an advanced system.

Results of studies on the ability of hydrous oxides of iron (HFO) and aluminum (HAO) to reduce Cu (initially 4.3 mg/L) to microgram per liter levels typical of increasingly stringent wastewater discharge limits were presented by Karthikeyan et al [Karthikeyan, K.G., H.A. Elliott and F.S. Cannon, "Adsorption and Coprecipitation of Copper with the Hydrous Oxides of Iron and Aluminum," *Environ. Sci. & Technol.*, Vol. 31, No. 10, pp. 2721-2725 (1997)]. Residual soluble Cu was compared following adsorption (ADS), where Cu was contacted with preformed oxide flocs and coprecipitation (CPT), where Cu was added prior to the precipitation of HFO or HAO. The amount of copper removed was affected by the hydrous oxide type and contact methodology. For the HAO-ADS system, soluble Cu levels were markedly undersaturated with respect to homogeneous precipitation (PPT) of $Cu(OH)_2(s)$ over the pH 6-9 range. In contrast, soluble Cu was lowered by HFO-ADS for pH <7.5 but comparable to PPT at higher pH.

Isotherms suggest a Cu surface precipitate formed on HAO with a solubility product lower than its HFO analogue. Compared to ADS, soluble Cu after CPT was similar for HAO but was dramatically lower for HFO. More Cu was incorporated internal to the HFO flocs during CPT, suggesting that there was some Cu substitution into the HFO lattice. The findings have implications regarding coagulant selection or dosing methods for achieving high copper removal in wastewater treatment.

Benson presented a paper at the May 1999 meeting of the American Society of Naval Engineers [Benson, J., I. Caplan, and R. Jacobs, "Blackwater and Graywater on U.S. Navy Ships: Technical Challenges"] that describes the status of U. S. Navy developments to provide shipboard systems to control and treat sewage (black water) and hotel-related wastes (graywater). The Navy has recognized the need to develop technologies that would lead to systems to control and treat black and graywater because it expects that environmental regulation will become more stringent, the cost of waste disposal will increase, and because it must be able to operate unimpeded in the littoral zone. In addition, the discharge of graywater in the coastal zone will be controlled by the Uniform National Discharge Standards, which have yet to be defined. The challenge is to develop marine pollution control devices that treat the wastes adequately and meet the Navy shipboard requirements, viz.; affordability; compactness; low manning and maintenance requirements; reliability and safety; and noise, vibration, and shock. The Navy is developing membrane-based ultrafiltration systems that use aerobic biological treatment as the first stage and ultraviolet light as the second to meet those requirements. (A secondary benefit of such a system is that metallic contaminants in the system are sorbed onto the biomass and/or entrapped by the membranes.) The project will demonstrate a process to treat shipboard nonoily wastewater to meet the anticipated national and international effluent standards. The system is an aerated membrane bioreactor that combines membrane separation with biological treatment into a single process. Benson also described the sequence of studies that are directed toward the pierside demonstration of such a system to process black and graywater; and the design, fabrication, and tests of an Engineering Developmental Model of a modified system to process graywater that will be evaluated in the laboratory before it is demonstrated on a ship.

W.E. Schwinkendorf and L.L. Nenninger reported on progress to identify and evaluate thermal and nonthermal destruction technologies as options to incineration for a variety of mixed waste streams. [W. E. Schwinkendorf and L.L. Nenninger, "Evaluation of Alternatives to Thermal Treatment for DOE Mixed Waste," *Proceedings of the 1994 International Incinerator Conference*, Houston, TX, May 1994, pp 13-18. See also McFee, J., Schwinkendorf, W.E., Hart, A.H., "Evaluation of Alternatives to Incineration For DOE Mixed Waste," (February 1995)]. The study was performed under auspices of the United States Department of Energy Mixed Waste Integrated Program (MWIP). MWIP had initiated the program because of the current and potential problems in permitting and operating incinerators and other high temperature systems. For the purposes of the study, they defined an alternative to thermal treatment as a process that operates at low temperatures ($<350^{\circ}\text{C}$). (The technology they considered could also be applied to waste that does not contain low level radioactive components.) They fell into three general classes: chemical oxidation, irradiated chemical oxidation, and electrolytic/electrochemical oxidation. The technologies included in the three classes were Wet Air Oxidation, Catalyzed Chemical Oxidation, Acid Digestion, Ultraviolet Oxidation, Electron Beam, Ultrasound (enhanced) Oxidation, the Persulfate Process, and Mediated Electrochemical Oxidation. (All of these technologies are discussed elsewhere in this report.) Evaluation criteria were based upon low temperature operation, applicability to materials targeted for one or more thermal processes, conversion of organics to nonhazardous species, volume reduction, and minimum safety hazards. The paper concluded that while the nonthermal technologies do not have the large volume off-gas problems associated with incineration and other thermal processes, they do have other general disadvantages, viz.: "(1) in some instances, depending on the waste constituents and the technology, the organic matter is not completely oxidized and intermediate compounds may be produced that require post destruction; (2) many processes cannot treat organic solids, and those that do either require extensive size reduction (to powder form) or can treat only a limited class of solids such as

ion exchange resins or soluble cellulose; and (3) the inorganic solids in the waste stream result in a sludge that requires further treatment."

J. M. DeSimone and his coworkers at the University of North Carolina, J.D. Londono and his coworkers at Oak Ridge National Laboratory, and D. Chillura-Martino and R. Triolo of the University of Palermo reported on the design of nonionic surfactants for Supercritical Carbon Dioxide (SCCO₂) [J. B. McClain, et al. "Design of Nonionic Surfactants for Supercritical Carbon Dioxide," *Science* 274, 20 Dec 1996, pp 2049-2052]. Neat CO₂ is a very poor solvent for biomolecules and describing it as an alkane analog is not appropriate. The U.S.-Italian team led by J. DeSimone created surfactants that form micelles and should help carbon dioxide dissolve greasy molecules. (The University of Pittsburgh had reported earlier that fluoroalkyl and fluoroether surfactants exhibit high solubility in CO₂ and form micelles in it [E. J. Beckman, "Carbon Dioxide Extraction of Biomolecules," *Science*, 271, 2 February 1996, pp 613-614]). DeSimone's group found a way to dissolve nonpolar molecules, a category that includes grease, oils, machine-cutting fluids, and many polymers, in CO₂, and created a new surfactant by linking a fluorinated, acrylate compound with a strand of polystyrene, a nonpolar polymer. The nonionic surfactants for CO₂ were capable of emulsifying up to 20% by weight of a CO₂ - insoluble hydrocarbon into CO₂.

The liquid membrane transport process is a new technology where specific materials are transported selectively and rapidly across a liquid membrane [S. Kilambi, "Reclaiming Metals and Organics From Industrial Wastewaters," *Pollution Engineering*, August 1996, pp 46-48]. A liquid membrane is a thin liquid film that contains materials that facilitate transport of specific species of interest across it. Transport of a metal ion across the membrane is accompanied by transport of another ion in the same or opposite direction. The second ion's concentration gradient is often the driving force for the metal ion transport, which makes it possible for the ions to travel from dilute to concentrated solutions. Supported Liquid Membranes (SLMs) can be used in metal ion separation, biotechnology, and reverse osmosis/ultrafiltration processes. SLMs require a good prefiltration system to avoid membrane fouling. Kilambi refers to the use of SLMs to remove copper, chrome, and zinc salts in the metal finishing industry and organic chemicals in the petrochemical industry. Argonne National Laboratory is using SLMs to separate metals [Dunks, K.L., Hodgson, K.M., "Integrated test plan for the field demonstration of the supported liquid membrane unit," Bechtel Hanford, Inc., Richland, WA (Jun 1995), DE96005708, NTIS Order Number DE96005708]. This Integrated Test Plan describes the operation and testing of a hybrid reverse osmosis/coupled transport (RO/CT) groundwater remediation test unit, also referred to as the Environmental Restoration Technology Demonstrations at the Hanford Site. The SLM will be used to remove uranium, technetium-99, and nitrate from a selected groundwater source at the Hanford Site. The overall purpose of this test is to determine the efficiency of the RO/CT membranes operating in a hybrid unit, the ease of operating and maintaining the SLM, and the amount of secondary waste generated as a result of processing. The goal of the SLM is to develop a RO/CT process that will be applicable for removing contaminants from almost any contaminated water.

STATUS OF NAVY PROGRAMS TO IMPROVE THE QUALITY OF SOME OF THE LIQUID WASTE STREAMS GENERATED BY SHIPS

OPNAV INSTRUCTION 5090.1B has mandated the following liquid waste discharge restrictions: [Nickens and Pizzino, "Shipboard Waste Management Program RDT&E Program Review," PE63721N, Project S0401, 26 September 1996; and Soto, M. and A. Lardis, "Hydrothermal Oxidation (HTO) for the Destruction of Shipboard Wastes," in *Proceedings of the International Conference on Incineration and Thermal Treatment Technologies*, Salt Lake City, UT, pp. 753-755 (1998)]

- Oily Waste (bilge water, ballast water, waste oil)

Current-National: Discharge <15 milligrams per liter (mg/l) everywhere, but if not possible beyond 12 nautical miles (nm) then <100 mg/l. No discharge in "special areas," if possible.

Current-state: Some states restrict discharges to no more than 10, 5, or 0 mg/l.

Anticipated: 15 mg/l everywhere discharge is allowed; UNDS (the Final Rule) is expected to take affect in FY 03.

- Sewage

Current: No discharge within 3 nm.

Anticipated: No discharge within 4 nm, treated sewage 4-12 nm.

- Graywater

Current-National: No restrictions, but most Navy ships combine graywater with sewage and consequently are subject to sewage restrictions.

Current-State: Several states attempting to restrict discharge.

Anticipated: No pending restrictions at Federal or international levels. Some states discourage discharges, and there is international interest in control of discharges: UNDS (The Final Rule) is expected to take affect in FY 03.

- Other liquid discharges

Current: No restrictions.

Anticipated: No pending restrictions at the Federal or international level; UNDS, which will establish performance standards for incidental liquid discharges, may take in effect in FY 03.

Control of the pollutants during the discharge of graywater, oily wastes from the bilge, and fuel-contaminated water from compensated ballast systems is the subject of major Navy developmental programs. It is anticipated that graywater discharged from Armed Forces vessels that are operating within the navigable waters of the United States and the in the water of the contiguous zone will be required to contain less than 50 mg/l of Biochemical Oxygen Demand (BOD₅), less than 100 mg/l of Total Suspended Solids (TSS), and less than 200-colonies/100 ml of fecal coliform. Oily wastes from bilges and other sources will be required to contain no more that 5 mg/l of oil. The Navy's approach to control the quality of black water, graywater, and oily water discharges is to separate and concentrate the pollutants by ultrafiltration, and then to hold or destroy the concentrate.

The Navy is exploring thermal destruction technologies to dispose of waste oil, concentrates from ultrafiltration membranes that process the graywater and oily water, and the relatively concentrated black water typical the vacuum collection systems that is installed in new ships. One program will develop a shipboard integrated liquid discharge system (ILDS) that couples volume reduction with thermal destruction to treat most shipboard liquid waste. The ILDS uses modern combustion techniques to destroy the foregoing liquid wastes in a vortex liquid waste incinerator similar to that used on certain classes of destroyers to destroy black water from low-flow vacuum collection systems. The study will optimize the nozzle type and its placement, characterize the operating performance, and model the flow characteristics to maximize the performance with minimal changes and cost [Brian Gullett, "Development of U.S. Navy Shipboard Systems for Solid and Liquid Waste Thermal Treatment," in *Proceedings of the International Conference on Incineration and Thermal Treatment Technologies*, Savannah GA, May 1996, pp. 809-815; Brown, S. H., E. B. White, T. L. Chaney and R. Garman, "Shipboard Integrated Liquid Discharge System Concept," in *Proceedings of the International Conference on Incineration and Thermal Treatment Technologies*, Salt Lake City, UT, pp. 675-679

(1998); and Adema, C.M., A.J. Rodriguez and C.H. Crane, "U. S. Navy Vision for Shipboard Thermal Destruction of Solid and Liquid Wastes," Presented at the *International Conference on Incineration and Thermal Treatment Technologies*, Orlando FL. (May 1999)].

Another program is considering thermal destruction in an Advanced Technology Demonstration (ATD) program that is developing a Plasma Arc Waste Destruction System (PAWDS) to process shipboard solid waste. PAWDS uses an ultra-high temperature plasma jet to dissociate complex organic materials and reduce them to simple pyrolytic gases and can melt all inorganic materials. Some of the work will address concentrates from the liquid waste streams and waste oil [Nolting, E.E., D.S. Vaughters, J.W. Cofield, M.J. Pechulis, and C.M. Kelly, "Navy Shipboard Plasma Arc System Development Program," in *Proceedings of the International Conference on Incineration and Thermal Treatment Technologies*, Oakland, CA, pp. 553-557 (1997) and Peterson, S.H., D. A. Counts, B. D. Sartwell, E.E. Nolting, and J. Cofield, "Current Status of Development of Plasma Arc Systems For Destruction of Navy Wastes," presented at *The International Conference on Incineration and Thermal Treatment Technologies*, Orlando FL, (May 1999)].

Studies of the use of ultrafiltration membranes to concentrate shipboard-generated graywater have been supported by the Strategic Environmental Research and Development Program and the Navy's Environmental Quality Applied Research Program. Those studies revealed that membranes (ultrafiltration and nanofiltration) alone could not treat the graywater (remove sufficient soluble low molecular weight oxygen-demanding organics) to meet the anticipated 5-day BOD requirement.

Benson reported the results of a study that investigated the ability of a two-stage membrane treatment system to treat shipboard-generated graywater at a rate of 3 gal/min [Benson, J., "Pierside Evaluation of a Prototype Graywater Treatment System," NSWCCD Technical Report NSWCCD-63-TR-1996/12 (Jan 1999)]. The first stage of the system used ultrafiltration to trap coarse and fine solids and to remove a significant amount of suspended organics and fecal coliform. A second stage nanofilter was intended to remove dissolved organics and consequently reduce the BOD₅ and suspended solids. The UF membrane reduced the BOD₅ (by 65%) and the TSS (by 99%). The nanofilter reduced the BOD₅ in the permeate issuing from the UF membrane by 15%. It could not maintain a stable flux and was difficult to maintain. The median concentration of the BOD₅ in the permeate leaving the system was 217 mg/l, much greater than the goal of 50 mg/l. There was a significant drop in the concentration of copper and zinc across the system. The results of pierside tests using proprietary *in-tank* hollow-fiber membranes in an aerated (aerobic biological) chamber were encouraging; the BOD₅ was less than 50 mg/l most of the time. Supporting studies to devise and install water saving fixtures and processes in the graywater system will reduce significantly the amount of fluid to be processed.

A project under Program Element 0603712N will demonstrate a process [the Aerated Non-Oily Wastewater Membrane Treatment System (AMTS)] to treat shipboard-generated non-oily (black and gray) wastewater to meet the anticipated national and international effluent standards of less than 50 mg/l of (BOD₅), 100 mg/l of TSS and 200 colonies/100 ml of fecal coliform. The project, an element of the Office of Naval Research's (ONR) Environmental Requirements Advanced Technology Program, will design, fabricate, and evaluate a hybrid membrane/bio-conditioning system that combines aerobic biological treatment, the proprietary *in-tank* hollow fiber microfiltration membranes discussed above, and an ultraviolet post-treatment element. The hybrid membrane/bio-conditioning system that will be produced by ZENON Environmental Systems under a sole-source, cost sharing contract. The feed will be a mixture of graywater and black water drawn from a ship that has a 300-man crew and a sewage vacuum-collection system. This risk reduction effort will demonstrate the viability of the AMTS process and serve as the basis for the design of a full-scale shipboard engineering development model. The development model will be able to treat sewage and graywater generated by a combatant over a 30-day period (without wasting sludge) to meet future 21st century water quality requirements and Navy mission requirements. In addition, a graywater treatment developmental model that can concentrate graywater 50:1 was evaluated by the Navy pierside at the Norfolk Naval Station from May - October 1999 to

determine system reliability, performance, and the ability to handle unanticipated upsets (toxic shocks). The Norfolk model used an *out-of-tank* bundled tubular membrane filtration system and ultraviolet disinfection. The system processed wastewater for a total of 1,805 hours at 2.3 gpm. The membrane resistance trend indicated that the membranes could have processed for another 4,900 hours (a total of 12.5 months), which exceeded the goal of 6 months before chemical cleaning. The effluent quality thresholds for the demonstration were: total suspended solids (TSS) less than 100 mg/L; fecal coliform bacteria (FC) less than 200 colony forming units/100 mL; and five-day biochemical oxygen demand (BOD₅) less than 50 mg/L. The prototype membrane bioreactor system using in-tank membranes demonstrated the ability to successfully process shipboard sanitary wastewater and meet stringent effluent quality goals for BOD₅, TSS, and FC. Further, it was able to process shipboard wastewater without the aid of chemicals to mitigate membrane fouling.

Membrane-based systems are also being considered for processing oily wastewaters so their oil content will not exceed 15 mg/l within the contiguous zone. Ultrafiltration membrane modules are being used to separate and concentrate the small amount of oil that remains in the effluent from the parallel plate separators used to treat oily waste on most of the Navy's ships. The results of recent studies of ceramic membranes used to concentrate the effluent from the parallel oil/water separator on USS Carney (DDG 64) showed that the parallel plate separator removed 98% of the oil. The membrane concentration system removed 99% of the oil (240 mg/l to 3.5 mg/l) that remained in the effluent leaving the separator. The 95th percentile was 7.6 mg/l, and the 95th percentile confidence limit was 8.6 mg/l. It is essential that the membranes used to polish the effluent of parallel plate oil/water separators remain impenetrable barriers to oil and continue to permeate water despite exposure to high levels of oil. High oil levels can arise either as a result of progressive or instantaneous upsets, or during operation at high concentration factors. The results of studies to (1) evaluate the response of the membrane to the intrusion of bulk oil from a defective oily/water separator, (2) determine the membrane's response to a simulated valve failure that would allow a gradual increase in the oil content of the recirculating loop, and (3) determine the ability of membranes to operate at concentration factors up to 1,000x, showed that the membranes rejected oil throughout the three studies. The concentration of the oil in the permeate issuing from the membranes in the first two studies never exceeded 5 mg/l. In the first tests, membranes processed oily waste that contained 54% oil and 96% oil before flux ceased abruptly (fail safe). Similarly, flux ceased abruptly in the third test at a concentration factor of 600x. Water flushing restored much of the efficiency of the membranes.

The results of recent studies on USS Arleigh Burke (DDG 51) to determine if sorbents can be used to polish the effluent from parallel plate oil water separators showed that they were not practicable. The sorbents were blinded by minor upsets of the oil water separator and were adversely affected by detergents that are normally found in the bilgewater. Fletcher and Upsher [Fletcher, L.E. and F.J. Upsher, "Hydrocarbon Adsorbents: A Potential Polishing Step to Treat Shipboard Oily-water Waste," Defense Science and Technology Organization Canberra (Australia) Technical Report DSTO-TR-0237, ADA307299 (Jan 1996)] also found that detergents in the bilge of ships has a negative affect on the sorbents they examined. Gallup, Isacoff, and Smith's work discussed earlier showed that sorbents must be protected from high concentrations of oil.

State-of-the-art of Environmentally Preferable Lubricants (EPLs) and functional fluids are being examined to determine shipboard applications that, because of design or function, warrant the use of less toxic, more biodegradable lubricants and functional fluids. Environmentally preferable lubricants and hydraulic fluids typically consist of vegetable oil, polyalkylene glycol, or synthetic ester base stocks and additive packages that have improved biodegradability and toxicity compared to conventional petroleum-based products. EPLs are designed for use in applications where inadvertent leakage or water wash-off of lubricants or fluids may occur, which could adversely affect the environment and wildlife. Industrial interest in the use of EPLs has grown rapidly over the last few years and there are numerous commercial products that meet customer needs for products with improved biodegradability, lower toxicity, and

excellent performance. The approach is to review available literature and manufacturers' product information on EPLs and determine shipboard applications for which their use is warranted. More biodegradable, less toxic lubricants will reduce environmental damage and reduce operational restrictions that can result from spills, incidental release during normal operations, and water wash-off of lubricants overboard. Oily waste disposal costs could also be decreased. Lower toxicity lubricants will also provide safer working conditions for shipboard personnel.

A database has been developed that contains commercial EPL information such as suppliers, performance properties, biodegradability, toxicity, and shipboard applications that may benefit from use of environmentally preferable lubricants or hydraulic fluids that have been identified. Work on potential shipboard EPL applications are already underway. The Naval Sea Systems Command has evaluated a Union Carbide hydraulic fluid (water, diethylene glycol, and polyalkylene glycol formulation) in power hydraulic units for diver tools. NAWCAD Lakehurst is working with ARL (Pennsylvania State University) and Union Carbide to develop a polyalkylene glycol monobutyl ether-based catapult lubricant. NSWCCD is developing an EPL wire lubricant ("Environmentally Preferable Lubricants for U.S. Navy Ships - Progress Report," NSWCCD-TR-63-97/02, June 1997.)

The Navy has four classes of compensated fuel/ballast ships: DD 963, DDG 993, CG 47, and DDG 51. Of these, the DDG 51 class is the newest and the only one in which ships are still being built. These vessels maintain varying amounts of fuel oil and compensating seawater in their fuel tanks. After refueling, the tanks are essentially full of fuel. Seawater is pumped into the tanks to enable the ship to maintain uniform sea keeping characteristics while the fuel is used. This compensating water is discharged overboard while the fuel tanks are filled with fuel. The fuel tank structures and geometries reduce the ships' fuel capacities by inducing seawater hideout, which, in turn, exacerbates the problem of fuel oil in the overboard discharge. The DoD, MARPOL, and the coastal states of the United States have varying (all very high) requirements on the quality of the water discharged. The requirements could limit the operation of compensated fuel/ballast ships by placing severe restrictions on their refueling.

Systems are being developed to ensure that compensated fuel/ballast ships comply with existing and anticipated effluent discharge standards for compensating water, and to increase compensated ships fuel capacity by reducing seawater hideout. The product of this task will ensure that these ships do not pollute while they refuel and will reduce or eliminate seawater hideout. Guidance will be proffered for the design of future compensated ships. Operational changes or simple tank modifications may be developed which could eliminate the need for more expensive treatment systems for ballast water or the elimination of compensated fuel/ballast-ships altogether. Work focuses on the DDG 51 class, because it would be easier to introduce design changes in that class while they are still being built, and data are available from earlier in-port and at-sea fueling tests on DDG-51. These studies use computational fluid dynamics models to simulate refueling, and physical models to validate them. Phase I will evaluate simple changes in tank structure and procedural modifications in refueling operations. Phase II will evaluate the effectiveness of modifications in fuel tank and fuel system design. Finally, Phase III will determine the effectiveness of these and additional design modifications across a tank group.

The Navy's 6.4 Shipboard Waste Management RDT&E Program has a project to demonstrate and validate maturing underwater hull cleaning and effluent treatment technology that will be used to maintain the quality of the coatings on hulls. This technology has transitioned from ONR's 6.2 Research and Exploratory Development and 6.3 Advanced Technology Development RDT&E programs to the demonstration and validation (DEMVAL) phase for final development, testing and evaluation prior to production scale configuration and deployment. The complete system incorporates the use of integrated hull cleaning and effluent treatment technologies that clean the ships underwater hull and capture, contain and treat the effluent generated during the process. It is anticipated that this technology will meet the developing UNDS Marine Pollution Control Device (MPCD) specification for discharges associated with hull cleaning operations under the Underwater Ship Hull Husbandry category. Use of the system will *assist in meeting toxic discharge requirements* and will reduce life cycle hull maintenance costs by

monitoring the status of various underwater hull systems. The vehicle is suitable for all antifouling (AF) paints, and is ideal for *cleaning future nontoxic, fouling release paints*, which may require periodic cleaning. The U.S. Navy needs a new method for underwater cleaning of marine fouling from toxic AF paints to save propulsive fuel, meet mission requirements for ship speed and range, and to reduce refueling at sea. Hull cleaning must be accomplished while reducing the release of cuprous oxide into harbors. The Navy spends \$500M/year in propulsive fuel, of which \$75M-\$100M is lost due to marine fouling on ship hulls. The current cleaning process is already under scrutiny and emerging regulations are preventing the Navy from cleaning copper hull coatings at some locations. The only options available for fouled hulls are underwater cleaning, dry-docking and refurbishment of the hull, or accepting large propulsive fuel losses. The requirement to maintain operational readiness in the face of shrinking budgets makes the latter unacceptable.

The hull-cleaning vehicle project will demonstrate the feasibility of integrating underwater vehicle technology with novel hull cleaning methods, advanced navigation and automated control, image analysis for fouling detection, and hull system sensors to develop an underwater hull maintenance system. The approach is built upon an earlier Applied Research Program that explored various technologies necessary for the vehicle. Those areas included acoustic and cavitating water jet cleaning, underwater image analysis, vehicle command and control, vehicle dynamic modeling, effluent capture and analysis, and sensor enhancement. The automated vehicle will follow preprogrammed trajectory paths along the ship hull using a computer navigation and control system developed by CDNSWC for an earlier vehicle. An underwater imaging system will detect the presence of fouling, and a computer based decision process will activate the vehicle's unique cleaning tool to remove that fouling with *a significant reduction in copper discharge as compared to present methods*. Sensors will provide needed data for vehicle navigation, measurements of both hull and paint thickness, and hull electropotential (a corrosion indicator). The vehicle will be equipped for video and still photography. Specialized sensors, such as those to detect de-bonding of submarine acoustic tiles, and to monitor environmental quality, can also be included. Subsystems that will capture, transport and treat effluent generated while the hull is being cleaned are also be developed and will be demonstrated. The treatment sub-system will be modeled after existing separation and filtering systems being developed by the National Shipbuilding Research Program and will be designed to remove constituents including copper, zinc and fouling debris from the process water.

The Navy Environmental Quality Research, Development, Test, and Evaluation Strategic Plan has identified the replacement of existing copper AF coatings as a high priority. Industry is claiming that reduced copper, self-polishing, antifouling coatings offer advantages over the current generation of copper ablative coatings especially with respect to fouling control, reduced environmental toxicity, and drag minimization. If proven true, this type of performance has the potential to save millions of dollars and meet the Navy's operational requirements while maintaining environmental responsibility.

ONR has a project in its Environmental Requirements Advanced Technology Program to develop advanced, self-polishing, reduced-copper coatings. The objective of the work is to develop a new generation of antifouling, self-polishing coatings that are environmentally sound. The new coatings will be demonstrated to minimize the risk associated with fleet implementation of these materials. The new coatings are to replace the current copper-containing ablative coatings on ships and submarines. Reduced copper antifouling coatings are a near to mid term solution to current increasing environmental pressures, especially as related to copper release from ship hull coatings. Because this technology is not a completely nontoxic system (copper plus booster agents are used together to control fouling), the effort will also address related environmental risks by considering release rate, which includes laboratory and *in-situ* field measurement techniques, to evaluate the actual flux of copper and booster agents into the environment. In addition, technology gaps in the area of environmental toxicity will be identified.

Self-polishing coatings were selected over other technologies as the focus of this effort for several reasons. Completely nontoxic antifouling systems such as silicone easy release coatings are being

developed as an environmentally friendly alternative to copper antifouling coatings. However, they have been demonstrated and transitioned only on a limited basis and do not meet the Navy's long term performance goals. They require further development and validation before these materials are transitioned to the Fleet. Consequently, easy release materials will not provide an effective near to mid term solution to the problem of long-term (5-7 year) fouling-control coating systems. Less technologically advanced approaches to reduce copper inputs take advantage of more traditional AF resin systems that use reduced copper loading in combination with booster agents (for example, microencapsulated agents) formulated for long-term controlled release. Copper release rates of these systems are also lower. However, self-polishing coatings are closer to fleet transition than microencapsulation technology or other reduced copper technologies, and it is expected that they will provide similar if not improved performance over these systems, and possibly even over traditional copper ablative systems. Therefore, it appears that self-polishing antifouling coatings are a logical mid-term solution to the problem.

The Naval Research Laboratory (NRL) has research programs to develop new materials and technologies to remove heavy metals generated during Navy ship and facility operations. One program is using genetic engineering techniques to develop bacterial-based biosorbents by cloning and expressing the gene of a very high affinity binding protein (*Metallothioneins*) into *e. Coli* and using this *e. Coli* as a heavy metal biosorbent. Another program at NRL is investigating the properties of both cyclic and acyclic chelators and their immobilization on solid surfaces in order to develop novel filtration materials specific for heavy metals. They will be used to remove the last traces of heavy metals in waste streams that present technologies cannot. A third program will take the metal-chelators and bind them to solid substrates in packed columns designed for high throughput. Finally, NRL is developing and demonstrating advanced "easy-release" antifouling or fouling-resistant hull coatings that do not depend upon the release of copper and are nontoxic and environmentally benign. Coatings based upon this technology could replace the current method of controlling marine fouling on U.S. Navy hulls, which depend on the use of copper-based ablative coatings. These copper-based paints pollute the marine environment and, when replaced, generate thousands of tons of hazardous materials annually.

Easy release coatings are part of an Environmental Security Technology Certification Program (ESTCP) that demonstrates the effectiveness of a new environmentally safe coating (www.estcp.org/projects/pollutn/199502.htm). ESTCP was established to demonstrate and validate innovative environmental technologies under real world conditions, to address the real most urgent environmental needs of DoD, and to promote the rapid implementation and direct technology insertion of advanced environmental technologies. These technologies provide a return on investment through cost savings and improved efficiency.

The Navy's Environmental Quality Applied Research Program provides transitionable technology that will lead to affordable environmental compliance and pollution prevention ashore and afloat. The specific ship-related objective is to develop and apply emerging technologies to manage all shipboard generated wastes so that ships of the 21st century can travel in any body of water unconstrained by, and in full compliance with, national, international, and local environmental regulations. The following is drawn from the Executive Summary of the FY 1999 Program Plan. It describes tasks that are related to the possible impact of UNDS.

Task EQ-4 Zero Discharge Industrial Wastewater Treatment Plant (IWTP). This task will develop and integrate technologies that will be needed by the Navy's IWTPs of the 21st century so they can comply with the Clean Water Act (CWA) and other regulatory requirements. It will identify and optimize the technical parameters of advanced technologies to remove and recover heavy metals, to

* The Los Alamos National Laboratory is developing water-soluble chelating polymers specially designed to bind selectively with metal ions in aqueous solutions.

mineralize organic compounds, and to polish the effluent so that industrial wastewater can be recycled. NFESC successfully demonstrated the potential of macrocyclic crown ether ligands to sequentially separate heavy metals in industrial wastewater. This ligand adsorptive metal removal system, generically called molecular recognition technology (MRT), was optimized in bench studies and scaled for field demonstration. The MRT operates efficiently with target ion concentrations in the parts per million or parts per billion ranges even in the presence of high concentrations of other species. The advantage of the system is that a much smaller footprint is required compared to ion exchange systems. (However there is a coincidental requirement that the system must be able to systematically elute the captured ions off the column; this may make it unattractive for shipboard systems.) Feasibility tests showed that MRT broke metal-chelated bond in acid/alkali wastewater samples from the NAS, North Island IWTP. The Puget Sound Naval Shipyard IWTP is serving as a full-scale demonstration/validation site in FY 1998-99. In addition to MRT, feasibility studies were completed for an ultrasonic advanced oxidation process (AOP) reactor that could treat Navy wastewaters contaminated with dilute toxic organic compounds. A "proof of concept" study began at NUWC Keyport in FY 98 to destroy anionic and nonionic surfactants found in IWTP wastewaters.

Task EQ-11 Alternative Approach to Copper Discharge Regulations. Copper is a high profile pollutant for the Navy. The EPA has established very low water quality criteria for copper, and many states have similarly low criteria. However, research over the past decade has shown that toxicity is not closely related to the total copper concentration because many forms of copper are bound to organic and inorganic materials in the water, which makes it less available, and therefore less toxic to marine organisms. This task will develop the information necessary to permit a more rational and scientifically valid approach to regulate Navy copper discharges.

Task EQ-12 Nonpolluting Marine Lubricants. Oily wastewater from steam catapults aboard Navy carriers is being discharged into the surrounding water, which causes a visible sheen. Methods to control these discharges have been identified as the number one priority for AIRLANT and AIRPAC type commanders. This task will develop a "drop-in replacement" for existing mineral lubricants that will provide similar performance and comply with environmental requirements. A base fluid was formulated that meets environmental requirements. It is a synthetic material that is a food grade lubricant. The base fluid was made into grease using a lithium complex thickener. Results show that greases that meet environmental and performance criteria could be formulated. This effort complements an effort by NAWCADLKE to develop an environmentally compliant replacement oil that can be used in the steam catapult power cylinders. This task will concentrate on the development of lubricating greases for the other catapult components.

Task EQ-13 Electrochemical Treatment of Non oily Wastewater. The Navy is developing a shipboard non oily wastewater treatment system to meet anticipated US EPA and international discharge requirements. The treatment system will use polymeric ultrafiltration membrane (UF) technology to treat non oily wastewater. However, UF membranes cannot remove enough of the five-day biochemical oxygen demand (BOD₅) to meet anticipated discharge requirements. This task will demonstrate the feasibility of using electrochemical oxidation in conjunction with UF membranes to remove BOD₅ and ensure consistent disinfection to meet anticipated water quality standards. This task demonstrated the feasibility of using electrochemical methods to treat shipboard graywater. Organic material in effluent from a graywater membrane treatment unit was successfully destroyed in a bench-scale electrochemical prototype. Biochemical oxygen demand in the water from the prototype was reduced to below 10 mg/l, there were no fecal coliforms, and residual chlorine was less than 10 mg/l.

Task EQ-14 Bilgewater Treatment with Liquid Carbon Dioxide Extraction. Parallel plate oil/water separators (OWS) that are being installed aboard Navy ships remove more than 90% of the oil in bilgewater. However, the oil concentration in the discharge from the OWS does not always meet the 15-mg/l-discharge requirement. While ultrafiltration membranes have been shown in recent shipboard evaluations to remove oil to less than 10 mg/l, anticipated regulations may require less than 5 mg/l in

restricted zones and harbors. This task will investigate the feasibility of using liquid CO₂ to extract oil from the OWS effluent to reduce its concentration to nearly zero ppm. While liquid CO₂ has been used to remove a variety of organic pollutants from industrial wastewater that includes water-soluble hydrocarbons, detailed design data on the extraction efficiency of liquid CO₂ is not available for emulsified oils and surfactants found in bilgewater. The design data will be obtained experimentally and will be used to design a prototype oil extraction system.

Task EQ-16 Nonfouling Coatings for Ceramic Membranes. Ceramic ultrafiltration membranes are being used in shipboard advanced oily wastewater treatment systems to remove trace amounts of oil and potentially toxic organic constituents from shipboard oil/water separator effluent. Membrane fouling is the most significant problem encountered and is a significant impact to lifecycle costs. This task will develop and test several fouling resistant coatings that can be applied to existing ceramic membranes used in the shipboard OWS. In addition, the University of Colorado has built a computerized, laboratory-scale test platform to test the effectiveness of back pulsing to control fouling on dense pack ceramic membranes. Initial tests were in batch mode at flow rate of approximately 20 L/min and a forward pressure of 25 psi. The permeate's oil content was between 1.0 and 2.5 mg/l, as compared to 250 mg/l in the feed. The highest permeate flux of over 50 gal/ft²-day, which was 80% of the clean membrane flux, was achieved with forward-filtration/back-pulse time ratio of 5:1.

Task EQ-17 Submarine Oil Pollution Control. This task investigated the feasibility of using water-based hydraulics for submarine external hydraulic systems. Findings and recommendations are included in an initiation decision report (IDR). Water-based hydraulics would reduce the environmental risks associated with oily discharges. Although water-based hydraulics would be feasible and beneficial, this task was discontinued under the Environmental Applied Research Program in favor of support from other sponsors because of other benefits that water-based hydraulics would offer over and above the environmental benefit.

Task EQ-19 Submarine Heat Exchanger Fouling Control. This task is attempting to apply pulsed power acoustics technology to systematically remove incipient fouling in submarine seawater heat exchangers. Marine fouling of mission-critical heat exchangers is a chronic problem for Navy submarines. Cleaning fouled heat exchangers is costly and significantly degrades overall ship availability. The approach to control biofouling is through aqueous chlorine; however, the discharge of chlorinated seawater from cooling systems may violate environmental discharge regulations. Dechlorinating systems would have to be designed, fabricated, and implemented to continue the use of chlorine.

The Defense Advanced Research Projects Agency (DARPA) and the Office of Naval Research (ONR) are sponsoring a joint effort to develop and demonstrate the shipboard feasibility of using hydrothermal oxidation (supercritical water oxidation) to treat concentrated black water, graywater, and hazardous organic liquids. The major technical challenges are corrosion due to the supercritical media and plugging due to the accumulation of salts and solids. This work will demonstrate acceptable treatment, configuration, and packaging under warship requirements and constraints. Two different HTO units (General Atomics and Foster Wheeler) have been fabricated and are undergoing extensive shoreside evaluations that began in November 1997. The evaluation has been designed to address Navy concerns about performance, operation, safety, reliability, and maintainability. The units will be delivered to the Navy for further testing when the evaluations at the contractors' facilities are completed. [Soto, M. and A. Lardis, "Hydrothermal Oxidation (HTO) for the Destruction of Shipboard Wastes," in *Proceedings of the International Conference on Incineration and Thermal Treatment Technologies*, Salt Lake City, UT, pp. 753-755 (1998) and; Morris, V.L. and M. Soto, "Hydrothermal Oxidation (HTO): A Systems Engineering Approach to Technology Validation," presented at *The International Conference on Incineration and Thermal Treatment Technologies*, Orlando FL, (May 1999)].

Finally, the Naval Surface Warfare Center Carderock Division is using the *Commerce Business Daily* to seek sources to provide technologies, procedures, concepts, alternative materials, or devices to replace, minimize, process, or otherwise control the pollutants in each of the twenty-five incidental liquid waste streams generated by Armed Forces vessels. An on-line search of *The Daily Journal of Commerce* on June 25, 1999 using a query string of "UNDS" listed twelve of the requests for sources.

ADVANCED PHOTOCHEMICAL OXIDATION PROCESSES

Many waste streams that must be treated are aqueous with organic constituents and may be suited to photochemical processing techniques. The advantage of a photochemical approach is that no chemicals are added that produce a secondary waste that may require extensive treatment. However, much of the photochemical equipment is effective on very dilute (parts per million) clear aqueous solutions and its efficiency is based upon the destruction of the original contaminate. Total oxidation would require all hydrogen and carbon to be converted to carbon dioxide and water if any process is to be competitive with incineration.

Gray, et al., [Gray, L.W., et al, "Aqueous Phase Oxidation Techniques as An Alternative To Incineration," *Proceedings of the International Incinerator Conference*, Albuquerque, NM, May 11-15, 1992, pp. 157-164] described three aqueous phase techniques that were being developed at the Lawrence Livermore National Laboratory (LLNL) to oxidize low concentrations (<5%) materials in waste water streams. They were 1) direct electrochemical oxidation; 2) mediated electrochemical oxidation using regenerable, strongly oxidizing cations such as Ag (II), Co (III), and Ce (IV) that can either attack oxidizable materials directly and/or indirectly by first reacting with water to generate the OH radical, which then attacks the oxidizable materials; and 3) using H₂O₂ and UV to generate OH radicals directly which in turn attack the oxidizable materials. The best results in studies of the mediated electrochemical oxidation of Trimsol (total destruction) were obtained with an electrolyte of AgNO₃ and HNO₃ at 70°C and at a current near the mass transport limit. However, the chloride liberated by the destruction of Trimsol precipitated as AgCl. (This system would find no place on a ship because of the pervasive presence of chloride in the feed.)

Dhooge [Dhooge, P.M., "Report on Study of Oxidation Reaction Rates," Los Alamos National Laboratory Subcontract Report No. 9-XT1-V6607-1, June 10, 1991] presented reaction rate data on the Delphi Research process which uses the reduction of Fe (III) to Fe (II). Results showed reaction rate constants in the range of 10⁻⁷ to 10⁻⁴ sec⁻¹, depending on the cocatalyst, type of anions, type of organic, and the ratio of Fe (III) to Fe (II). The chloride anion was found to reduce significantly the reaction rate constant for many of the organics. The authors found this to be surprising because chloride ions increase the redox potential of the Fe (III)/Fe (II) couple, and thus might be expected to increase the reaction rate constant. They expected much greater amounts of iron to be maintained in the solution. Later, Dhooge [Dhooge, P.M., "Continued Investigations of The DETOX Wet Oxidation Process for Mixed Waste Volume Reduction/Recycling," *Proceedings of the International Incinerator Conference*, Albuquerque, NM, May 11-15, 1992, pp. 779-781.] reported that while preliminary studies had shown that low to moderate concentrations of chloride had led to greatly reduced reaction rate constants, subsequent studies showed that the reaction rate constants for organics oxidation in chloride-containing solutions cease decreasing at chloride concentrations above 10 molar, and begin increasing at chloride concentrations of 20 molar or greater. The increase in reaction rate constants combined to give 10 to 100 times greater total amount of reaction than can be achieved in sulfate solutions. Moderate to high concentrations of phosphate anion severely decreased oxidation reaction rate constants. The results demonstrated that 99.99+% of the organics were destroyed by the oxidation solution. Delphi Research's DETOXSM Catalyzed Wet Oxidation System is included among other technologies in the EPA VISITT Data Base (now REACHIT).

Strong absorption of short wavelength UV by water will reduce penetration of light to a negligible value; so just as glass used for windows imposes a lower wavelength of about 190 nm, water imposes a wavelength of 185 nm. At longer wavelengths, hydrogen peroxide, ozone, and many organic compounds can be excited. At about 200 nm, ozone can be dissociated to give O_2 and O which is an extremely powerful oxidizer. However, the application of ozone to streams with reasonably high concentrations of organics is not particularly practical because of its poor solubility, 70 ppm at 20°C and at 1 atmosphere. The use of the more favored hydrogen peroxide – it was capable of destroying a variety of organic compounds when dissolved in aqueous solutions at concentrations up to 1 weight percent – engenders logistics problems because unlike ozone, it is not practicable to generate it in-situ.

APO Technologies

This section draws heavily from the EPA's Handbook on *Advanced Photochemical Processes*, EPA report EPA/625R-98/004, December 1998, and quotes directly from its Executive Summary. The handbook discusses the applicability of advanced photochemical oxidation (APO) technologies for treatment of contaminated water, air, and solids (soil, sediment, and ash). APO has been shown to be an effective technology for treatment of contaminated water. These processes generally involve generation and use of powerful but relatively nonselective transient oxidizing species, primarily the hydroxyl radical ($\cdot OH$) and in some cases the singlet oxygen. The $\cdot OH$ can be generated by both photochemical and nonphotochemical means to oxidize environmental contaminants. The primary purpose of the handbook is to summarize commercial-scale APO system performance and cost data for treatment of contaminated water, air, and solids. It presents similar information drawn from pilot-scale and bench-scale evaluations of APO technologies as a supplement to the commercial-scale data. Pilot-scale results are presented in greater detail than bench-scale results. In addition, pilot- and bench-scale results are presented only where they supplement commercial-scale APO system evaluation results or where they fill information gaps, such as those associated with byproduct formation.

APO technologies can be divided into the following groups: (1) vacuum ultraviolet (VUV) photolysis, (2) ultraviolet (UV)/oxidation processes, (3) the photo-Fenton process, and (4) sensitized APO processes. These technologies and their variations are briefly described below.

VUV Photolysis

Photolysis of water using UV radiation of a wavelength shorter than 190 nanometers yields OH and hydrogen radicals ($H\cdot$). A contaminant can be degraded in water or in moist air through oxidation by $\cdot OH$ or reduction by $H\cdot$. Commercial-scale VUV photolysis systems are not currently available. However, bench-scale study results indicate that VUV photolysis is effective in treating contaminated water and humid air streams.

UV/Oxidation Processes

UV/oxidation processes generally involve generation of $\cdot OH$ through UV photolysis of conventional oxidants, including hydrogen peroxide (H_2O_2) and ozone (O_3). Both UV/ H_2O_2 and UV/ O_3 processes are commercially available. Some APO technology vendors also offer variations of these processes (for example, UV/ O_3/H_2O_2 and UV/ H_2O_2 proprietary catalyst). The commercial-scale UV/oxidation systems available for contaminated water treatment include the 1) Calgon Carbon Corporation (Calgon) peroxpure™ and Rayox® UV/ H_2O_2 systems; 2) Magnum Water Technology, Inc. (Magnum), CAV-OX® UV/ H_2O_2 systems; 3) WEDECO UV-Verfahrenstechnik (WEDECO) UV/ H_2O_2 and UV/ O_3 systems; and 4) U.S. Filter/Zimpro, Inc. (U.S. Filter), UV/ O_3/H_2O_2 system. The only commercial-scale UV/oxidation system available for contaminated air treatment is the Process Technologies, Inc. (PTI) UV/ O_3 system. UV/oxidation treatment systems for contaminated solids generally treat contaminated slurry or leachate generated using an extraction process such as soil washing.

Photo-Fenton Process

Decomposition of H_2O_2 using ferrous iron (Fe (II)) or ferric iron (Fe (III)) under acidic conditions yields $\cdot\text{OH}$. The rate of removal of organic pollutants and the extent of mineralization using the Fe (II)/ H_2O_2 and Fe (III)/ H_2O_2 reagents are improved considerably by irradiation with near-UV radiation and visible light. This process is called the photo-Fenton reaction. The only commercial-scale photo-Fenton system available is the Calgon Rayox[®] ENOX water treatment system.

Sensitized APO Processes

These APO processes can be broadly categorized as dye-sensitized and semiconductor-sensitized processes.

- In a dye-sensitized APO process, visible light is absorbed by a sensitizing dye, which excites the dye molecules to a higher energy state. The excited dye then transfers some of its excess energy to other molecules present in the waste stream, producing a chemical reaction. When dissolved oxygen accepts energy from the excited dye molecule (for example, methylene blue or rose bengal), the dissolved oxygen is converted to singlet oxygen, a powerful oxidant. The process has not yet become commercially viable.
- In a semiconductor-sensitized APO process, metal semiconductors are used to destroy environmental contaminants by means of light-induced redox reactions. These reactions involve generation of conduction band electrons and valence band holes by UV irradiation of semiconductor materials such as titanium dioxide (TiO_2). In this process, the formation and availability of $\cdot\text{OH}$ is maximized by addition of oxidants such as H_2O_2 and O_3 .

The Matrix UV/ TiO_2 system is a commercial-scale sensitized APO system for contaminated water treatment. The commercial-scale sensitized APO systems for contaminated air treatment include the (1) Zentox Corporation (Zentox) UV/ TiO_2 system; (2) Matrix Photocatalytic, Inc. (Matrix) UV/ TiO_2 system; and (3) KSE, Inc. (KSE) Adsorption-Integrated-Reaction (AIR) UV/catalyst system. EPA Report EPA/540/R-97/503 (May 1997) is an Innovative Technology Report on the Matrix Photochemical Oxidation Technology.

PERTINENT SUPERFUND INNOVATIVE TECHNOLOGY EVALUATION PROGRAMS

The Environmental Protection Agency's Superfund Innovative Technology Evaluation (SITE) Program evaluates new and promising treatment technologies for the cleanup of hazardous waste sites. It was established to encourage the development and routine use of innovative treatment technologies. It assesses but does not approve or endorse technologies. "Superfund Innovative Technology Evaluation Program—Technology Profiles Ninth Edition," EPA/540/R-97/502, December 1996 lists some technologies that may be applied to shipboard incidental liquid wastes. They are discussed below. Appendix A to this report is a more complete list that was taken directly from the ninth edition. Current SITE information and data can be downloaded from <http://www.epa.gov/ORD/SITE>. This source is updated periodically and one can download the technical information about each program together with the related EPA reports. EPA Report EPA/540R-95/522 of July 1995, "The Superfund Technology Evaluation Program, Annual Report to Congress," FY 1994, stated that technologies for on-site aqueous treatment are of low priority for SITE and that some of the more important breakthroughs are anticipated in *chemical conversion technologies*. Technologies that rely on chemical conversion rather than destruction will end the remediation process *at treatment*. EPA Report EPA-542-R-95-008 of September 1995, "EPA Innovative Treatment Technologies: Annual Status Report," Seventh Edition, analyzes the selection and use of innovative treatment technologies in the EPA Superfund Program, technologies at some non-Superfund sites subject to corrective action under the RCRA Program, and those addressed by DoD and DOE.

The SITE Emerging Technology Program provides an opportunity to perform research and to develop technologies at the bench and pilot scales. The goal is to promote and support the development of alternate technologies for field applications at Superfund sites. The SITE Demonstration Program develops reliable engineering, performance, and cost data on innovative, alternative technologies so that the potential user can evaluate a technology's application for a specific waste site. Demonstrations are carried out at hazardous waste sites such as National Priorities List (NPL) sites, and state sites under conditions that simulate actual hazardous wastes.

Some of these technologies are included in the EPA's "The Remediation and Characterization Innovative Technologies" system (REACHIT) and in EPA report 542/B/-94/013 of October 1995, "Remediation Technologies Screening Matrix and Reference Guide" prepared by the DoD Environmental Technology Transfer Committee. REACHIT is a searchable internet-based (i.e., no downloading) source of information on the availability, performance, and application of remediation and characterization technologies. It combines information from the downloadable remediation and characterization Vendor Information System for Innovative Treatment Technologies (VISITT) and Vendor FACTS, and EPA's Innovative Treatment Technology databases. Its URL address is <http://www.epareachit.org>.

The Institute of Gas Technology's (IGT) Two-Stage Fluidized-Bed Cyclone Agglomerating Combustor is designed to destroy solid, liquid, and gaseous waste. The two-stage combustor can destroy organic contaminants in gaseous, liquid, and solid wastes that includes soils and sludges. The solids particle size must be less than 6 mm to support fluidized-bed operation; therefore wastes must be pulverized before they are processed by the system. Solid, nonvolatile, inorganic contaminants are combined within a glassy matrix consisting of discrete pebble-sized agglomerates. The first stage of the combustor is an agglomerating fluidized-bed reactor that can operate under substoichiometric conditions or with excess air. The system can also gasify materials with high caloric values such as municipal waste. Most of the fluidized-bed is maintained at 1500 to 2000°F, while the central spout temperature can be varied between 2000 and 3000°F. The combustible portion of the waste is rapidly gassified and combusted. The solid fraction containing inorganic and metallic components is agglomerated in the hot zone. Product gas from the fluidized bed is fed to a second stage of the combustor where it is further combusted at 1800 to 2400°F. The second stage is a cyclone combustor and separator that provides sufficient residence time to oxidize CO and organic compounds to CO₂ and water. This stage has a combined destruction efficiency greater than 99.99%.

ZenoGem™ Wastewater Treatment Process, ZENON Environmental Systems, removes organic compounds from wastewater by integrating aerobic biological treatment, maintained by diffused aeration, and membrane-based ultrafiltration. The system combines biological treatment to remove biodegradable organic compounds with ultrafiltration to separate residual suspended solids from biologically treated effluent. EPA report EPA/540/MR-954/503, dated March 1995, presented the results of a demonstration of the process at a Superfund site in New Jersey. The groundwater at this site was contaminated with methyl methacrylate (MMA) and volatile organic compounds. The system achieved average removal efficiencies >99% for MMA and 89% for the COD. Zenon reduced the flow rate and was able to achieve an average removal rate of 98 % when a carbon filter was used to polish the effluent.

The Ultrox, A Division of Zimpro Environmental, Inc., Ultraviolet Radiation and Oxidation Process uses ultraviolet (UV) radiation, ozone, and hydrogen peroxide to destroy organic compounds in water. The process oxidizes compounds that are toxic or refractory to parts per million or parts per billion levels. Tank size and approximate UV intensity and oxidant doses are determined by pilot scale studies. Off-gases from the treatment tank passes through an ozone destruction unit. This unit also destroys volatile organic compounds that have been stripped off in the treatment tank. A field demonstration was completed in 1989. The test was designed to evaluate system performance for several combinations of pH, retention time, ozone dose, hydrogen peroxide dose, and UV intensity. The technical report, EPA/540/5-89/012, was published in January 1990. The Applications Analysis Report presents the results from seven case studies. While the technology was able to reduce the organics in the wastewater

to applicable discharge levels, pretreatment was required where the wastewater contained high levels of iron, manganese, oil and grease, and suspended solids. At one facility, the effluent met discharge standards when the influent contained oil and grease at the 3% level. The technology is fully commercial.

The Matrix Photocatalytic, Inc. photocatalytic oxidation system removes and destroys dissolved organic contaminants from water in a continuous flow process at ambient temperatures. When excited by light, titanium dioxide (TiO_2) semiconductor catalyst generates hydroxyl radicals that oxidatively break the carbon bonds of organic compounds. The catalyst also generates electron holes, which are powerful reducing species. Given sufficient time, the organics are broken down to carbon dioxide, water and, if halogenated organics were present, acids. Typically, efficient destruction occurs between 30 seconds and 2 minutes actual exposure time. The Matrix system was originally designed to destroy organics in drinking and plant process water. The Matrix system was accepted into the SITE Emerging Technology Program in May 1991. A demonstration site at DOE's Oak Ridge complex has been established. The Matrix system has treated effluents, such as solvents and alcohols with concentrations as high as 30,000 ppm (3 per cent), and has achieved effluent qualities as low as 5 parts per trillion. Modular systems have been developed for high flow rates with capacity increments of 5 gallons per minute. Two peer-reviewed journal articles are available, PB93-222883 and PB93-130184. EPA report EPA/540/R-97/503 (May 1997), which is an Innovative Technology Report on the Matrix Photochemical Oxidation Technology, is also available.

Pulse Sciences, Inc. X-Ray Treatment of Aqueous Solutions is based on the in-depth deposition of ionizing radiation. X-rays collide with matter, generating a shower of lower energy secondary electrons within the contaminated waste material. The secondary electrons ionize and excite the atomic electrons, break up the complex contaminant molecules, and form radicals. The radical react with the organic material to form nontoxic byproducts such as water, carbon dioxide, and oxygen. This is similar to electron beam processing, an effective method to destroy contaminants in aqueous solutions. However, the X-rays effective penetration is much deeper than that of the electron of the same energy level and allows the treatment of thicker waste volumes. This technology was accepted into the SITE Emerging Technology Program in 1992 and demonstrated in 1994. Contamination concentrations of 200 to 10,000 parts per billion (ppb) were reduced to less than 0.1 to 1 ppb by X-ray doses of 5 to 70 kilorads for contaminants that react well with the hydroxyl radical. Contaminants that do not react well with the hydroxyl radical required doses from 100 to 200 kilorads to destroy initial concentrations of 180 to 2,000 ppb.

Wheelabrator Clean Air Systems, Inc. (formerly Chemical Waste Management, Inc.) PO*WW*ER™ Technology reduces the volume of aqueous wastes and catalytically oxidizes the volatile components. It is used to treat and reduce complex industrial and hazardous waste waters containing mixtures of inorganic salts, volatile and nonvolatile organics, volatile inorganics, and radionuclides. The technology combines evaporation with catalytic oxidation to concentrate and destroy contaminants, producing a high-quality product condensate. Wastewater is first pumped into an evaporator where most of the water is removed and contaminants are volatilized and removed. The residue is concentrated (about 30:1) into a small volume. The vapors are passed over a catalyst and oxidized. The vapors are condensed to produce water, if required. The technology was accepted into the SITE Demonstration in 1991. The EPA has the following reports available: the Application Analysis Report (EPA/540/AR-93/505), the Technology Evaluation Report (EPA/540/R93/506, September 1993) and the Technology Demonstration Summary (EPA/540/SR-93-506, September 1994), and the Technology Evaluation Technical Report (PB94-160637, June 1992).

Energy and Environmental Engineering, Inc. PhotoCAT™ Process photochemically oxidizes organic compounds in wastewater using a chemical oxidant, ultraviolet (UV) radiation and a photocatalyst. The photochemical reaction reduces saturated concentrations of organics in wastewater to "nondetectable" levels. The process can be used as a final treatment step to reduce the organic concentration in industrial wastewater. The existing bench-scale system treats solutions containing up to

several parts per million of total organic carbon at the rate of 3 gallons per minute. Typically the contaminated water is pumped through a filter to remove particles. Next, the filtrate is mixed with hydrogen peroxide and fed to the photochemical reactor and irradiated. Reaction products are carbon dioxide, water, and the appropriate acid if halogenated organics are present in the wastewater. Destruction efficiencies of three orders of magnitude were demonstrated on simulated textile dying operations. Two orders of magnitude were observed in the destruction of chlorobenzene, chlorophenol, and phenol. UV Technologies was formed to commercialize the technology. EPA report, EPA/540/SR/92/080 discusses the work. Subsequent work is underway under EPA Small Business Industry Research.

High Voltage Environmental Applications, Inc. High-Energy Electron Beam Irradiation treats a variety of organic compounds including petroleum residues. Irradiation of aqueous solutions with high-energy electrons results in the formation of the aqueous electron, hydrogen radical ($H\bullet$), and the hydroxyl radical ($OH\bullet$). These reactive transient species initiate chemical reactions that destroy organic compound in aqueous solutions, oxidizing them to carbon dioxide, water, and salt. An aqueous solution is directed over a weir where it falls in a thin sheet. At the other end of the system is a 1.5-million volt insulated core transformer (ICT) electron accelerator that generates electrons and accelerates them to "about 97% of the speed of light" typically stated as $\beta = v/c = 0.97$. The electrons are propelled in a concentrated beam toward the aqueous solution where the reaction occurs. Studies were carried out at 120 gpm. The process can treat complex mixtures in drinking water and wastewater containing up to 5% solids. Initial studies showed that the process removes greater than 99% of trichloroethane, tetrachloroethane, chloroform, benzene, toluene, and phenol in aqueous streams. The technology was accepted into the SITE Emerging Technology Program in 1993. EPA Emerging Technology Bulletin EPA/540/F-92/009, dated October 1992, and EPA Innovative Technology Evaluation Report EPA/540/R-96/504, dated August 1997, describe the process and presents the results of an evaluation.

The General Environmental Corporation's CURE Electrocoagulation Wastewater Treatment System was developed to remove suspended materials and an extremely broad range of dissolved metals, that can form precipitates (lead, nickel, copper, zinc), from water. It does not remove soluble organic compounds. The wastewater passes through coagulation tubes where the contaminants coagulate with the metal and metal hydroxide cations generated by the process. It is described in report EPA 542-N-96-002, Issue No. 23 (June 1996).

The Membran Corporation's Membrane Gas Transfer Device is based upon fluidized hollow fiber membrane technology that dissolves high concentrations of oxygen, methane, or hydrogen by exploiting the high gas permeabilities of hollow-fiber microporous membranes. Membrane technology can dissolve gases without bubbles, which eliminates many of the problems associated with conventional gas transfer devices. The ability to supply oxygen to an aerobic reactor without bubbles improves the process and eliminates emissions and the need for air pollution equipment. The technology was accepted into the SITE Emerging Technology Program in 1994.

PERTINENT PROJECTS WITHIN THE STRATEGIC ENVIRONMENTAL RESEARCH AND DEVELOPMENT PROGRAMS

Congress established the Strategic Environmental Research and Development Program (SERDP) to address environmental matters of concern to the Department of Defense and the Department of Energy. It identifies research, technology, and other information developed by DoD and DOE that could be useful to others who develop energy and environmental technologies. SERDP furnishes other governmental organizations with pertinent data, and it identifies technologies within the private sector that could be useful to DoD and DOE for environmentally related defense activities. It is a Department of Defense program; planned, managed, and executed in full partnership with DOE and the Environmental Protection Agency. It seeks to identify, demonstrate and transition technology from six areas: cleanup, compliance,

conservation, pollution prevention, energy conservation/renewable resources, and global environmental change.

There are several research projects within SERDP related to the targeted waste streams. Some of them were summarized in SERDP's FY 1998 Annual Report to Congress and the SERDP Scientific Advisory Board's (SAB) FY 1998 Annual Report to Congress. SERDP's annual reports to Congress summarize its activities, the most significant accomplishments during that fiscal year, its plans for the following year, and new initiatives that will be undertaken during the following fiscal year. The Appendix to SERDP's FY 1998 report presents one to two page project summaries for most of its projects in each of the four thrust areas. The SAB's report provides critiques and recommendations related to projects, programs, and information exchange. Both of these reports and a list of FY 1998 and 1999 new starts, ongoing programs, completed programs are available at the SERDP web site. The URL is www.serdp.com. The list below was drawn from those sources. Appendix B contains copies of some of the project summaries listed in the Annual Report together with summaries procured from the SERDP archives.

New Starts

- CP-1136 Purification of Oily Wastewaters by a One-Step Advanced Biodegradation Process that Produces No Secondary Wastestream
- CP-1132 Thermally Actively Controlled Sludge Treatment

Ongoing

- CP-1107 Electrochemical Advanced Oxidation Process for Shipboard Final Purification of Filtered Black Water, Graywater and Bilge Water
- CP-1108 Novel Nonporous-Fouling Resistant Composite Nanofiltration Membranes and Membrane Separation Systems in Wastewater Treatment
- PP-1111 Environmentally Advantaged Substitutes for Ethylene Glycol for Aircraft Ice Control
- PP-1112 Recycle and Reuse of Industrial Rags Using Liquid CO₂ and Surfactant Additives as a Cleaning Agent

Completed

- CP-29 Shipboard Non-Oily Wastewater Treatment System
- CP-34 Compact Closed Loop Waste Incinerator
- CP-35 Supercritical Water Oxidation of Organic Wastes
- CP-364 Kinetics of Supercritical Water Oxidation
- PP-756 Fluorinated Ship-Hull Coatings for Non-Polluting Fouling Control
- CP-887 Demonstration of Compact Closed Loop Controlled Waste Incineration
- CP-180 Hydrothermal Reduction of Energetic Wastes
- CU-387 Removal and Encapsulation of Heavy Metals in Groundwater
- CU-1084 Selective Removal of Heavy Metals from Aqueous Wastes Electrosorption on Functionalized Carbo Aerogels

RELATED PROGRAMS SPONSORED BY THE ENVIRONMENTAL PROTECTION AGENCY'S OFFICE OF RESEARCH AND DEVELOPMENT

The EPA's Office of Research and Development (ORD) focuses on the advancement of peer-reviewed scientific research and implementation of cost-effective common sense technology. ORD provides data and technical support to solve current problems and build a science knowledge base to manage ecological resources, understand how pollutants affect health, and prevent or reduce future environmental risks [*Waste Research Strategy*, EPA /600/R-98/154, dated February 1999]. Fundamental to ORD's mission is a partnership with the academic and scientific community through extramural research grants and fellowships. The National Center for Environmental Research and Quality Assurance (NCERQA) maintains a searchable and downloadable website that provides brief descriptions of each of their programs. This site and the "Search Option" at EPA's internet site provided most of the information in Appendix C. The National Risk Management Research Laboratory has developed an on-line, searchable version of the Treatability Database on the effectiveness of proven treatment technologies in the removal/destruction of chemicals in various types of media, including water, wastewater, soil, debris, sludge and sediment. That database was used to develop Table 2 of this report.

RELATED PROGRAMS SPONSORED BY THE DEPARTMENT OF ENERGY'S OFFICE OF SCIENCE AND ENVIRONMENTAL MANAGEMENT OFFICE OF SCIENCE AND TECHNOLOGY

The Office of Science and Technology (OST) that is within the DOE's Office of Environmental Management develops new technologies that could accelerate cleanup, reduce costs, reduce risks to clean up workers, or enable cleanup activities for which no cost-effective technologies exist. OST is organized into five focus areas for specific remediation activities and a lead national laboratory is assigned to each of them. Although OST is responsible for technology development, DOE's waste sites are responsible for selecting the technologies they will use. DOE's selection is subject to review and approval by the EPA and the state agencies that regulate DOE's cleanups. Technology selections are made with input from the public involved with the site.

Appendix D contains briefs of selected research programs. They were drawn from the DOE web site and from a compact disk, "Environmental Management Science Program," 1998 Project Summaries, July 1998, graciously supplied by Mark Gilbertson, Director DOE EM-52. All published Innovative Technology Summary Reports are available on the OST Web site under "Publications."

DOE's FY 1998 Report on the Mixed Waste Focus Area features progress on two alternate organic oxidation technologies. Direct Chemical Treatment uses peroxydisulfate to chemically oxidize organic contaminants that are dispersed in soil or water. Targeted contaminants include detergents, solvents, and water-insoluble oils and greases. A 15-kg/day pilot plant successfully treated PCB wastes at the Hanford Reservation. Catalytic Chemical Oxidation uses catalysts and high temperatures to decompose organic chemicals. The process can accommodate both organic and aqueous mixtures and achieve 99.999% efficiency. Lawrence Berkley National Laboratory performed treatability studies and identified it as a viable technology in terms of ease of use, availability, cost, and chemical applicability.

The Energy Environmental Research Center at the University of North Dakota has entered into cooperative program with the DOE Morgantown Energy Technology Center to develop, demonstrate, and commercialize environmental technologies to clean up contamination at nuclear weapons facilities. One of the activities involves the use of Centrifugal Membrane Filtration (SpinTech) to remove heavy metals from large volumes of water. SpinTech Membrane Systems, Inc. has developed a uniquely configured centrifugal membrane process to produce a clean, filtered waste stream and a low volume concentrate stream.

EPA's BEST DEMONSTRATED AVAILABLE TECHNOLOGIES FOR WASTEWATERS SIMILAR TO THOSE GENERATED BY NAVY SHIPS

The U.S. Environmental Protection Agency proposed technology-based limits for the discharge of pollutants into *navigable* waters of the United States and into publicly-owned treatment works (POTW) by existing and new facilities that are engaged in the treatment of industrial waste from off-site facilities. The new and existing facilities that treat off-site wastes before the wastes are discharged into a POTW are called centralized waste treatment facilities. The agency periodically revises the best demonstrated available technology (BDAT) treatment standards for constituents regulated in hazardous wastewater. These hazardous wastes are defined in Title 40, Code of Federal Regulations (40 CFR), Section 261-31. EPA prefers to use appropriate wastewater treatment performance data from well-designed and well-operated wastewater treatment units to develop wastewater treatment standards whenever possible because they represent the performance of *actual* treatment technologies. [If the individual concentrations of all the regulated constituents (organics, inorganics, metals) in a waste, as generated, are lower than or equal to their respective concentration-based treatment standards, then treatment of that waste is not required before it is disposed on land.] *Wastewaters* are defined as wastes containing less than 1% (weight basis) total suspended solids (TSS) and less than 1% (weight basis) total organic carbon. Liquid wastes not meeting this definition are classified as *nonwastewaters* and must comply with nonwastewater treatment standards. Most of the incidental *wastewaters* generated aboard ships meet the EPA definition of wastewater.

EPA's proposed *technology-based limits* were contained EPA 821-R-95-006, "*Development Document For Proposed Effluent Limitations Guidelines and Standards For the Centralized Waste Treatment Industry*," January 1995; and recently, a follow-up to this document, EPA 821-R-020, December 1998. These limits apply to centralized waste treatment facilities that collect wastes from offsite waste suppliers. The EPA places these centralized treatment facilities into categories or subcategories that depend on the type of waste they treat. For example, centralized facilities that treat oily wastes would be placed in the Oily Waste Subcategory.

Different pollutant parameters are used to characterize raw wastewater and wastewater discharged by Centralized Waste Treatment facilities. These include:

- Total Suspended Solids (TSS)
- Biochemical Oxygen Demand (BOD₅)
- pH
- Oil and Grease

A summary of the raw wastewater pollution parameter levels is presented in the Table 3. It was adapted from the table on page 4-8 of EPA 821-R-95-006.

Table 3. Influent Concentration Ranges for Selected Pollutant Parameters

Pollutant Parameter	Influent Concentration Range (mg/l)					
	Metals Subcategory		Oils Subcategory		Organics Subcategory	
	Min	Max	Min	Max	Min	Max
TSS	86	152,767	190	22,258	44	3,700
BOD ₅	4	30,000	4,520	10,067	4,100	48,675
Oil & Grease	3	5,995	492	180,000	16	626

Total solids in wastewater are the residue remaining upon evaporation at just above the boiling point. Total suspended solids (TSS) is the portion of the total solids that can be filtered out of the solution using a 1-micron filter. Raw wastewater TSS content is a function of the type and form of waste accepted for treatment. (Typically, the higher the TSS content the more concentrated the waste stream.) TSS can also be a function of a number of other external factors, including stormwater runoff and runoff from working or storage areas. The total solids are composed of matter that is settleable, in suspension, or in solution and can be organic, inorganics, or a mixture of both. Settleable portions of the suspended solids can be removed in a variety of ways, such as during the metal precipitation process or by multimedia filtration, depending on a facility's operation. BOD₅ is one of the most important gauges of pollution potential of a wastewater and varies with the amount of biodegradable matter that can be assimilated by biological organisms under aerobic conditions. The nature of chemicals discharged into wastewater affects the BOD₅ due to the differences in susceptibility of different molecular structures to microbiological degradation. Compounds with lower susceptibility to decomposition by microorganisms tend to exhibit lower BOD₅ values, even though the total organic loading may be much higher than compounds exhibiting substantially higher BOD₅ values. Oil and grease in raw wastewater is an important parameter in Centralized Waste Treatment Industry wastewater, especially for the Oils Subcategory. Oil and Grease can interfere with the operation of wastewater treatment plants and, if not removed prior to discharge, can interfere with biological life streams and/or create films along surface waters.

The predominant priority and nonconventional pollutants detected in waste streams treated by centralized waste treatment facilities were metals. Metals were detected in all samples collected. Table 4 is a summary of the metal pollutants in raw wastewater by subcategory. It was drawn from page 4-10 of EPA 821-R-95-006 and includes only those metals related to this study.

Table 4. Range of Metal Pollutant Influent Concentrations (mg/l)

Pollutant	Metals Subcategory		Oils Subcategory		Organics Subcategory	
	Minimum	Maximum	Minimum	Maximum	Minimum	Maximum
Aluminum	2.867	2,090	1.200	192.58	1,498	157.94
Antimony	0.015	1,160	0.027	0.242	0.066	1,540
Cadmium	0.019	307	0.038	0.498	0.009	0.049
Chromium Hexavalent	0.011	40,000				
Chromium - Total	0.102	16,300	0.363	7.178	0.063	1.265
Copper	0.199	21,000	1.200	80.482	0.224	2.690
Iron	4.450	3,745	43.60	567.69	2.360	88.828
Lead	0.208	4,390	0.607	21.725	0.094	0.687
Magnesium	3.210	1,360	22.40	247.12	6.310	23.800
Mercury	0.001	3.100	0.5	0.007	0.001	0.007
Nickel	0.581	1,700	0.313	62.824	0.069	2.610
Phosphorus	5.931	456				15.900
Silver	0.076	6.060	0.033	7.740		
Sulfur	708.55	24,100			972	1,990
Tin	0.145	15,100	0.592	6.216	0.200	2.530
Vanadium	0.086	264				
Zinc	0.600	7,735	10.349	94.543	0.516	2.352

The material in this section *draws heavily from both EPA centralized waste treatment documents because the wastewaters contain components at concentrations similar to the incidental wastewaters generated on Navy ships.* Some technologies used to mitigate the pollutants in the Centralized Waste Treatment Industry could be used on ships. In addition, it is an excellent tutorial that describes the process EPA uses to develop the technologies to treat the wastewaters. Technology-based limits would establish effluent limitations guidelines for direct dischargers based on the following treatment technologies: "best practicable control technology" (BPT), "best conventional pollutant control technology" (BCT), and "best available technology economically achievable" (BAT). New source performance standards are based on "best demonstrated technology."

Best Practicable Control Technology (BPT)

In the guidelines, EPA defines BPT effluent limits for conventional, priority, and nonconventional pollutants. EPA looks at a number of factors. EPA first considers the cost of achieving effluent reductions in relation to the effluent reduction benefits. Next it considers the age of the equipment and facilities, the processes employed and any required process changes, engineering aspects of the control technologies, nonwater quality environmental impacts (including energy requirements), and other such factors as deemed appropriate. Traditionally, EPA establishes BPT effluent limitations based on the average of the best performances of facilities within the industry, processes, or other common characteristics. Where, however, existing performance within a category or subcategory is uniformly inadequate, EPA may require higher levels of control than are in place in an industrial category (or subcategory) if the Agency determines that the technology can be practically applied. BPT may be transferred from a different subcategory or category.

EPA efforts emphasized the achievement of BPT limitations for control of the "classical" pollutants (TSS, pH, BOD₅) in the initial stages of Clean Water Act (CWA) regulation. However, nothing on the face of the statute explicitly restricted BPT limitation to such pollutants. Following passage of the Clean Water Act of 1977 with its requirement for point sources to achieve best available technology limitations to control discharges of pollutants, EPA shifted its focus to address the listed priority pollutants under the guidelines program. BPT guidelines continue to include limitations to address all pollutants.

Best Conventional Pollutant Control Technology (BCT)

The 1977 Amendments added Section 301 (b)(2)(E) to the Act establishing BCT for discharges of conventional pollutants from existing industrial point sources. Section 304(a)(4) designated the following as conventional pollutants: biochemical oxygen demanding pollutants (BOD), total suspended solids (TSS), fecal coliform, pH, and any additional pollutants defined as conventional. EPA designated oil and grease as an additional conventional pollutant on July 30, 1979. BCT is not an additional limitation, but replaces BAT for the control of conventional pollutants. BCT limitations are established in light of a two-part "cost-effectiveness" test. EPA's current methodology for the general development of BCT limitations was issued in 1986.

Best Available Technology Economically Achievable (BAT)

In general, BAT effluent limitation guidelines represent the best economically achievable performance of plants in the industrial subcategory or category. The CWA establishes BAT as a principal means to control the direct discharge of priority and nonconventional pollutants to waters of the United States. The factors considered in assessing BAT include the cost of achieving BAT effluent reductions, the age of equipment and facilities involved, the process employed, potential process changes, and nonwater quality environmental impacts, including energy requirements. EPA retains considerable discretion in assigning the weight to be accorded these factors. Unlike BPT limitations, BAT limitations

may be based on effluent reductions attainable through changes in a facility's processes and operations. As with BPT, where existing performance is uniformly inadequate, BAT may require a higher level of performance than is currently being achieved based on technology transferred from a different subcategory or category. BAT may be based upon process changes or internal controls, even when these technologies are not common industry practice.

Metal-Bearing Waste Treatment and Recovery Subcategory

This subcategory applies to discharges resulting from the treatment or recovery of metal-bearing waste. EPA proposes to regulate the conventional, priority, and nonconventional pollutants in this subcategory.

Oily Waste Treatment and Recovery Subcategory

This subcategory applies to discharges resulting from the treatment or recovery of oily waste. EPA proposes to regulate conventional, priority, and nonconventional pollutants in this subcategory. Most of the waste accepted for treatment and recovery in 1989 was stable oil-water emulsions resulting from cleaning fluids and lubricants that are difficult to treat. Other types of oily waste accepted for treatment include bilge waters and tank cleaning wastewater.

Organic Waste Treatment and Recovery Subcategory

This subcategory applies to discharges resulting from the treatment and recovery of organic waste. Organic recycling processes, such as solvent recycling, are not included in this regulation. The wastes accepted for treatment in this subcategory are typically less concentrated than the wastes treated in the other subcategories. Wastes from clean up of groundwater and landfill leachate are the predominate sources of wastewater. EPA proposes to regulate the conventional, priority, and nonconventional pollutants in this subcategory. It will not be discussed further in this report.

Metal Subcategory BPT (1995)

The EPA proposed the following options for metals:

- Option 1: Chemical precipitation, Solid-Liquid separation, and Sludge dewatering
- Option 2: Selective Metals Precipitation, Pressure Filtration, Secondary Precipitation and Solid-Liquid Separation
- Option 3: Selective Metal Precipitation, Pressure Filtration, Secondary Precipitation Solid-Liquid Separation, and Tertiary Treatment,

EPA selected the BPT limitations based on Option 3. EPA's decision to base BPT limitations on Option 3 treatment considered three factors: the degree of effluent reduction attainable, the cost, and the potential nonwater quality benefits.

Oils Subcategory Current Performance

Organic pollutants were detected in waste streams treated by centralized waste treatment facilities at varying amounts dependent on the subcategory of the facility sampled. In the Metals subcategory, organic compounds were detected at low levels since the organic compounds were incidental components of the waste receipts. The type of organics detected at Oils and Organics Subcategory facilities varied depending on the subcategory. Organic compounds in the Oils subcategory were more petroleum-based, such as alkanes and glycols, than in the Organics Subcategory.

The types of oils that are accepted for treatment can be characterized as stable or unstable oil-water emulsion. Stable oil-water emulsions are difficult to separate because the emulsions were created to make a specific product, such as lubricants and coolants. Chemical emulsion breaking is necessary to separate the mixture. Emulsion breaking is a highly effective treatment technology for separating oil from water. Typically, emulsions that contain of 5 to 10 percent oil can be reduced to about 0.01 percent (100 mg/l). Emulsion breaking is a common process in the Centralized Waste Treatment Industry; it is used by most of the facilities identified as belonging in the Oils Subcategory. An advantage of the emulsion breaking process is the high removals that are possible. A disadvantage, however, is the high operating costs for treatment chemicals and heat generation. One way to minimize operating costs is to pretreat the oil/water mixture to physically separate any free oil that may be present before emulsion breaking is performed. Unstable oil-water emulsions are easier to separate than stable emulsions. Gravitational (parallel plate) settling is usually sufficient to separate the oil and water phases. The wastewater generated from chemical emulsion breaking and settling requires treatment before it is discharged. The effluent from chemical-emulsion breaking was characterized to be similar to the unstable oil-water emulsions prior to settling.

Oils Subcategory BPT (1995)

EPA evaluated a variety of different treatment methods used within this subcategory to determine BPT for the Oily Subcategory. Treatment varies depending on the type of oils accepted for treatment and other on-site operations. A majority of facilities, 29 out of 34, use chemical emulsion breaking as a means to separate stable oil-water emulsions. The remaining facilities treat less stable oily wastes by gravity separation, dissolved air flotation, or in flocculation clarification treatment systems designed for a wide variety of waste streams. Wastewater resulting from emulsion breaking can be treated by a variety of methods. Most facilities that use emulsion-breaking treat the resulting wastewater in a flocculation/clarification treatment system designed to treat a variety of waste streams. Only one facility treated the wastewater resulting from emulsion breaking in a system specifically designed for the pollutants in an oily waste stream. EPA identified four regulatory options (identified from operations at the one facility that was specifically designed for the treatment of oily wastes) for consideration to reduce the discharge of pollutants by Centralized Waste Treatment facilities:

- *Option 1 - Emulsion-Breaking.* BPT limitations would be based on present performance of emulsion-breaking processes using acid and heat to separate oil-water emulsions. Stable oil-water emulsions require some emulsion-breaking treatment because gravity separation or flotation alone is inadequate to breakdown the oil-water waste stream.
- *Option 2 - Ultrafiltration.* BPT limitations are based on the use of ultrafiltration for treatment of less concentrated, unstable oily waste receipts or for the additional treatment of wastewater from the emulsion -breaking process.
- *Option 3 - Ultrafiltration, Carbon Adsorption, and Reverse Osmosis.* BPT effluent limitations are based on carbon adsorption and reverse osmosis in addition to Option 2 technology. The reverse osmosis unit removes metals compounds found at significant levels for this subcategory. Inclusion of a carbon adsorption unit is necessary in order to protect the reverse osmosis unit by filtering large particles that may damage the reverse osmosis unit or decrease membrane performance.
- *Option 4 - Ultrafiltration, Carbon Adsorption, Reverse Osmosis, and Carbon Adsorption.* This option is similar to Option 3 except for the additional carbon adsorption unit for final effluent polishing.

Table 5. Technology Basis for BPT Effluent Limitations (from EPA 821-R-95-006, January 1995)

Metal-Bearing Waste Treatment and Recovery	Selective Metals Precipitation, Pressure Filtration, Secondary Precipitation, Solid-Liquid, Separation, and Tertiary Precipitation Pretreatment by Alkaline Chlorination at specific operating conditions
Oily Waste Treatment and Recovery	Option 1: Ultrafiltration Option 2: Ultrafiltration, Carbon Adsorption, and Reverse Osmosis
Organic Waste Treatment and Recovery	Equalization, Air Stripping, Biological Treatment, and Multimedia Filtration

Of these four options, the EPA proposed two in 1995 for BPT effluent limitations for the Oily Waste Subcategory as shown in Table 5. The two options in Table 5 are the same as options 2 and 3 listed above. The EPA preliminarily concluded that both options represent best practicable control technologies. The technologies are in use in the industry, and the data collected show that the limitations are being achieved. For a service industry whose service is wastewater treatment, the pertinent factors for establishing the limitations are the cost of treatment, the level of effluent reductions obtainable, and nonwater quality effects.

EPA proposed different technologies in their 1998 documents. The agency proposed BPT limitations based upon batch precipitation followed by liquid solid separation, secondary precipitation and sand filtration for the Metal-Bearing Waste Subcategory; and emulsion breaking/gravity separation, secondary gravity separation followed by dissolved air flotation for the Oily Waste Treatment and Recovery Subcategory. Comments to the 1995 proposal and the 1996 Notice of Data Availability encouraged EPA to consider alternate technology options to emulsion breaking/gravity separation and ultrafiltration. This was driven in large measure by the fact that many of the facilities were "small businesses" *and the cost of installing, operating and maintaining ultrafiltration systems was quite high.* Many commentators stated that ultrafiltration is a sophisticated technology that would be difficult to operate and maintain with a majority of the waste streams. The commentators also noted that the Agency did not consider the nonwater impact adequately – particularly the disposal of the concentrate.

INNOVATIVE AND EMERGING TECHNOLOGIES THAT COULD BE USED TO PROCESS, TREAT, AND CONCENTRATE INCIDENTAL SHIPBOARD LIQUID WASTES

Innovative treatment technologies to treat hazardous and mixed wastes are being developed and demonstrated by the U.S. Department of Energy and the U.S. Environmental Protection Agency. DOE demonstrations generally focus on radioactive and mixed waste treatments, and are funded by the DOE Office of Technology Development (EM-50) through the mixed waste integrated program (MWIP). Technologies are developed and demonstrated at national laboratories such as Los Alamos National Laboratory, Sandia National Laboratories, Lawrence Livermore National Laboratory, Oak Ridge National Laboratory, Idaho National Engineering Laboratory, Brookhaven National Laboratory, and Pacific Northwest Laboratories; or at installations such as the Savannah River Site, the Hanford Site, the Oak Ridge Reservation, and the Rocky Flats Plant. The Risk Reduction Engineering Laboratory and the

* Mr. Marshall Looper of the Westinghouse Savannah Company provided several of the technology descriptions. Private communications January 1995.

Superfund Innovative Treatment Evaluation (SITE) program discussed earlier support EPA technology demonstrations.

Biological Treatment Methods

Biological treatment methods have been used to treat organic wastes for many years. This treatment method relies on microorganisms to degrade organic compounds to simpler compounds (such as carbon dioxide and water). Sanitary wastewater treatment plants rely on biological methods to treat domestic wastewater before it is discharged to surface water. Several industrial wastewaters (such as phenolic, and pulp and paper wastes) are also treated using biological methods. Complete degradation (mineralization) of complex hydrocarbons (such as polychlorinated biphenyls [PCBs] or polyaromatic hydrocarbons) is not generally achieved. Degradation rates are controlled by available energy from breaking chemical bonds and factors affecting enzymatic activity (such as water solubility, pH, temperature, and metals concentration). In general, biological treatment methods are most effective for simple, water-soluble organics. Biological treatment of aqueous-phase organics in industrial wastes often results in the production of metal-contaminated sludges.

Innovative approaches to biological treatment include in-situ treatment of contaminated groundwater by alternating aerobic and anaerobic conditions, using microorganisms (such as white rot fungus, which may be more effective for hydrophobic compounds), and using special substrates and nutrients to select microorganisms to degrade refractory compounds.

Biosorption

Biosorption consists of the separation and volume-reduction of dilute aqueous-phase metals and nitrate salts. Liquids and salts are fed to a bioreaction system where metals are concentrated and supernated through biosorption. The bacteria are grown in a bioreactor and are recycled to a biosorption tank where they are mixed with the liquids and salts. The bacteria biosorb the metals and are removed by filtration to generate a biomass sludge which can be volume reduced and stabilized through incineration or vitrification. The filtrate, which contains nitrate salts, organics, and low levels of metals, flows to the bioreactor where the nitrate salts are reduced to nitrogen gas and bicarbonate solution and any remaining metals are further adsorbed by the bacteria. After filtration, the effluent from the bioreactor is a salt solution. This process has been demonstrated in the laboratory and is in a scale-up design for field demonstration at the Idaho National Engineering Laboratory. The process should be intrinsically safe (it operates at standard temperature and pressure with natural bacteria), energy-efficient, and cost-effective.

Chemical Treatment Methods

Chemical treatment methods have traditionally been used to treat both organic and inorganic wastes. These methods can be applied to hazardous and mixed wastes and are compatible with liquids, solids, sludges, and gases. Direct chemical oxidation processes use a chemical oxidizer (oxygen, nitric acid, or an oxidizing cation) to decompose and oxidize organic contaminants that are either in solution or suspension in the reacting medium. All direct chemical oxidation processes operate with highly reactive media making corrosion and compatibility with materials a major issue. These reactions are most effective on soluble organic compounds, although some immiscible liquids may also be treated. The liquids require mixing for the reactions to take place in a reasonable period of time. These reactions are most effective on soluble organic compounds, although some immiscible liquids may also be treated. Secondary wastes can include organic reaction byproducts, products of incomplete reaction, inorganic sludges, and depleted acids.

There are two basic types of chemical treatment methods: chemical extraction and chemical destruction. Chemical extraction technologies separate the contaminants from the waste stream, while chemical destruction technologies either destroy the hazardous constituent or neutralize their hazardous

characteristic. The type of chemical treatment method applied to a waste stream is dependent on its physical and chemical properties. Innovative approaches to chemical treatment include catalyzed oxidation-reduction methods, supercritical water oxidation, and ultraviolet oxidation.

Catalyzed Chemical Oxidation

Catalyzed (or mediated) chemical oxidation refers to the class of reactions that use oxidizing agents with a catalyst to oxidize organic chemicals to CO_2 , H_2O , mineral acids, and less toxic organic materials. An example is the use of Fe (III) as an oxidizing agent in an HCl solution in the DETOX™ system being developed by Delphi Research Inc. Such oxidizing agents are stronger than oxygen. It operates at 100 to 300°C and at 35 to 215 psig depending on the waste form and composition. The low temperature process produces no NO_x , SO_x , dioxins, or furans. Cocatalysts increase the oxidation rate for organics; the Fe (II), formed in the organic oxidation process is oxidized back to Fe (III) by a second catalyzed reaction with oxygen. The process is capable of treating dilute organic solutions. However, care must be taken to control the concentration of the organic wastes in the aqueous solution to prevent dilution. The secondary wastes produced by the process are residual solids, heavy metal salts precipitated from the reaction solution, condensate, and exhausted reaction solution. [See Dhooge, P.M., "Continued Investigations of the DETOX Wet Oxidation Process for Mixed Waste Volume Reduction/ Recycling," *Proceedings of the International Incinerator Conference*, Albuquerque, NM, May 11-15, 1992, pp. 779-782; and Dhooge, P. M., "Report on Study of Oxidation Reaction Rates," Los Alamos National Laboratory Subcontract Report No. 9-XT1-V6607-1, June 10, 1991]. The findings in these reports are elsewhere in the text, and the Delphi Research's DETOX™ Catalyzed Wet Oxidation System is included in the EPA VISITT Data Base. The DETOX system being developed for Rocky Flats uses both an iron catalyst and a co-catalyst to degrade the organics in a strong acid solution. The system operates at temperatures much below those used in incineration and utilizes moderate pressures (expected operating conditions are approximately 150 F and 70 psig). Both solid and liquid wastes can be treated, and most metals are dissolved and concentrated in the reaction solution.

A process that has gained recent attention for rapidly oxidizing biorefractory compounds is the catalyzed decomposition of hydrogen peroxide by iron (II), which is commonly known as Fenton's reagent. Catalyzed hydrogen peroxide chemistry is well documented in the fundamental chemistry literature. Haber and Weiss [Haber, F., and J. Weiss, "The catalytic oxidation of hydrogen peroxide by iron salts," *Proc. Royal Soc. London* 1934, 147, 332.] first proposed that hydroxyl radical ($\text{OH}\cdot$) is the oxidant in hydrogen peroxide-iron (Fe II) systems. Fenton's chemistry has been used extensively for the treatment of aqueous organic wastes. Barbeni et al [Barbeni, M., C. Minero, and E. Pelizzetti, "Chemical Degradation of Chlorophenols with Fenton's Reagent," *Chemosphere* 1987 16, 2225] investigated the oxidation of chlorophenols and documented their transformation to carbon dioxide, water, and chloride. A Fenton-like reaction using iron (Fe III) was also shown to oxidize a formaldehyde waste stream. In addition, catalyzed hydrogen peroxide has been used for the pretreatment of industrial wastewaters containing chlorophenols, which are inhibitory to microbial metabolism.

EPA report, "Field Applications of In Situ Remediation Technologies: Chemical Oxidation," EPA 542-R-98-008, dated September 1998, describes completed and ongoing pilot demonstrations of *in situ* chemical oxidation technologies for the remediation of soil and groundwater at fifteen waste disposal and spill sites. *In situ* chemical oxidation is based on the delivery of chemical oxidants to contaminated media in order to destroy the contaminants by converting them to innocuous compounds. The oxidants used were hydrogen peroxide at 6 sites, potassium permanganate at 4 sites, ozone at 4 sites, and dissolved oxygen at 1 site. The most common field application is based on Fenton chemistry. The report presents site-specific technical references and a set of extensive general references. The sites that used ozone are of special interest because it is not yet practicable to generate hydrogen peroxide on a ship. The processes were able to significantly reduce the concentration of total hydrocarbons (THC); trichloroethane (TCE);

pentachlorophenol (PCP); polycyclic aromatic hydrocarbons (PAH); and benzene, toluene, ethylbenzene, and xylene (BETX) in the water table.

Biological/Chemical Treatment

Biological/chemical treatment technology involves a two-stage process to treat waste streams contaminated with organics (fuel, hydrocarbons, and any biodegradable material) and metals. The process includes chemical leaching of the waste to remove metals and bioremediation to remove organics and metals. The process results in an end product of recovered, saleable metal or metal salts, biodegraded organic compounds, and stabilized residues. The incoming waste stream is first exposed to the leaching solution and sized to separate oversized particles that may require shorter leaching times. The leaching solution removes metal compounds from the waste. The metal compounds form metal ions in the aqueous leachate and can be removed by liquid ion exchange, resin ion exchange, or reduction. After the metals are extracted, the slurried waste is allowed to settle and neutralize. The slurry is then transferred to a bioreactor where micronutrients are added. The residual leaching solution and biodegradable organic compounds are aerobically degraded in the bioreactor. Bench-scale tests show that heavy metals and organic pollutants can be remediated by this process. The combined metal leaching and bioremediation process may be less expensive than separate processes.

Gas-Phase Chemical Reduction

The process uses a gas-phase reduction reaction of hydrogen with organic compounds. The process occurs at elevated temperatures to convert aqueous and oily hazardous contaminants to a gaseous, hydrocarbon-rich product. The process takes place in a specially designed reactor. A mixture of atomized waste, steam, and hydrogen is injected into the reactor. The mixture swirls down an outer reactor wall and passes a series of electric heaters that raise the temperature to 850°C. The reduction reaction occurs as the gases travel toward the scrubber where hydrogen chloride (if chlorinated organic compounds are present), water, and particulates partition out.

Gas-phase chemical reduction is suitable for the treatment of PCB, dioxins, and chlorinated solvents. Demonstration tests were performed on a wastewater stream containing an average PCB concentration of 4,600 mg/l and a waste oil stream containing an average of 24.5 percent PCBs. Destruction Removal Efficiencies of 99.9999 percent were attained during the test runs that were conducted for the EPA's SITE Demonstration Program at a Toxic Substances Control Act (TSCA/RCRA) permitted landfill. This is a completed EPA SITE Demonstration Program. The technology project was with ELI Eco Logic International, Inc. The technology is listed in the EPA SITE Emerging Technology Program and in the EPA REACHIT Data Base (see Appendix A).

Steam Reforming is a waste system in which liquid and mixed wastes are gasified by exposure to superheated steam. Commercial steam reforming has been shown to destroy most of the organic solvents and polymeric organics commonly found in mixed wastes. The gasified organic materials are sent to an electrically heated detoxification reactor where they are converted to nontoxic vapors by thermal decomposition. Steam reforming chemistry reacts the organic compounds in the vapor phase with superheated steam to produce a gas comprised mostly of hydrogen and carbon monoxide. The chemistry is reductive and endothermic. Consequently, dioxins and furans that may be produced when halogens are present during incineration are not a problem with steam reforming. The product gases (CO, CO₂, H₂, and water) can be led to adsorber beds to remove trace organics, metals, and halogens. The product gases are oxidized catalytically to carbon dioxide and water and vented to the atmosphere.

Steam reforming is being tested for its applicability to mixed wastes and may prove to be a viable alternative to incineration. DOE reported that steam reforming was able to destroy kevlar/nylon parachutes at the Allied Signal Kansas City plant. A current project includes demonstration tests collaborated by the Sandia National Laboratory and Synthetica Technologies [see Schwinkendorf, W.E.,

"Alternatives to Incineration, Technical Area Status Report," DOE/MWIP-25, prepared for the U. S. Department of Energy (Nov. 1994)]. That unit consists of a two-stage destruction process. In the first stage, heat and high temperature steam in a waste-feed evaporator volatilize the organics. The hydrocarbons are vaporized within the evaporator under exposure to superheated steam at 300°C to 600°C, which begins the steam reforming chemistry to thermally decompose and fragment the organic molecules. The gases generated in the evaporator pass to a catalytic, high-temperature steam-reforming reactor operated at 1200°C, where they are mixed with superheated steam, and the reaction proceeds to completion. The Savannah River Site (SRS) also is evaluating a commercial steam-reforming unit. The project focuses on the destruction of organics, the decomposition of nitrates, and the processing of mercury. While the system has demonstrated destruction and removal efficiencies greater than 99.99 percent for a simulated benzene waste stream, carbon formations have caused prohibitive pressure drops within the system. The current acceptable waste stream is limited to low-heating value organics because of carbon limitations. Waste acceptance may also be limited to aqueous liquids and dry, heterogeneous solids. (The DOE is considering the use of a plasma arc furnace together with steam rather than air. The endothermic reaction produces CO and H₂. The low Btu product gases would be consumed in a secondary oxidizer.)

Wet Chemical Oxidation (Acid Digestion)

The wet chemical oxidation, or acid digestion, process is under investigation at the SRS for its applicability to treat hazardous and mixed waste streams. This process is described by Schwinkendorf, W. E., P. W. Hart, and McFee, "Low Temperature Alternatives to Incineration For DOE Mixed Waste," *Proceedings of The Symposium on Waste Management*, Tucson, AZ (Feb. 1995). It uses nitric acid, air, (and a catalyst) to oxidize liquid and solid organic wastes. The process works especially well for cellulosic materials and is suitable for polymers and nonvolatile organic compounds. Waste streams with high ash or metal content may produce large secondary wastes. An advantage of such a process is that it can occur at moderate temperatures and pressures.

Several parameters of this process are still under investigation. Research on operating temperatures, catalysts, and oxidant concentrations has limited the application and feasibility studies. Early experiments, however, have shown promising results for treating specific waste types. The applicability of the system to a variety of waste streams is difficult to predict. Theoretically however, this process should be able to successfully treat many waste streams. Unfortunately, the current system could produce large amounts of secondary waste products, such as spent acids that would require additional treatment.

Wet Air Oxidation

The wet air oxidation (WAO) process is a treatment method used to destroy organic contaminants in liquid waste. It is a commercialized process that involves the aqueous-phase oxidation of dissolved or suspended organic substances with oxygen. Typical reactor temperatures range from 150 to 325°C, and pressures of 300 to 3000 psi are maintained to control evaporation and to maintain the liquid state. The oxidation of organic substances can degrade them into carbon dioxide and water. Wet air oxidation is not a highly predictable process, and the design is usually based on bench-scale tests on specific compounds. The degree of oxidation of organics and inorganics is limited by the solubility of oxygen in water. Up to 95% to 99% destruction in 15 to 60 minutes can be achieved; however, only 60 to 70% destruction is achievable with highly resistive compounds such as PCBs. Although WAO has a high destruction and removal efficiency for many organic compounds, the compounds are rarely completely mineralized and some other hazardous compounds can be produced as the result of oxidation. The oxidized effluent may require further treatment to meet standards.

Conventional wet air oxidation methods are limited to treating dilute (less than 10 percent by weight of organics) liquid streams; however, the addition of a metal catalyst can drastically alter the treatability of the waste stream. A metal catalyst may allow degradation of halogenated aromatic compounds (such as PCBs) and condensed-ring compounds. A bench-scale method that uses a metal catalyst to assist in the waste treatment process is being tested for treating hazardous, radioactive and mixed wastes. This method has been proven successful in treating liquid wastes as well as solid wastes. The bench-scale studies have been performed on a batch oxidation reactor and a continuous oxidation reactor; both show promising results. The bench-scale tests have proven that sufficient oxidation rates can be achieved using wet oxidation methods with the addition of a metal catalyst. Experiments showed that oxidation rates for organic solids are highly dependent on its surface area and the interfacial contact area in the reaction vessels; therefore, efficient mixing is very important. A scheme has also been identified to allow separation of radioactive and toxic metals from the process solution.

Supercritical Water Oxidation

Supercritical water oxidation (SCWO), sometimes referred to as Hydrothermal Oxidation (HTO), is an aqueous-phase oxidation process that treats waste entrained in high-pressure water with oxidants such as O_2 and H_2O_2 . [The Winter 1998 edition of *Environmental Progress* (Vol. 17, No. 4) and the *Proceedings of the International Conference on Incineration and Thermal Treatment Technologies*, Salt Lake City, UT (1998)] featured papers on SCWO. Martin A. Abraham, who introduced the subject in *Environmental Progress*, noted that despite the gains in understanding the science of supercritical fluids, SCWO is only now being applied in real applications and supercritical water is only beginning to be accepted as a viable solvent.

Supercritical water oxidation is a closed loop system. The process takes place above the critical pressure [218 bars (3208 psi)] and critical temperature [374 °C (705 °F)] of water. It reduces the organic constituents to water, carbon dioxide, various biodegradable acids, no chain-growth compounds, and mostly molecular nitrogen rather than the NO_x that is produced in incinerator and plasma systems. Oxidation is performed above the critical point of water because the water in the liquid waste stream becomes an extremely good solvent for the organic materials contained in the waste. Typically, temperatures of 400°C to 600°C and pressures of about 250 bar yield complete conversion of any organic hydrocarbon molecule to water and carbon dioxide in a matter of seconds. Heteroatoms such as chlorine, sulfur, phosphorous, and fluorine are converted to inorganic acids that can be neutralized to produce salts. The large changes that occur in the solvation character of water from an ambient liquid state can be effectively exploited to provide a very robust process for detoxifying hazardous organic compounds. For example, supercritical water will dissolve gases such as oxygen and nonpolar aromatic and aliphatic hydrocarbons such as benzene and propane to provide a single-phase mixture for oxidation. In addition, heteroatoms are removed as precipitated inorganic salts, such as NaCl or Na_2SO_4 , which have very low solubility (100 ppm or less) in supercritical water. Although this process occurs at relatively low temperatures (400 °C to 600 °C) compared to incineration (1000 °C to 1200 °C), there is concern over process containment and the effects of corrosion.

The Savannah River Site (SRS) tested this treatment method as a bench-scale system using cutting oil containing a simulated radionuclide. Oxidation efficiencies of the oil were greater than 99 percent; however, the resulting solid effluent contained levels of the simulated radionuclides that would cause the solid to be a radiological hazard. Oxidation of the oil is encouraging because the Navy system under study will encounter oily waste and waste oil.

Research at MIT that began in the middle 1990's (<http://scwo.mit.edu>) focused on improved understanding of phenomena that affect the performance of subcritical and supercritical water oxidation as a process to treat aqueous wastes and remediate contaminated soils. In particular, they concentrated efforts on 1) chemical kinetics of hydrolysis and oxidation, 2) mixing and transport processes, 3) corrosion and behavior of materials, 4) phase partitioning and precipitation rates of salts, and 5) physical

property unit process step models for flow-sheet simulation. Research efforts are at three levels. (1) Molecular-level modeling of chemical and physical pathways including free radical and ionic mechanisms for oxidation and hydrolysis and molecular simulation of salt-water-organic thermodynamics at supercritical conditions. Of particular importance here are the effects of high fluid pressure and density in determining which elementary reactions are controlling the output of a complex reaction networks. Even the oxidation of simple compounds such as CH_2Cl_2 or CH_3OH involves hundreds of elementary reactions. (2) Engineering science level studies experimentally characterize and correlate rates of chemical reactions and product distributions and their dependence on mixing, temperature, pressure, density, and residence time. In addition, salt solubilities, nucleation, and crystallization rates are studied in high pressure, high temperature optically accessible cells. Electrochemical effects are also monitored under well-defined conditions to establish corrosion rates and expected service lifetimes. (3) Engineering process modeling studies utilize existing chemical process, flowsheet simulation software as a framework and add enhancements that deal with the chemical and physical steps unique to supercritical fluid processing. For example, PVTN equations of state and transport property models were developed to accurately represent supercritical phase behavior and mixing phenomena in reacting flows.

Evaporation and Catalytic Oxidation

The evaporation and catalytic oxidation system treats a variety of hazardous liquid wastes by reducing the waste volume and oxidizing volatile contaminants. The system consists of 1) an evaporator that reduces the influent volume, 2) a catalytic oxidizer that oxidizes the volatile contaminants in the vapor stream, 3) a scrubber that removes acidic gases produced during oxidation, and 4) a condenser that condenses the vapor stream leaving the scrubber. Aqueous wastes containing mixtures of metals, volatile and nonvolatile organics, and volatile inorganics are the primary source for treatment. The technology destroys volatile organic contaminants and produces a nontoxic condensate and a small concentrate containing the inorganic wastes and those organic wastes that are not destroyed or volatile at about 220 °F (2 psig). Pilot-scale facilities have been developed to treat radioactive, hazardous, and mixed waste streams under EPA's SITE Demonstration Program. (This should be of special interest in the Navy's study because it deals with the evaporation of aqueous wastes containing small amounts of organic material, and it can tolerate metals and salts.) This is Wheelabrator Clean Air System Inc.'s PO*WW*ER™ Technology described in "Superfund Innovative Technology Evaluation Program-Technology Profiles Ninth Edition," EPA/540R-97/502, December 1996 (see Appendix A). "CWM PO*WW*ER™ Evaporation-Catalytic Oxidation Technology, Applications Analysis Report," EPA/540/AR-93/506, September 1993, is an evaluation of this system. The process achieved a total solids concentration of about 32:1.

Electrochemical Treatment Methods

Electrochemical treatment is a direct oxidation process that is used to treat liquid wastes containing recoverable metals or cyanide. This process involves immersing cathodes and anodes in a waste liquid and introducing a direct electric current. Electrolytic recovery of single metal species can be high and may yield pure or nearly pure forms; however, process times are lengthy. DOE is developing innovative electrochemical treatment processes to demonstrate oxidation of organics and the biocatalytic destruction of nitrate and nitrite salts. Some are discussed in the section on the Superfund Innovative Technology Evaluation (SITE) Program and in Appendices A and D.

Electrochemical Oxidation

Electrochemical treatment of hazardous and mixed waste is a direct oxidation process. There are two methods in which oxidation of the organic constituents of the waste stream can occur in the electrochemical cell. The process can take place at the cell anode by direct oxidation or with the addition of an oxidizing agent to react with the organics in the cell. The oxidizing agent is a cation (usually Ag

(II)) in a nitric acid solution that produces highly reactive OH and NO₃ radicals. The cation and free radicals attack organic compounds converting most of them to CO₂ and water. The resultant Ag (I) is recycled to Ag (II) at the anode of an electrochemical cell to maintain the supply of oxidant and minimize the consumption of Ag. The Ag (II) migrates back into the bulk electrolyte to continue the oxidation process. A microporous membrane is usually placed between the electrode to prevent the oxidizer produced at the anode from being reduced at the cathode. This process is limited to the treatment of liquid wastes and has been confined to lab-scale demonstrations. Pilot-scale and commercial systems are being developed, and large-scale experiments using a commercially available industrial electrochemical cell have been performed at the Lawrence Livermore National Laboratory. The Navy's Applied Research Program for Environmental Quality is considering electrochemical treatment technologies to process the nonoily wastewater generated by ships. The objective of that study is to demonstrate the feasibility of applying electrochemical oxidation (pretreatment or post treatment) of nonoily wastewater combined with ultrafiltration to reduce the total BOD₅ levels and ensure disinfection to meet emerging international water quality standards.

Physical Treatment Methods

Physical treatment methods are diverse and rely on physical properties, such as electromagnetic or particulate radiation, high pressure, or gravity. Innovative physical treatment technologies include the use of sound waves to separate particulates from aqueous-phase liquids, the use of electron beams to treat hazardous organics in groundwater, the use of pressure filters to remove metals, and the use of precipitation following coagulation and chemical binding. Radiation-induced oxidation technologies destroy dilute organics in water, which eliminates the need for separation processes and subsequent treatment of concentrated wastes. Radiation is used to generate OH radicals in an aqueous solution, which, in turn, attack the oxidizable materials. Various radiation sources have been used (such as ultraviolet radiation, ultrasound, electron beams, and x-rays), along with oxidation agents such as H₂O₂, O₃ and catalysts (such as metal ions), to generate the hydroxyl radicals.

Ultrasound-Enhanced Oxidation

This process is described in Schwinkendorf, W.E., P.W. Hart, and McFee, "Low Temperature Alternatives to Incineration For DOE Mixed Waste," *Proceedings of The Symposium on Waste Management*, Tucson, AZ (Feb. 1995). Ultrasound affects organic oxidation primarily through cavitation, which is the growth and collapse of a gas-filled or vapor-filled bubble in a liquid. "... The highly localized transient temperatures (thousands of degrees Kelvin) and pressures (hundreds of atmospheres) in the center of the bubble cause direct pyrolysis of organic vapors within the collapsing bubbles, and decomposition of water molecules into free radicals that propagate outward into the surrounding fluid to react with organic material." The technical feasibility of this process has been demonstrated in small batch units at the Argonne National laboratory. The process can be used to treat a wide array of organics, due to the nonspecific nature of the process, and should be able to handle aqueous streams with moderate amounts of suspended solids and low light transmissivity.

High-Energy Electron Beam Irradiation

High-energy electron irradiation of aqueous solutions and sludges removes various hazardous organic compounds from aqueous waste streams with up to 8 percent solids and less than 5% percent organics. The process of irradiation produces large quantities of free radicals in the form of aqueous electrons, hydrogen radicals, and hydroxyl radicals. The hydroxyl ions can recombine to form hydrogen peroxide. These very reactive chemical species react with organic contaminants, oxidizing them to nontoxic byproducts, such as carbon dioxide, water, and salts. The electron irradiation process equipment consists of an electron accelerator that accelerates a beam of electrons to 95 percent of the speed of light. The beam is directed into a thin stream of wastewater or sludge where free radicals are produced to react

with the hazardous organics. Although the electron beam is a form of ionizing radiation, the process does not produce residual radioactivity. Both a full-scale facility and a mobile demonstration unit have been developed. The process was demonstrated at the Savannah River Site. In addition, DOE's Los Alamos National Laboratory evaluated the suitability of electron irradiation to treat mixed waste streams and sludges contaminated with organics and nitrates. Electron irradiation may be suitable for the treatment of halocarbons, aromatics, and nitrates. Disadvantages of the process include power requirements and interferences from solids. This technology is a project in the EPA SITE Emerging Technology Program and is an innovative technology listed in EPA's REACHIT Data Base. EPA report EPA/540/R-97/503 (May 1997) is an Innovative Technology Report on the results of an evaluation of the process.

Ultraviolet Oxidation

Ultraviolet oxidation has been a common treatment for industrial and municipal wastewater (EPA lists it as the best available control technology (BACT) for treating PCBs, cyanides, and polyaromatic hydrocarbons in water). (See also the earlier discussion of Advanced Photochemical Oxidation Processes). It works best on clear aqueous dilute streams. Although commercial systems are available for dilute waste forms, destruction of high organic concentrations requires additional oxidizing agents such as ozone and hydrogen peroxide. Ultraviolet radiation breaks down the hydrogen peroxide to products that chemically convert organic materials into carbon dioxide and water (and chloride ions when chlorinated hydrocarbons are present). While this technology operates at near-ambient conditions and generates a minimal amount of secondary waste, it operates at a slower destruction rate than other technologies.

The Ultraviolet Radiation and Oxidation process developed by ULTROX, a Division of Zimpro Environmental, Inc. is one such unit. Magnum Water Technology's CAV-OX[®] process uses the combination of hydrodynamic cavitation and ultraviolet radiation to oxidize organic contaminants in water. Hydrogen peroxide is added only if required. Heterogeneous photocatalytic oxidation has been gaining attention as technique to destroy hydrocarbons and halocarbons in water. The catalyzed process is activated by illumination of a semiconductor catalyst, commonly titanium dioxide with ultraviolet or near ultraviolet light in order to create electron excitation within the solid. Titanium dioxide is nontoxic, insoluble and comparatively inexpensive [M. Anheden, D.Y. Goswami, and G. Svedberg, "Photocatalytic Treatment of Wastewater From 5-Fluorouracil Manufacturing," *Trans of The ASME*, 118, February 1996, pp 2-8]. Matrix Photocatalytic's Photocatalytic Water Treatment System removes and destroys dissolved organic contaminants in a continuous flow process at ambient temperatures. When excited by light, a titanium dioxide semiconductor generates hydroxyl radicals that break the carbon bonds of organic compounds. The catalyst also generates electron-hole pairs, which are powerful reducing species. Some of the hole-pairs react with adsorbed molecules at the particle surface. These processes are described in EPA's, "Superfund Innovative Technology Evaluation Program - Technology Profiles Ninth Edition," EPA/540/R-97/502, December 1996 (see Appendix A). The technology used by the DOE is fully commercial and processes waste stream flow rates ranging from 5 to 1,050 gallons per minute. See also the description of the work at the Lawrence Livermore National Laboratory described by Gray, et al., [Gray, L.W., et al., "Aqueous Phase Oxidation Techniques as An Alternative To Incineration," *Proceedings of the International Incinerator Conference*, Albuquerque, NM, May 11-15, 1995, pp. 157-164] earlier in this text.

X-Ray Treatment of Aqueous Wastes

X-ray treatment of organically contaminated aqueous solutions is based upon their in-depth deposition of ionizing radiation. X-rays collide with matter, generating a shower of lower energy secondary electrons within the contaminated material. The secondary electrons ionize and excite the atomic electron, break up the complex contaminant molecules, and form radicals. The radicals react with the organic material in the waste to form H₂O, CO₂, and O₂. This is similar to the electron beam

processing; however, the x-rays penetrate much deeper for the same energy and allow the treatment of thicker waste volumes. Experiments to date have been on fairly dilute solutions. The process is described in report EPA/540/R-97/502, "Superfund Innovative Technology Evaluation Program – Technology Profiles Ninth Edition," December 1996 (see also Appendix A).

Chemical Treatment and Ultrafiltration

The chemical treatment and ultrafiltration process is used to remove trace concentrations of dissolved metals from wastewater. The process produces volume-reduced water that can be treated ultimately for disposal. Wastewater is passed through a refilter to remove suspended particles. The prefiltered wastewater is sent to a conditioning tank for pH adjustment and the addition of water-soluble macromolecular compounds that form complexes with heavy metal ions. Next, a polyelectrolyte is added to achieve metal particle enlargement by forming metal-polymer complexes (see Polymer Filtration, below). The chemically treated wastewater is circulated through a cross-flow ultrafiltration membrane. The filtered water is drawn off, while the contaminants are recycled through the ultrafiltration membrane until the desired concentration is reached. The concentrated stream can be withdrawn for further treatment, such as some of those discussed herein. Initial bench and pilot-scale tests were successful; however, field demonstrations showed that pretreatment methods need further evaluation. DOE is considering alternative methods of wastewater pretreatment for ultrafiltration, including the use of water-soluble chelating polymers for actinide removal and the use of reagents and polymeric materials that exhibit selectivity for cations of heavy metals.

Electrochemical Treatment Processes

These processes are being evaluated and developed for the destruction of organic compounds and nitrates/nitrites and the removal of other hazardous species from liquid wastes stored throughout the DOE complex. This activity consists of five major tasks: 1) evaluation of different electrochemical reactors for the destruction and removal of hazardous waste components, 2) development and validation of engineering process models, 3) radioactive laboratory-scale tests, 4) demonstration of the technology in an engineering-scale size reactor, and 5) analysis and evaluation of testing data. The development program team is comprised of individuals from federal, academic, and private industry. Work is being carried out in DOE, academic, and private industrial laboratories.

Electric-Field Enhanced Technologies

Muralidhara reviewed the state of the art of electric fields to enhance existing separation technologies and make them more efficient. [H. S. Muralidhara, "Enhance Separations With Electricity," *CHEMTECH*, May 1994, pp. 36-41.] While ac and dc fields have long been used to improve the efficiency of conventional separation processes, the lack of proper electrodes discouraged the commercial development these technologies. However, recent advances have made corrosion resistant electrodes available and have led to the commercialization in this area of separation. Electrophoresis is the movement of solids or charged species through a relatively stationary fluid and electroosmosis is the movement of fluid through a porous medium. "Electroosmosis occurs near the electrodes while electrophoresis occurs in the bulk fluid. In processes such as electrofiltration, electrosedimentation, electrothickening, electrocoagulation, or electrodewatering, both electrophoresis and electroosmosis occur simultaneously. Electrocoagulation (see the Appendices), electrocoalescence, electropasmoyllis, electroflocculation, electrocentrifuge, dielectrophoresis, electroosmosis, electrophoresis, electrofiltration, electrodewatering, electrokinetic thickening, and electroacoustic dewatering are commercial processes to separate liquids and solids. All except electropasmoyllis use dc technology. The conventional methods of filtration, dewatering, or thickening are inefficient for fine particles in suspension, relying as they do on bulk hydraulic flow, which decreases drastically with particle size. The electric field-enhanced technologies are based on surface and colloid characteristics, and use particle surface charges to enhance

filtration, dewatering or particle mobility." Dielectrophoresis causes particles to cluster. The main parameter in this process is the difference between the dielectric constant of the liquid medium and the particles to be separated.

Chemical Binding/Precipitation/Physical Separation of Metals

Chemical binding/precipitation/physical separation of radionuclides is an innovative technology used to treat contaminated low-level radioactive and mixed wastewater, sludges, and soils. The treatment method combines a chemical binding process and a physical separation. The initial step of the combined treatment process involves rapid mixing of the waste stream with a fine powder containing reactive binding agents, such as complex oxides. The binding agents react with most of the radionuclides and heavy metals in the waste by absorption, adsorption, or chemisorption. The reactions yield precipitates or coagulum in the processed slurry. Water is then separated from the solids. This involves a two-stage process that combines clarifier technology and microfiltration (to separate solid material by particle-size and density) and dewatering using a sand filter. The resulting waste form is material containing heavy metals and other solids that can be stabilized for disposal.

Heavy Metal Polishing Filter

The heavy metals polishing filter uses a colloidal sorption method to remove ionic colloidal, complex, and chelated heavy metals from wastewater streams. This technology must be combined with an oxidation process in order to treat wastewater that is also contaminated with hydrocarbons or hazardous organics. This technology consists of a colloidal sorption unit that contains a high-efficiency, inorganic, pressure-controlled filter bed. Pollutants are removed from the wastewater via surface sorption and chemical complexing in which trace inorganics, metals, and low-level wastes can be efficiently treated. The polishing filter can be used for batch or continuous flow processing.

Membrane Microfiltration

The membrane microfiltration system is designed to remove solid particles from liquid wastes. This technology can treat hazardous waste suspensions and process wastewaters containing heavy metals. The system uses an automatic pressure filter with a special Tyvek filter made of spunbonded olefin. The material is a thin, durable plastic with tiny openings that allow water and smaller particles (less than one ten-millionth of a meter in diameter) to pass, while larger particles accumulate on the filter to form a filter cake. The filter cake can be collected for further treatment prior to disposal. This technology is best suited for liquid waste that contains less than 5,000 mg/l solids; however, the system is capable of treating wastes containing volatile organics because the system is enclosed. The technology demonstrated encouraging results, including removal efficiencies from 99.75 to 99.99 percent and filter cake that passed RCRA TCLP standards.

Polymer Filtration

This is a technology developed at Los Alamos National Laboratory (LANL) to recover valuable or regulated metal ions selectively from process or wastewaters. (See the foregoing Chemical Treatment and Ultrafiltration.) Water-soluble chelating polymers are specially designed to bind selectively with metal ions in aqueous solutions. Advantages of polymer filtration relative to extant technologies are rapid binding kinetics, high selectivity, low energy and capital costs, and a small footprint. The polymers' molecular weight is large enough so they can be separated and concentrated using available ultrafiltration technology. Water and smaller unbound components of the solution pass freely through the ultrafiltration membrane. The polymers can then be reused by changing the solution conditions to release the metal ions that are recovered in concentrated form. LANL is conducting small-scale testing of the chelating polymer systems for the required solubility, ultrafiltration properties, selectivity and binding constants;

and an assessment at a larger scale for comparison to competing separation technologies. The work focuses on metal ion contaminants in waste streams at facilities at LANL and Rocky Flats.

Sorption

Available sorbent materials can be categorized by composition (organic, inorganic, or synthetic) and by performance (selective, chemical or specialty) [C. Mouche, "Managing Used Oil," *Pollution Engineering*, October 1995, pp. 40-43; Dentel, S., K., and S. Ko, "Use of Organo-clay Adsorbent Materials for Groundwater Treatment Applications," Final Report Submitted to Delaware State Water Research Institute, Department of Civil and Environmental Engineering, University of Delaware, Period 6/1/95-5/31/96; and Knaebel, K., S., "For Your Next Separation Consider Adsorption," *Chem Eng.* pp 92-102 (Nov 1995)]. Organic sorbents are produced from charred carbon-based materials such as coal, coconut shells, wood, and paper. Inorganic sorbents are derived from clay granules, perlite, and vermiculite. Selective sorbents contain media that absorb particular fluids. For example, petroleum sorbents selectively remove oil from water. Chemical or universal sorbents can be used with most liquids. They will absorb most all fluids or combinations of them. Synthetic or specialty sorbents are produced from petroleum-based or plastics-based materials. These materials can be tailored to have an affinity for, or repel water or oil-based fluids. Some encapsulate the liquid into a gel through polymers. One major advantage is that these materials do not produce dust.

The Navy considered the use of sorbents to polish the effluent from the oil-water separators on certain ships. It became clear that while use of sorbents may be a mature technology, it is not ready to be the basis of a system to polish the effluent of parallel plate oil water separators on a ship until a plethora of problems are resolved. Most of the problems relate to the inability to control the variability of the contents of the waste stream to and from the separator on a ship and the inability of the OWS to produce a predictable effluent with narrow enough characteristics to be a basis for a rational design based upon sorbents. Sorbents are adversely affected (sometimes irreversibly) by small diameter ($<20\mu$) oil droplets, bulk oil, detergents and surfactants, intermittent high oil concentrations, expected contaminants such as solids and sea salts, channeling within the canisters, and poor quality control when the sorbents are packed within canisters or other containers.

Plugflow Dissolved Air Flotation

In conventional dissolved air flotation (DAF), the treated liquid is removed from the bottom of the tank and the floated particles and oils are removed from the top of the tank. Research is being conducted to counteract the negative flow effects that reduce conventional dissolved air flotation efficiencies. Most is directed to reduce the counter-current flow of the two streams that cause turbulence and mixing in the flotation tank. [Baeyens, J., I. Y. Mochtor, S. Liers, and H. DeWit, "Plugflow Dissolved Air Flotation," *Water Environment Research*, Nov/Dec 1995, Vol. 67, No. 6, pp. 1027-1035; and G. C. Yeh, "Advancing the Science of Dissolved Air Flotation," *Environ. Technology*, Nov/Dec 1996, pp. 26-30]. Baeyens, et al., found that it is essential to establish a plugflow condition throughout the flotation process, both in the bubble-solids contact zone and in the agglomerate separation zone, and to develop a design that prevents disturbance of the formed layer. Thermodyne Corporation has marketed a dissolved air flotation process that purports to use plugflow.

Freeze Crystallization

Freeze crystallization is based upon differences in waste stream component concentrations during solid and liquid phases that are in equilibrium. As an aqueous waste stream is cooled, water usually crystallizes as a pure material, and dissolved contaminants of the waste concentrate into a reduced volume. The freeze crystallization system will be capable of concentrating aqueous waste streams by removing most of the water and separating organic and inorganic contaminants. Freeze crystallization

can be used to decontaminate liquid mixed wastes containing inorganics, organics, and heavy metals. The technology offers many advantages over other processes. For example the process offers high decontamination and volume reduction factors, it requires no waste stream additives, and it operates at low temperatures and pressures making it intrinsically safe and energy efficient.

Thermal Treatment Technologies

Thermal treatment technologies use high temperatures to convert organic waste constituents to carbon dioxide and water vapor. Inorganic waste constituents are concentrated in secondary waste streams (such as ash or blowdown), are captured in off-gas treatment systems (such as high efficiency particulate air [HEPA] filters or baghouses), or are emitted through the stack for some volatile compounds. Removal efficiencies of metals are dependent on the chemical and thermodynamic properties of the element or compound. Incineration technologies have been used to destroy the organic portion of hazardous wastes, and incineration is the EPA-specified BDAT for many hazardous organics (such as solvents and PCBs).

Unvented Thermal Process

The unvented thermal process for treating mixed wastes is under development at Argonne National Laboratories. The primary treatment unit is a fluidized-bed processor. The processor contains a bed of calcined limestone, which reacts with the off-gases produced during the oxidation of organic constituents in the waste stream. Such gases include carbon dioxide, sulfur dioxide, and water. The water vapor is collected and removed through a condenser, and the remaining gases (mostly nitrogen) are mixed with oxygen and returned to the oxidizer. This process does not release any gas from the system and is therefore a more attractive treatment method to the general public. The only hazardous byproducts would be mixed with cement-making materials to form a solid cement. The unvented system favors certain types of wastes over others depending on the cost of oxygen and the avoidance of emissions. Such wastes include wastes containing chlorinated hydrocarbons, solid and liquid mixed wastes, and hospital waste. Mixed waste (those that contain some low level radioactive material) treatment is especially suited to the unvented system because incineration process emissions may contain radioactive volatile matter or fine particulates that might escape filtration methods.

Packed Bed Reactor/Silent Discharge Plasma Apparatus

The packed bed, reactor/silent discharge plasma apparatus is a two-stage oxidation system for destroying hazardous liquid wastes. It combines a thermal oxidation process in an excess air stream and a process to destroy the organic constituents from the reactor exhaust. The packed bed provides thermal oxidation, and the silent discharge plasma unit provides the organic destruction. The plasma unit is operated at ambient temperature and pressure. Most hazardous waste destruction occurs in the packed bed reactor by heat provided externally (no open flame). The reactor exhaust is treated in a cold plasma that is generated by electrical discharges in the silent plasma unit. Bench-scale tests have predicted destruction and removal efficiency greater than 99.9 percent for PCBs. The production of hydroxide gas through the oxidation process could cause corrosion problems if the system is operated for an extended period of time. (See J.T. Gill and M.R. Cage, "Destruction Efficiency Tests Using A Mixed Waste Surrogate as Feed to a Packed Bed Reactor/Silent Discharge Plasma Apparatus," *Proceedings of the 1994 International Incinerator Conference*, Houston, TX, May 1994, pp 457-463.)

Cyclonic Furnace

The cyclonic furnace is designed to treat solid, liquid, soil slurries, or gaseous wastes by high temperature combustion and vitrification. The high turbulence in the combustion chamber helps ensure that temperatures are high enough (2400 to 3000°F) to melt high ash content materials. The process

could be adapted to treat the "concentrated" liquid wastes of Navy interest. The waste that enters the cyclonic furnace is melted, and the organics are destroyed in the resurging gas phase or in the molten slag layer that forms on the inner wall of the furnace barrel.

Catalytic Combustion in a Fluidized Bed Reactor

The method of catalytic combustion in a fluidized bed reactor at low temperatures (525 to 600°C) to treat waste is in an active research and development stage. Several advantages are offered by burning waste in a fluidized bed reactor and using a catalytic after-burner rather than using high-temperature incineration. Two of the advantages are the elimination of the need for a refractory lining in the reactor and the elimination of undesirable gases that emit from the fluidized bed.

SUMMARY

Table 6 is a matrix that assigns technologies, unit operations, and management practices that could control the quality of the shipboard incidental waste streams.

Table 6. Technologies, Unit Operations, and Management Practices That Could Be Used To Process Shipboard Incidental Wastes Discharges Requiring Control

Discharges Requiring Control	Technology, Unit Operation or Management Practice
Aqueous film-forming foam	Management practices control the discharge
Catapult water brake tank and post-launch retraction exhaust	Management practices control the discharge. Non-polluting lubricants are being developed.
Chain locker effluent	DoD prohibits discharge within 12 nm
Clean ballast	Management policy will mandate open ocean ballast water exchange
Compensated fuel ballast	Operational guidelines reduce the probability to overfill tanks or discharge or discharge excessive amounts of fuel entrained in the displaced compensating water.
Controllable pitch propeller hydraulic fluid	Management practices dictate that the repair procedures require that containment booms and skimming equipment be staged
Deck runoff	Management practices control the discharge
Dirty ballast	The technologies listed for Surface Vessel Bilgewater Oil/water Separator Discharge
Distillation and reverse osmosis brine	MPCDs in the form of reverse osmosis plants to replace the distillers on some vessels and limiting the use of distillers within 12 nm
Elevator pit effluent	Adsorption; environmentally-acceptable lubricant; liquid waste stored or processed through the oil/water separator
Firemain systems	Dry firemain system; Sorption systems that can process large volumes of water; Alternate piping material less prone to erosion or corrosion
Gas turbine water wash	Management dictates that the discharge be held in a holding tank while the vessel is in coastal waters.
Graywater	Aerated tubular ultrafiltration membrane units followed by ultraviolet oxidation with/without ozone; submerged

	membrane bioreactor; biological treatment; a combination of carbon adsorption and biological treatment; chemical oxidation; wet air oxidation; liquid carbon dioxide extraction; catalyzed chemical oxidation; mediated electrochemical oxidation; gas-phase chemical reduction; steam reforming; supercritical water oxidation; evaporation and catalytic oxidation, electrochemical oxidation; ultrasound-enhanced oxidation; high-energy electron beam irradiation; ultraviolet oxidation with ozone; x-ray treatment; freeze crystallization
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Table 6. (Continued)	
Hull coating leachate	TBT paints have been phased out. ESTCP should yield easy-release non-leaching coatings before 2004. Self-polishing reduced copper release coatings developed under ERAT will become available as a mid term solution.
Motor gasoline compensating discharge	Management practices demonstrate the availability of controls to mitigate adverse affects on the environment.
Non-oily machinery wastewater	The Navy has a program to install new sonar domes that do not have TBT-impregnated internal surfaces.
Photographic laboratory drains	Current practices and the availability of digital photographic systems demonstrate that MPCDs are available.
Seawater cooling overboard discharge	A high flow rate adsorption system or a change in metallurgy that could reduce corrosion and erosion
Seawater piping biofouling prevention	Existing operational controls limit the residual chlorine discharged. A Navy program is studying the use of pulsed-power acoustics technology that would remove fouling as it occurs as an alternative to chlorination
Small boat engine wet exhaust	Replace existing outboard engines with reduced emission engines and inboard engines with dry exhaust systems.
Sonar dome discharge	New and replacement sonar domes will not have TBT-impregnated internal surfaces.
Submarine bilgewater	Parallel plate oil-water separator followed by ultrafiltration membranes
Surface vessel bilgewater/oil-water separator discharge	Parallel plate gravity coalescence oil/water separator followed by ultrafiltration membranes, dissolved air flotation followed by ultrafiltration membranes, reverse osmosis semipermeable microporous membrane filtration followed by ultrafiltration membranes, liquid carbon dioxide extraction, catalyzed chemical oxidation, mediated electrochemical oxidation, steam reforming, evaporation and catalytic oxidation, electrochemical oxidation, ultrasound-enhanced oxidation, high-energy electron beam irradiation, ultraviolet oxidation with ozone, mechanical centrifugal oil/water separator, hydrocyclone.

Table 6. (Continued)

Underwater ship husbandry	The Navy has policies that minimize the number of hull cleanings and procedures to use the least abrasive cleaning equipment. The Automated Underwater Hull Maintenance/Monitoring System being developed will reduce significantly the discharge of copper.
Welldeck discharge	Existing containment and cleanup practices demonstrate that there are ways to reduce the contamination of these discharges.

ABBREVIATIONS USED IN TEXT

AFFF	Aqueous film-forming foam
AIRLANT	Naval Air Force, Atlantic Fleet
AIRPAC	Naval Air Force, Pacific Fleet
AMTS	Aerated Non-Oily Wastewater Membrane Treatment System
BAT	Best available technology economically achievable
BCT	Best conventional pollutant control technology
BDAT	Best demonstrated available technology
BOD	Biochemical oxygen demand
BPT	Best practicable control technology
CDNSWC	Carderock Division, Naval Surface Warfare Center
CFR	Code of Federal Regulations
CMA	Calcium magnesium acetate
CO ₂	Carbon dioxide
CPP	Controllable pitch propeller
CWA	Clean Water Act
CWT	Centralized Waste Treatment
DAF	Dissolved air flotation
DARPA	Defense Advanced Research Projects Agency
DOE	Department of Energy
DoD	Department of Defense
DRE	Destruction and removal efficiency
EPA	Environmental Protection Agency
ERAT	Environmental Requirements Advanced Technology
ESTCP	Environmental Security Technology Certification Program
FC	Fecal coliform
gal/min	Gallons per minute
GRP	Glass Reinforced Plastic
IGT	Institute of Gas Technology
TTS	Integrated Thermal Systems Treatment Study
LLNL	Lawrence Livermore National Laboratory
MARPOL	International Maritime Convention for the Prevention of Pollution from Ships
mg/l	milligrams per liter
MPCD	Marine Pollution Control Device
MWIP	Mixed waste integrated program
MOGAS	Motor gasoline
NAVFAC	Naval Facilities Engineering Command
NEPSS	Naval Environmental Protection Support Service
nm	Nautical mile
nm	nanometers

NRL	Naval Research Laboratory
ONR	Office of Naval Research
OWS	Oil/Water Separator
PAC	Powder activated carbon
PACT	Powdered Activated Carbon Technology
PCB	Polychlorinated biphenyl
ppm	parts per million
psi	Pounds per square inch
REACHIT	The Remediation and Characterization Innovative Technologies system
RCRA	Resource Conservation and Recovery Act
RDT&E	Research, Development, Test and Evaluation
RO	Reverse Osmosis
SCWO	Supercritical water oxidation
SERDP	Strategic Environmental Research and Development Program
SESO	Ships Environmental Support Office
SITE	Superfund Innovative Treatment Evaluation
SLM	Supported liquid membrane
SRS	Savannah River Site
STP	Site Treatment Plan
TBT	Tributyl tin
TSCA	Toxic Substances Control Act
TOC	Total organic carbon
TSS	Total suspended solids
UF	Ultrafiltration
UNDS	Uniform National Discharge Standards
UV	Ultraviolet
VISITT	Vendor Information System for Innovative Treatment Technologies
WAO	Wet Air Oxidation

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APPENDICES

APPENDIX A

**Selected Technologies from the Superfund Technology Evaluation Program
Technology Profiles, Ninth Edition
(December 1996)**

APPENDIX A

Superfund Innovative Technology Evaluation Program (SITE)

The Superfund Innovative Technology Evaluation Program (SITE) is an integral part of the EPA's research into alternative cleanup methods for hazardous waste sites around the nation. It encourages the development and implementation of (1) innovative treatment technologies for hazardous waste site remediation, and (2) characterization and monitoring technologies for evaluating the nature and extent of hazardous waste site contamination. Under the Program, the EPA enters into cooperative agreements with technology developers, who research and refine their technologies at the bench scale or pilot scale and then demonstrate them, with EPA support, at hazardous waste sites.

The SITE Program was established by the EPA's Office of Solid Waste and Emergency Response and the Office of Research and Development (ORD) in response to the 1986 Superfund Amendments and Reauthorization Act (SARA), which recognized a need for an "Alternative or Innovative Treatment Technology Research and Demonstration Program." The SITE Program is administered by ORD's National Risk Management Research Laboratory (NRMRL), headquartered in Cincinnati, Ohio.

The SITE Program has four components:

- **Demonstration Program** – Conducts and evaluates demonstrations of promising innovative technologies to provide reliable performance, cost, and applicability information for site cleanup decision-making.
- **Emerging Technology Program** – Provides funding to developers to continue research efforts from the bench-scale and pilot-scale levels to promote the development of innovative technologies.
- **Characterization and Monitoring Program** – Evaluates technologies that detect, monitor, and measure hazardous and toxic substances to provide better, faster, and more cost-effective methods for real-time data during site characterization and remediation.
- **Technology Transfer Program** – Disseminates technical information, which includes engineering, performance, and cost data, on innovative technologies to remove impediments for using innovative technologies.

The Technology Profiles document ("Superfund Innovative Technology Evaluation Program, Technology Profiles," Ninth Edition, USEPA, Office of Research and Development, Washington DC, EPA540/R-97/502, December 1996), a product of the Technology Transfer Program, describes completed and ongoing projects in the Demonstration, Emerging, and Characterization and Monitoring Programs. Each two-page technology profile contains (1) a technology developer and process name, (2) a technology description that includes a process schematic or a photograph of the process, (3) a discussion of waste applicability, (4) a project status report, and (5) EPA project manager and technology developer contacts. The profiles also include summaries of demonstration results, if they are available. The developer prepares the technology description and waste applicability sections. The EPA prepares the status and demonstration results sections.

The Technology Profiles, Ninth Edition, was reviewed for technologies potentially applicable to shipboard liquid wastes. Those that could be applied to Navy shipboard liquid wastes (41 technologies) were selected and included in this appendix. The page numbers were preserved for reference to the original document.

The Ninth Edition is the latest version the Technology Profiles. However, each component of the SITE Program produces a series of reports and documents, and some may contain information later than that available in the Ninth Edition. Some of the reports and documents are available for review at the SITE website (www.epa.gov/ORD/SITE/).

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PROJECT DESCRIPTIONS

AMERICAN COMBUSTION, INC.
(PYRETRON® Thermal Destruction)

TECHNOLOGY DESCRIPTION:

The PYRETRON® thermal destruction technology controls the heat input during incineration by controlling excess oxygen available to oxidize hazardous waste (see figure below). The PYRETRON® combustor relies on a new technique for mixing auxiliary oxygen, air, and fuel to (1) provide the flame envelope with enhanced stability, luminosity, and flame core temperature, and (2) increase the rate of heat released.

The technology is computer-controlled to automatically adjust the temperatures of the primary and secondary combustion chambers and the amount of excess oxygen. The system adjusts the amount of excess oxygen in response to sudden changes in contaminant volatilization rates in the waste.

The technology fits any conventional incineration unit and can burn liquids, solids, and sludges. Solids and sludges can also be coincinerated when

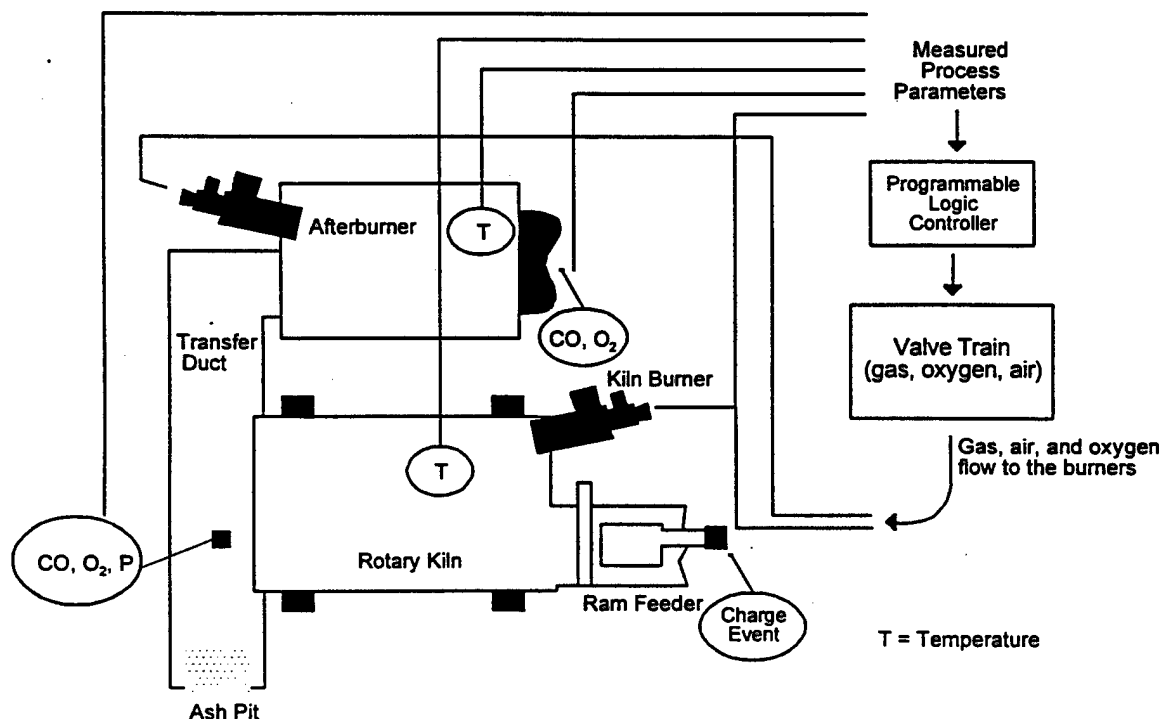
the burner is used with a rotary kiln or similar equipment.

WASTE APPLICABILITY:

The PYRETRON® technology treats high- and low-British thermal unit solid wastes contaminated with rapidly volatilized hazardous organics. In general, the technology treats any waste that can be incinerated. It is not suitable for processing Resource Conservation and Recovery Act heavy metal wastes or inorganic wastes.

STATUS:

The PYRETRON® technology was demonstrated at EPA's Incineration Research Facility in Jefferson, Arkansas, using a mixture of 40 percent contaminated soil from the Stringfellow Acid Pit Superfund site in Glen Avon, California and 60 percent decanter tank tar sludge (K087) from coking operations. The demonstration began in November 1987 and was completed at the end of January 1988.



PYRETRON® Thermal Destruction System

Both the Technology Evaluation Report (EPA/540/5-89/008) and Applications Analysis Report (EPA/540/A5-89/008) are available from EPA.

DEMONSTRATION RESULTS:

The polynuclear aromatic hydrocarbons naphthalene, acenaphthylene, fluorene, phenanthrene, anthracene, and fluoranthene were selected as the principal organic hazardous constituents (POHC) for the demonstration. The PYRETRON® technology achieved greater than 99.99 percent destruction and removal efficiencies for all six POHCs in all test runs. Other results are listed below:

- The PYRETRON® technology with oxygen enhancement doubled the waste throughput possible with conventional incineration.
- All particulate emission levels from the scrubber system discharge were significantly below the hazardous waste incinerator performance standard of 180 milligrams per dry standard cubic meter at 7 percent oxygen. This standard was in place until May 1993.

- Solid residues were contaminant-free.
- There were no significant differences in transient emissions of carbon monoxide between air-only incineration and PYRETRON® oxygen-enhanced operation with doubled throughput rate.
- Cost savings increase when operating and fuel costs are high and oxygen costs are relatively low.
- The system can double the capacity of a conventional rotary kiln incinerator. This increase is more significant for wastes with low heating values.

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BABCOCK & WILCOX CO. (Cyclone Furnace)

TECHNOLOGY DESCRIPTION:

The Babcock & Wilcox Co. (Babcock & Wilcox) cyclone furnace is designed to combust coal with high inorganic content (high-ash). Through cofiring, the cyclone furnace can also accommodate highly contaminated wastes containing heavy metals and organics in soil or sludge. High heat-release rates of 45,000 British thermal units (Btu) per cubic foot of coal and high turbulence in cyclones ensures the high temperatures required for melting the high-ash fuels and combusting the organics. The inert ash exits the cyclone furnace as a vitrified slag.

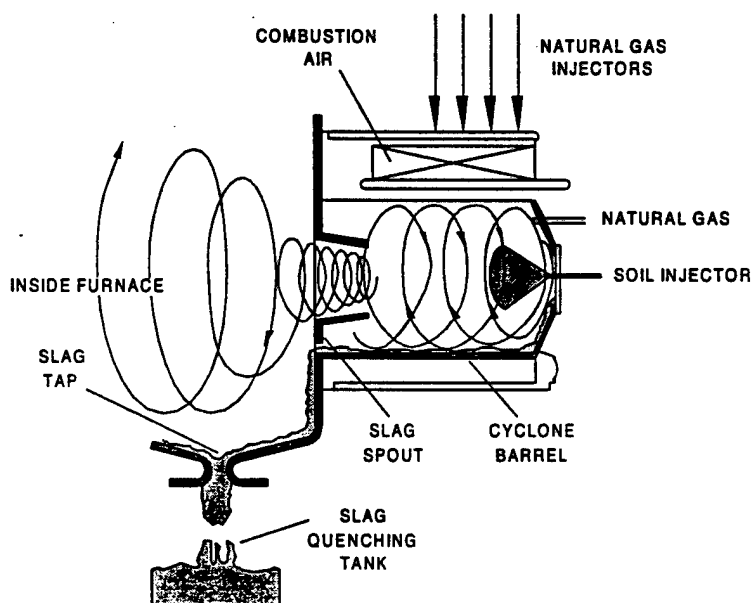
The pilot-scale cyclone furnace, shown in the figure below, is a water cooled, scaled-down version of a commercial coal-fired cyclone with a restricted exit (throat). The furnace geometry is a horizontal cylinder (barrel).

Natural gas and preheated combustion air are heated to 820 °F and enter tangentially into the cyclone burner. For dry soil processing, the soil

matrix and natural gas enter tangentially along the cyclone furnace barrel. For wet soil processing, an atomizer uses compressed air to spray the soil slurry directly into the furnace. The soil or sludge and inorganics are captured and melted, and organics are destroyed in the gas phase or in the molten slag layer. This slag layer is formed and retained on the furnace barrel wall by centrifugal action.

The soil melts, exits the cyclone furnace from the tap at the cyclone throat, and drops into a water-filled slag tank where it solidifies. A small quantity of soil also exits as fly ash with the flue gas from the furnace and is collected in a baghouse. In principle, this fly ash can be recycled to the furnace to increase metal capture and to minimize the volume of the potentially hazardous waste stream.

The energy requirements for vitrification are 15,000 Btu per pound of soil treated. The cyclone furnace can be operated with gas, oil, or coal as the supplemental fuel. If the waste is high in organic content, it may also supply a significant portion of the required fuel heat input.



Cyclone Furnace

Particulates are captured by a baghouse. To maximize the capture of particulate metals, a heat exchanger is used to cool the stack gases to approximately 200 ° F before they enter the baghouse.

WASTE APPLICABILITY:

The cyclone furnace can treat highly contaminated hazardous wastes, sludges, and soils that contain heavy metals and organic constituents. The wastes may be solid, a soil slurry (wet soil), or liquids. To be treated in the cyclone furnace, the ash or solid matrix must melt (with or without additives) and flow at cyclone furnace temperatures (2,400 to 3,000 ° F). Because the furnace captures heavy metals in the slag and renders them nonleachable, it is particularly suited to soils that contain lower-volatility radionuclides such as strontium and transuranics.

STATUS:

Based on results from the Emerging Technology Program, the cyclone furnace technology was accepted into the SITE Demonstration Program in August 1991. A demonstration occurred in November 1991 at the developer's facility in Alliance, Ohio. The process was demonstrated using an EPA-supplied, wet synthetic soil matrix (SSM) spiked with heavy metals (lead, cadmium, and chromium), organics (anthracene and dimethylphthalate), and simulated radionuclides (bismuth, strontium, and zirconium). Results from the demonstrations have been published in the *Applications Analysis Report* (EPA/520/AR-92/017) and *Technology Evaluation Report*, Volumes 1 and 2 (EPA/504/R-92/017A and EPA/540/R-92/017B); these documents are available from EPA.

DEMONSTRATION RESULTS:

Vitrified slag leachabilities for the heavy metals met EPA toxicity characteristic leaching procedure (TCLP) limits. TCLP leachabilities were 0.29 milligram per liter (mg/L) for lead, 0.12 mg/L for cadmium, and 0.30 mg/L for chromium. Almost 95 percent of the noncombustible SSM was incorporated into the slag. Greater than 75 percent

of the chromium, 88 percent of the strontium, and 97 percent of the zirconium were captured in the slag. Dry weight volume was reduced 28 percent. Destruction and removal efficiencies for anthracene and dimethylphthalate were greater than 99.997 percent and 99.998 percent, respectively. Stack particulates were 0.001 grain per dry standard cubic foot (gr/dscf) at 7 percent oxygen, which was below the Resource Conservation Recovery Act limit of 0.08 gr/dscf effective until May 1993. Carbon monoxide and total hydrocarbons in the flue gas were 6.0 parts per million (ppm) and 8.3 ppm, respectively.

An independent cost analysis was performed as part of the SITE demonstration. The cost to remediate 20,000 tons of contaminated soil using a 3.3-ton-per-hour unit was estimated at \$465 per ton if the unit is on line 80 percent of the time, and \$529 per ton if the unit is on line 60 percent of the time.

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BIOTROL®
(Biological Aqueous Treatment System)

TECHNOLOGY DESCRIPTION:

The BioTrol biological aqueous treatment system (BATS) is a patented biological system that treats contaminated groundwater and process water. The system uses naturally occurring microbes; in some instances, however, a specific microorganism may be added. This technique, known as microbial amendment, is important if a highly toxic or recalcitrant target compound is present. The amended microbial system removes both the target contaminant and the background organic carbon.

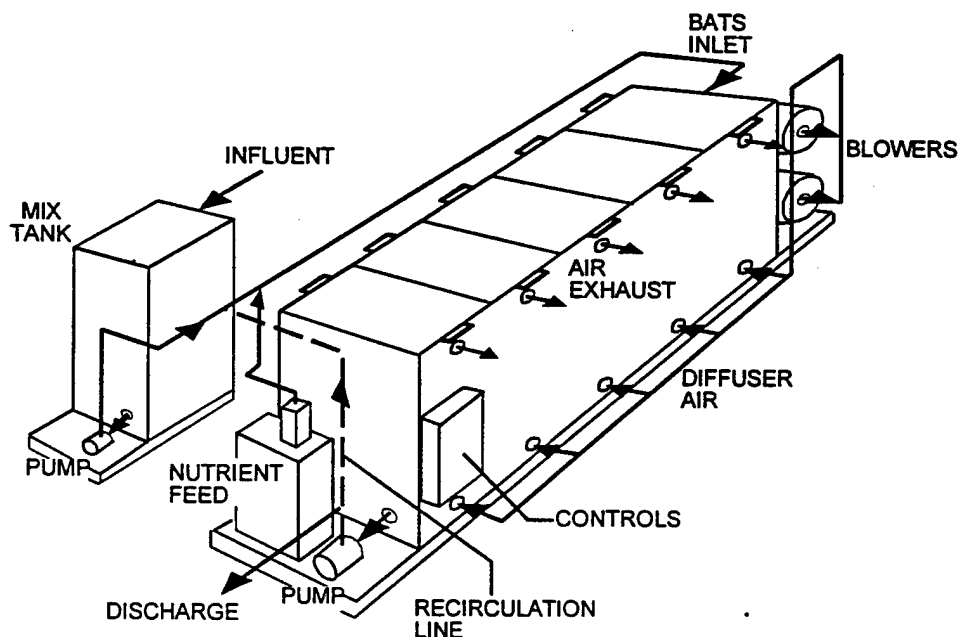
The figure below is a schematic of the BATS. Contaminated water enters a mix tank, where the pH is adjusted and inorganic nutrients are added. If necessary, the water is heated to an optimum temperature with a heater and a heat exchanger, to minimize energy costs. The water then flows to the bioreactor, where the contaminants are biodegraded.

The microorganisms that degrade the contaminants are immobilized in a multiple-cell, submerged, fixed-film bioreactor. Each cell is filled with a highly porous packing material to which the microbes adhere. For aerobic conditions, air is supplied by fine bubble membrane diffusers mounted at the bottom of each cell. The system may also run under anaerobic conditions.

As water flows through the bioreactor, the contaminants are degraded to biological end-products, predominantly carbon dioxide and water. The resulting effluent may be discharged to a publicly owned treatment works or reused on site. In some cases, discharge with a National Pollutant Discharge Elimination System permit may be possible.

WASTE APPLICABILITY:

The BATS may be applied to a wide variety of wastewaters, including groundwater, lagoons, and



BioTrol Biological Aqueous Treatment System (BATS)

process water. Contaminants amenable to treatment include pentachlorophenol (PCP), creosote components, gasoline and fuel oil components, chlorinated hydrocarbons; phenolics, and solvents. Other potential target waste streams include coal tar residues and organic pesticides. The BATS may also be effective for treating certain inorganic compounds such as nitrates; however, this application has not yet been demonstrated. The system does not treat metals.

STATUS:

The BATS was accepted into the SITE Demonstration Program in 1989. The system was demonstrated under the SITE Program from July to September 1989 at the MacGillis and Gibbs Superfund site in New Brighton, Minnesota. The system operated continuously for 6 weeks at three different flow rates. The Applications Analysis Report (EPA/540/A5-91/001), the Technology Evaluation Report (EPA/540/5-91/001), and the Demonstration Bulletin (EPA/540/M5-91/001) are available from EPA.

During 1986 and 1987, BioTrol performed a successful 9-month pilot-scale field test of the BATS at a wood preserving facility. Since that time, the firm has installed more than 20 full-scale systems and has performed several pilot-scale demonstrations. These systems have successfully treated waters contaminated with gasoline, mineral spirit solvents, phenol, and creosote.

DEMONSTRATION RESULTS:

For the SITE demonstration, the BATS yielded the following results:

- Reduced PCP concentrations from about 45 parts per million (ppm) to 1 ppm or less in a single pass
- Produced minimal sludge and no PCP air emissions
- Mineralized chlorinated phenolics
- Eliminated groundwater biotoxicity
- Appeared to be unaffected by low concentrations of oil and grease (about 50 ppm) and heavy metals in groundwater
- Required minimal operator attention

The treatment cost per 1,000 gallons was \$3.45 for a 5-gallon-per-minute (gpm) pilot-scale system and \$2.43 for a 30-gpm system.

FOR FURTHER INFORMATION:

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CALGON CARBON OXIDATION TECHNOLOGIES
(formerly VULCAN PEROXIDATION SYSTEMS, INC.)
(perox-pure™ Chemical Oxidation Technology)

TECHNOLOGY DESCRIPTION:

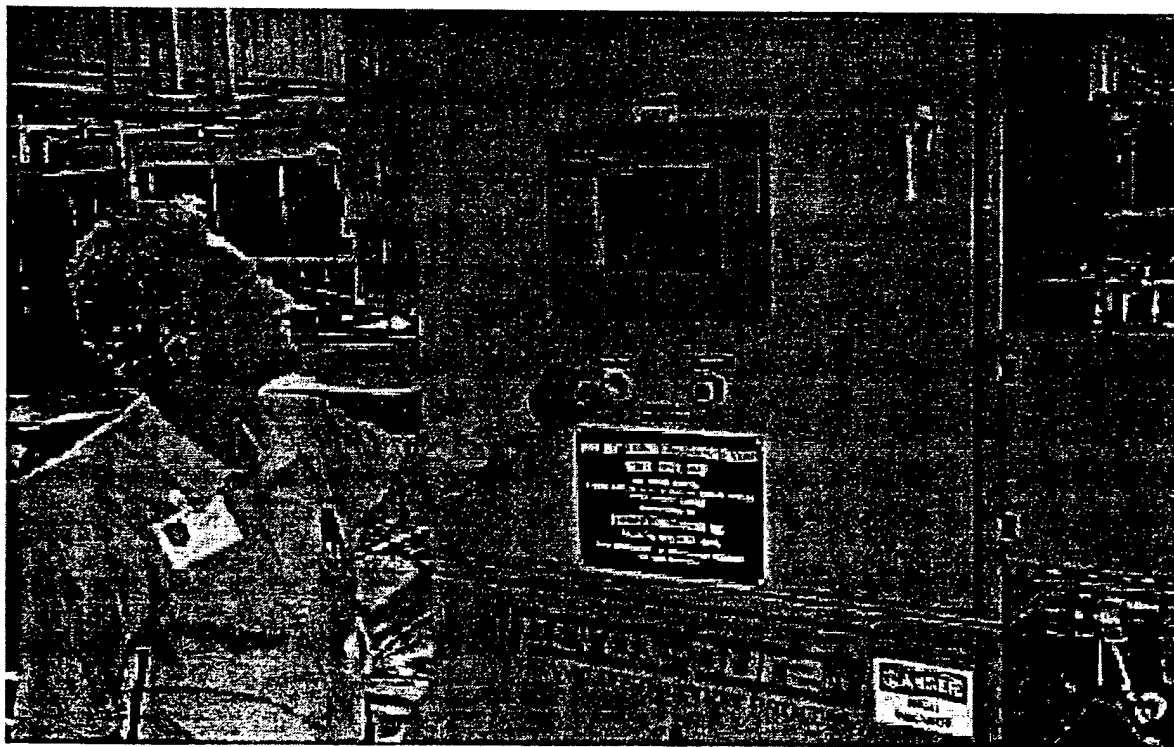
The perox-pure™ treatment system is designed to destroy dissolved organic contaminants in groundwater or wastewater with an advanced chemical oxidation process that uses ultraviolet (UV) radiation and hydrogen peroxide. Hydrogen peroxide is added to the contaminated water, and the mixture is then fed into the treatment system.

The treatment system's oxidation section contains one or more reaction chambers. Each chamber contains one high-intensity UV lamp mounted in a quartz sleeve. The contaminated water flows in the space between the chamber wall and the quartz sleeve in which each UV lamp is mounted. The perox-pure™ equipment includes circular wipers attached to the quartz sleeves. These wipers periodically remove solids that may accumulate on the sleeves, a feature designed to maintain maximum treatment efficiency.

UV light catalyzes chemical oxidation of organic contaminants in water by affecting the organics so they react with hydrogen peroxide. Many organic contaminants that absorb UV light change chemically or become more reactive with chemical oxidants. More importantly, UV light catalyzes hydrogen peroxide breakdown to produce hydroxyl radicals, which are powerful chemical oxidants. Hydroxyl radicals react with and destroy organic contaminants, ultimately producing harmless by-products such as carbon dioxide, halides, and water. The treatment system produces no air emissions.

WASTE APPLICABILITY:

The perox-pure™ technology treats groundwater and wastewater contaminated with chlorinated solvents, pesticides, polychlorinated biphenyls, phenolics, ethers, fuel hydrocarbons, and other organic compounds. It is effective on



perox-pure™ Model SSB-30

concentrations ranging from low parts per billion to several hundred parts per million (ppm). In certain instances, when used in conjunction with photocatalysts, it can be competitive for contaminated concentrations of several thousand ppm. In some cases, the combination of the **perox-pure™** technology with activated carbon, air stripping, or biological treatment will provide a more economical approach than would be obtained by using only one technology.

STATUS:

The **perox-pure™** technology was accepted into the SITE Demonstration Program in April 1991. A Model SSB-30 (see photograph on previous page) was demonstrated in September 1992 at the Lawrence Livermore National Laboratory Superfund site in Altamont Hills, California. The purpose of this demonstration was to measure how well the **perox-pure™** technology removed volatile organic compounds from contaminated groundwater at the site. The Demonstration Bulletin (EPA/540/MR-93/501), Technology Demonstration Summary (EPA/540/SR-93/501), Applications Analysis Report (EPA/540/AR-93/501), and Technology Evaluation Report (EPA/540/R-93/501) are available from EPA.

This technology has been successfully applied to over 150 sites throughout the United States, Canada, the Far East, and Europe. The treatment units at these sites have treated contaminated groundwater, industrial wastewater, contaminated drinking water, landfill leachates, and industrial reuse streams (process waters). Equipment treatment rates range from several gallons to several thousand gallons per minute.

DEMONSTRATION RESULTS:

Operating parameters for the treatment system were varied during the demonstration. Three reproducibility tests were performed at the optimum operating conditions, which were selected from the initial test runs.

In most cases, the **perox-pure™** technology reduced trichloroethene, tetrachloroethene, chloroform, trichloroethane, and dichloroethane to below analytical detection limits. For each organic contaminant, the **perox-pure™** technology complied with California action levels and federal drinking water maximum contaminant levels at the 95 percent confidence level. The quartz sleeve wipers effectively cleaned the sleeves and eliminated the interference caused by tube scaling.

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CF SYSTEMS CORPORATION
(Liquified Gas Solvent Extraction [LG-SX] Technology)

TECHNOLOGY DESCRIPTION:

The CF Systems Corporation (CF Systems) liquified gas solvent extraction (LG-SX) technology uses liquified gas solvents to extract organics from soils, sludges, sediments, and wastewaters. Gases, when liquified under pressure, have unique physical properties that enhance their use as solvents. The low viscosities, densities, and surface tensions of these gases result in significantly higher rates of extraction compared to conventional liquid solvents. These enhanced physical properties also accelerate treated water's gravity settling rate following extraction. Due to their high volatility, gases are also easily recovered from the suspended solids matrix, minimizing solvent losses.

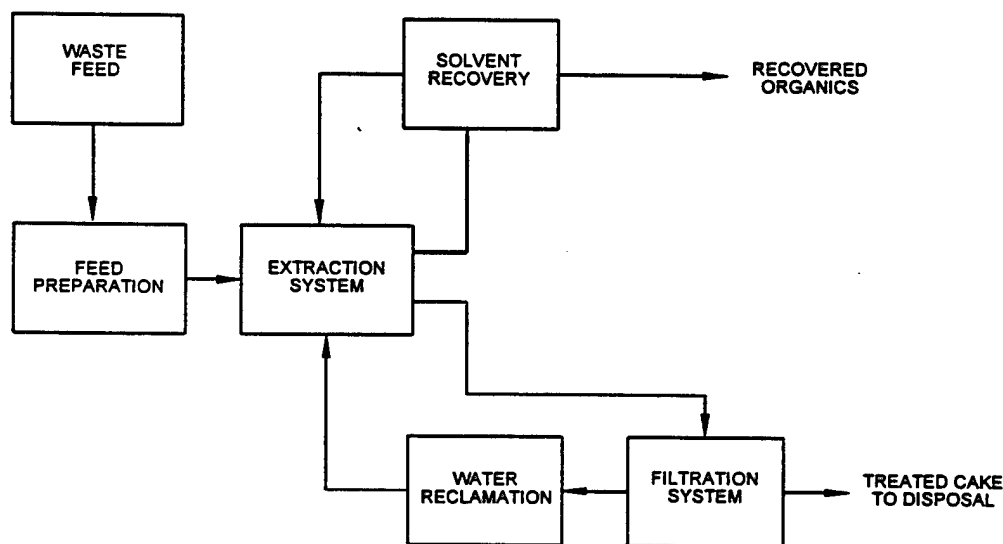
Liquified propane solvent is typically used to treat soils, sludges, and sediments, while liquified carbon dioxide is typically used to treat wastewater. The extraction system uses a batch extractor-decanter design for solids and sludges and a continuous trayed tower design for waste-waters and low-solids wastes. Typical treatment costs for non-pumpable soils and sludges range

from \$80 to \$300 per ton of feed, excluding excavation and disposal.

Contaminated solids, slurries, or wastewaters are fed into the extraction system along with solvent (see figure below). Typically, more than 99 percent of the organics are extracted from the feed. After the solvent and organics are separated from the treated feed, the solvent and organic mixture passes to the solvent recovery system. Once in the solvent recovery system, the solvent is vaporized and recycled as fresh solvent. The organics are drawn off and either reused or disposed of. Treated feed is discharged from the extraction system as a slurry. The slurry is filtered and dewatered. The reclaimed water is recycled to the extraction system and the filter cake is sent to disposal or reused.

WASTE APPLICABILITY:

The LG-SX technology can be applied to soils and sludges containing volatile and semivolatile organic compounds and other higher boiling point complex organics, such as polynuclear aromatic hydrocarbons (PAH), polychlorinated biphenyls



Liquified Gas Solvent Extraction (LG-SX) Technology

(PCB), dioxins, and pentachlorophenol (PCP). This process can also treat refinery wastes and wastewater contaminated with organics.

STATUS:

This technology was accepted into the SITE Demonstration Program in 1988. Under the SITE Program, a pilot-scale mobile demonstration unit was tested in September 1988 on PCB-laden sediments from the New Bedford Harbor Superfund site in Massachusetts. PCB concentrations in the harbor sediment ranged from 300 parts per million (ppm) to 2,500 ppm. The Technology Evaluation Report (EPA/540/5-90/002) and the Applications Analysis Report (EPA/540/A5-90/002) are available from EPA.

A pilot-scale treatability study was completed on PCB-contaminated soil from a Michigan Superfund site. Analytical data showed that the treatment reduced PCB levels to below 5 ppm, representing a 98 percent removal efficiency for this waste. A Project Summary (EPA/540/SR-95/505), which details results from this work, is available from EPA.

CF Systems completed the first commercial on-site treatment operation at Star Enterprise in Port Arthur, Texas. The propane-based solvent extraction unit processed listed refinery K- and F-wastes, producing Resource Conservation and Recovery Act treated solids that met EPA land-ban requirements. The unit operated continuously from March 1991 to March 1992 and was on-line more than 90 percent of the time. Following heavy metals fixation, the treated solids were disposed of in a Class I landfill.

EPA Region 6 and the Texas Natural Resources Conservation Commission selected the LG-SX technology to clean an estimated 115,000 tons of contaminated soil at the United Creosoting Superfund Site in Conroe, Texas. The 250 tons per day unit is on site and is anticipated to begin full scale operation in December 1996. The soil is contaminated with PAHs, PCP, and chlorinated isomers of furan and dioxin.

DEMONSTRATION RESULTS:

This technology was demonstrated concurrently with dredging studies managed by the U.S. Army Corps of Engineers. Contaminated sediments were treated by the LG-SX technology, using a liquified propane and butane mixture as the extraction solvent. The demonstration at the New Bedford site yielded the following results:

- Extraction efficiencies were 90 to 98 percent for sediments containing PCBs between 360 and 2,575 ppm. PCB concentrations were as low as 8 ppm in the treated sediment.
- Volatile and semivolatile organics in aqueous and semisolid wastes were extracted with 99.9 percent efficiency.
- Operating problems included solids retention in the system hardware and foaming in receiving tanks. The problems were corrected in the full-scale operations at Star Enterprise.
- Projected costs for PCB cleanup were estimated at \$150 to \$450 per ton, including material handling and pre- and posttreatment costs. These costs are highly dependent on the utilization factor and job size, which may result in lower costs for large cleanups.

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DEHYDRO-TECH CORPORATION

(Carver-Greenfield Process® for Solvent Extraction of Wet, Oily Wastes)

TECHNOLOGY DESCRIPTION:

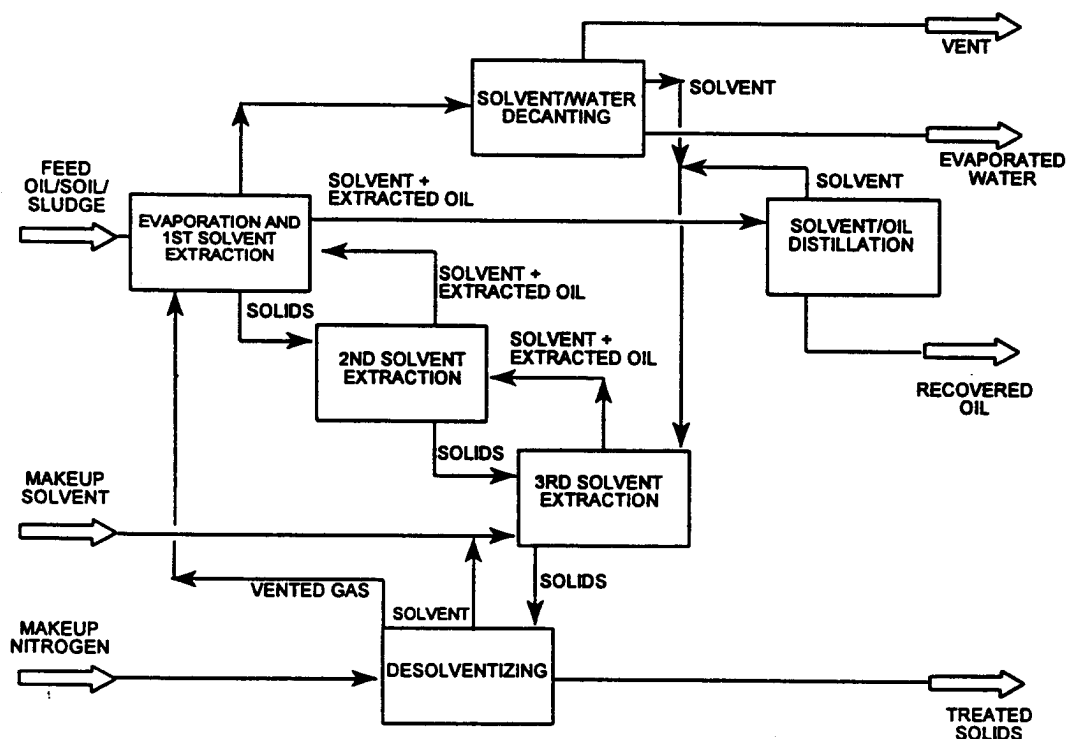
The Carver-Greenfield Process® (C-G Process™) combines dehydration and solvent extraction technologies to separate wet, oily wastes into their constituent solid, water, and oil phases (see figure below).

Waste is first mixed with a low-cost hydrocarbon solvent. The resultant slurry mixture is fed to an evaporator system that vaporizes water and initiates solvent extraction of the indigenous oil. Depending on the water content of the feed, single-effect or energy-saving multi-effect evaporators may be used. Next, the slurry of dried solids is treated in a multistage solvent extraction unit, where solids contact recycled solvent until the target amount of indigenous oil is removed.

Finally, solids are centrifuged away from the solvent, followed by "desolventizing," an operation that evaporates residual solvent. The final solids product typically contains less than 2 percent water and less than 1 percent solvent. The spent solvent, which contains the extracted indigenous oil, is distilled to separate the solvent for reuse, and the oil for recovery or disposal.

The C-G Process yields (1) a clean, dry solid; (2) a water product virtually free of solids, indigenous oil, and solvent; and (3) the extracted indigenous oil, which contains the hazardous hydrocarbon-soluble feed components.

The C-G Process combination of dehydration and solvent extraction has the following advantages: (1) any emulsions initially present are broken and



Carver-Greenfield Process® Schematic Diagram

potential emulsion formation is prevented; (2) solvent extraction is more efficient because water is not present; and (3) the dry solids product is stabilized more readily if required (for example, if metals contamination is a concern).

WASTE APPLICABILITY:

The C-G Process can treat sludges, soils, sediments, and other water-bearing wastes containing hydrocarbon-soluble hazardous compounds, including polychlorinated biphenyls, polynuclear aromatic hydrocarbons, and dioxins. The process has been commercially applied to municipal wastewater sludge, paper mill sludge, rendering waste, pharmaceutical plant sludge, and other wastes.

STATUS:

The C-G Process was accepted into the SITE program in 1990. The pilot-scale SITE demonstration of this technology was completed in August 1991 at EPA's research facility in Edison, New Jersey. Spent petroleum drilling fluids from the PAB oil site in Abbeville, Louisiana were used as process feed. The Applications Analysis Report (EPA/540/AR-92/002), Technology Demonstration Summary (EPA/540/SR-92/002), and Technology Evaluation Report (EPA/540/R-92/002) are available from EPA.

DEMONSTRATION RESULTS:

The SITE demonstration of the C-G Process yielded the following results:

- The process successfully separated the petroleum-contaminated sludge into its solid, indigenous oil, and water phases. No detectable levels of indigenous total petroleum hydrocarbons were present in the final solid product.

- The final solid product was a dry powder similar to bentonite. A food-grade solvent comprised the bulk of the residual hydrocarbons in the solid.
- Values for all metals and organics were well below the Resource Conservation and Recovery Act toxicity characteristic leaching procedure limits for characteristic hazardous wastes.
- The resulting water product required treatment due to the presence of small amounts of light organics and solvent. Normally, it may be disposed of at a local publicly owned treatment works.
- A full-scale C-G Process can treat drilling fluid wastes at technology-specific costs of \$100 to \$220 per ton of wet feed, exclusive of disposal costs for the residuals. Site-specific costs, which include the cost of residual disposal, depend on site characteristics and treatment objectives.

FOR FURTHER INFORMATION:

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**E.I. DUPONT DE NEMOURS AND COMPANY, and
OBERLIN FILTER COMPANY**
(Membrane Microfiltration)

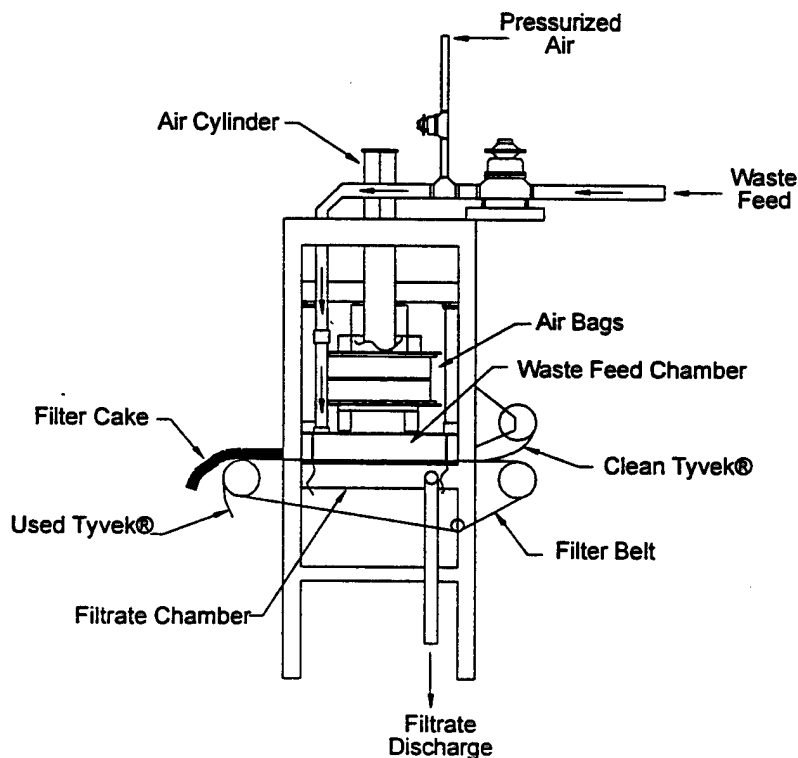
TECHNOLOGY DESCRIPTION:

This membrane microfiltration system is designed to remove solid particles from liquid wastes, forming filter cakes typically ranging from 40 to 60 percent solids. The system can be manufactured as an enclosed unit, requires little or no attention during operation, is mobile, and can be trailer-mounted.

The membrane microfiltration system uses an automatic pressure filter (developed by Oberlin Filter Company), combined with a special Tyvek® filter material (Tyvek® T-980) made of spun-bonded olefin (invented by E.I. DuPont de Nemours and Company) (see figure below). The filter material is a thin, durable plastic fabric with tiny openings about 1 ten-millionth of a meter in diameter. These openings allow water or other liquids and solid particles smaller than the openings to flow through. Solids in the liquid stream that are too large to pass through the openings

accumulate on the filter and can be easily collected for disposal.

The automatic pressure filter has two chambers: an upper chamber for feeding waste through the filter, and a lower chamber for collecting the filtered liquid (filtrate). At the start of a filter cycle, the upper chamber is lowered to form a liquid-tight seal against the filter. The waste feed is then pumped into the upper chamber and through the filter. Filtered solids accumulate on the Tyvek® surface, forming a filter cake, while filtrate collects in the lower chamber. Following filtration, air is fed into the upper chamber at a pressure of about 45 pounds per square inch. Air removes any liquid remaining in the upper chamber and further dries the filter cake. When the filter cake is dry, the upper chamber is lifted, and the filter cake is automatically discharged. Clean filter material is then drawn from a roll into the system for the next cycle. Both the filter cake and the filtrate can be collected and



Membrane Microfiltration System

treated further before disposal, if necessary.

WASTE APPLICABILITY:

This membrane microfiltration system may be applied to (1) hazardous waste suspensions, particularly liquid heavy metal- and cyanide bearing wastes (such as electroplating rinsewaters), (2) groundwater contaminated with heavy metals, (3) constituents in landfill leachate, and (4) process wastewaters containing uranium. The technology is best suited for treating wastes with solids concentrations of less than 5,000 parts per million; otherwise, the cake capacity and handling become limiting factors. The system can treat any type of solids, including inorganics, organics, and oily wastes, with a wide variety of particle sizes. Moreover, because the system is enclosed, it can treat liquid wastes that contain volatile organics.

STATUS:

The membrane microfiltration system, accepted into the SITE Program in 1988, was demonstrated at the Palmerton Zinc Superfund site in Palmerton, Pennsylvania. The demonstration was conducted over a 4-week period in April and May 1990. Groundwater from the shallow aquifer at the site was contaminated with dissolved heavy metals, including cadmium, lead, and zinc. This contaminated groundwater served as the feed waste for the demonstration. The system treated waste at a rate of about 1 to 2 gallons per minute.

The Applications Analysis Report (EPA/540/A5-90/007), the Technology Evaluation Report (EPA/540/5-90/007), and a videotape of the demonstration are available from EPA.

Since 1991, about 12 commercial installations of the technology have been operational.

DEMONSTRATION RESULTS:

During the demonstration at the Palmerton Zinc Superfund site, the membrane microfiltration system achieved the following results:

- Removal efficiencies for zinc and total suspended solids ranged from 99.75 to 99.99 percent (averaging 99.95 percent).
- Solids in the filter cake ranged from 30.5 to 47.1 percent.
- Dry filter cake in all test runs passed the Resource Conservation and Recovery Act paint filter liquids test.
- Filtrate met the applicable National Pollutant Discharge Elimination System standards for cadmium, lead, zinc, and total suspended solids.
- A composite filter cake sample passed the extraction procedure toxicity and toxicity characteristic leaching procedure tests for metals.

FOR FURTHER INFORMATION:

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WASTE APPLICABILITY:

The Sponge can scavenge metals in concentration levels of parts per million and parts per billion from industrial discharges, municipal sewage, process streams, and acid mine drainage. The Sponge is particularly useful when treating water with low contaminant levels, especially in polishing or end-of-pipe treatments. Because of the low capital investment required, the Sponge is well-suited for use in short-term remediation projects and for sporadic flows conditions.

STATUS:

This technology was accepted into the SITE Demonstration Program in June 1991. The Sponge was demonstrated in April 1994 at the National Lead Industry site in Pedricktown, New Jersey. The Demonstration Bulletin (EPA/540/MR-94/522), Technology Capsule (EPA/540/R-94/522a), and Innovative Technology Evaluation Report (EPA/540/R-94/522) are available from EPA.

The Sponge has also effectively removed trace heavy metals from acid mine drainage at three locations in Colorado. In bench-scale tests, the Sponge reduced mercury, lead, nickel, cadmium, and chromium in groundwater from various Superfund locations to below detectable levels. The Sponge was also demonstrated in a field-scale installation at a photoprocessing operation. The process reduced chromate and silver by 75 percent at a cost of \$1,100 per month. In bench-scale tests, the Sponge

has removed lead, mercury, and copper from pourable sludges such as simulated municipal sewage, and from soils slurried with water.

DEMONSTRATION RESULTS:

Treatment performance from the SITE demonstration was as follows:

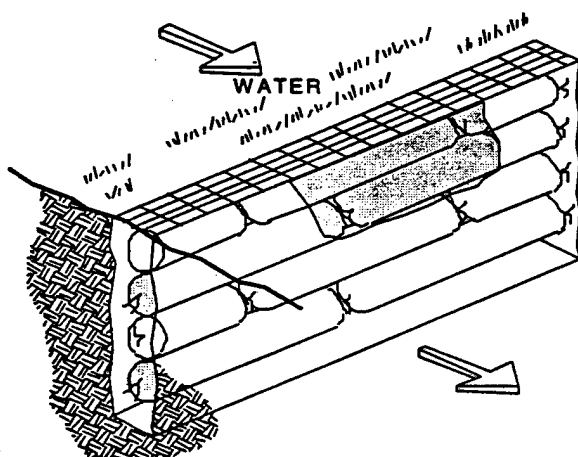
Analyte	Average Influence Concentration ($\mu\text{g/L}$)	Percent Removal
Cadmium	537	90
Copper	917	97
Lead	578	97
Chromium ^{III}	426	32

In 1996, the Sponge, configured in a column, was employed in a pump-and-treat remediation of 360,000 gallons of water that had accumulated as a result of a fuel handling operation. The water, containing 0.2 parts per million (ppm) arsenic, was treated at 12 gallons per minute (0.1 bed volume per minute) to produce an effluent having a nondetect level of arsenic.

FOR FURTHER INFORMATION:

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Fishnet Bags Placed Horizontally in a Trench

ELI ECO LOGIC INTERNATIONAL INC.
(Gas-Phase Chemical Reduction Process)

TECHNOLOGY DESCRIPTION:

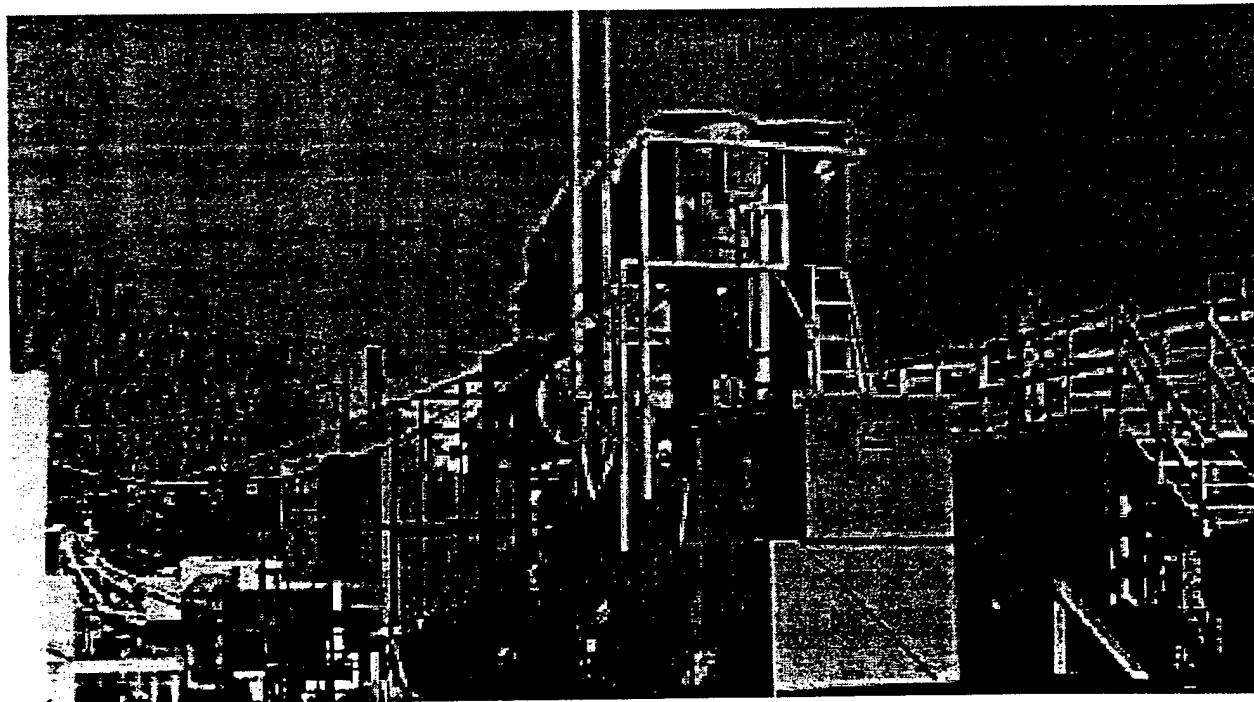
The patented ELI Eco Logic International Inc. (Eco Logic), process (see photograph below) uses a gas-phase reduction reaction of hydrogen with organic and chlorinated organic compounds at elevated temperatures to produce a hydrocarbon-rich gas product. During the SITE demonstration, soils were pretreated within Eco Logic's thermal desorption unit (TDU), which was operated in conjunction with the reduction reactor. For further information on Eco Logic's TDU, see the profile in the Demonstration Program section (completed projects).

The gas-phase reduction reaction takes place within a specially designed reactor at ambient pressure. Separate nozzles inject gaseous atomized waste, steam, and hydrogen into the reactor. As the mixture swirls down between the outer reactor wall and a central ceramic tube, it passes a series of electric glo-bar heaters, raising the temperature to 850 °C. The reduction reaction takes place as the

gases enter the ceramic tube through inlets at the bottom of the tube and travel up toward the scrubber. The scrubber removes hydrogen chloride, heat, water, and particulate matter. If necessary, scrubber liquid may be recycled through the system for additional treatment.

For waste with a low organic content, the majority of the hydrogen-rich gas recirculates to the reactor; the remainder can be used as a supplementary fuel for a propane-fired boiler that produces steam. Processing waste with a high organic content produces excess gas product, which can be compressed and stored for later analysis and reuse as supplementary fuel.

The unit is mounted on two standard, drop-deck, highway trailers. A computerized process control system allows the operator to monitor process variables such as temperature, pressure, hydrogen content, and oxygen levels. In addition, an on-line mass spectrometer is used to continually monitor selected organic compounds.



Gas-Phase Chemical Reduction Process

WASTE APPLICABILITY:

The Eco Logic process is designed to treat aqueous and oily waste streams and soil or sludge contaminated with hazardous organic waste such as polychlorinated biphenyls (PCB), polynuclear aromatic hydrocarbons, chlorinated dioxins and dibenzofurans, chlorinated solvents, chlorobenzenes, and chlorophenols. Wastes with high water content are easily handled by the process since water is a good source of hydrogen.

STATUS:

In October and November 1992, the Eco Logic process was demonstrated at the Middleground Landfill in Bay City, Michigan, under a Toxic Substances Control Act research and development permit. The demonstration was conducted in cooperation with Environment Canada and the Ontario Ministry of the Environment. The test was performed using PCB-contaminated wastewater, waste oil, and soil from the site. The Demonstration Bulletin (EPA/540/MR-93/522) and the Applications Analysis Report (EPA/540/AR-93/522) are available from EPA.

Since the SITE demonstration, Eco Logic has developed a commercial-scale system (the SE25) which is designed to treat 100 to 300 tons per day of contaminated soil or sediment and 20 tons per day of PCB liquid. The SE25 combines the reduction reactor, which treats PCB oils and aqueous wastes, with a redesigned TDU, which treats contaminated soils and sediments and an SBV for treating bulk solids such as electrical equipment, drums, and personal protective equipment.

Two commercial-scale SE25 treatment units are currently in operation; one in Perth, Western Australia, and the other at a General Motors of Canada Ltd (GMCL) facility in Ontario. Both are currently treating a variety of waste matrices, including DDT residues and PCBs in soil, oils, electrical equipment, concrete, and other solids. Following the GMCL project, the unit will be relocated to Toronto, Ontario where General Electric (GE) and Eco Logic have a contract to destroy PCB-impacted materials stored

aboveground at GE's Lansdowne and Davenport facility. Eco Logic has also been awarded a contract through the Department of Energy's Morgantown Energy Technology Center for treatment of hazardous wastes, radioactive mixed low-level wastes, and energetics-explosives.

DEMONSTRATION RESULTS:

During the demonstration, two separate waste feed conditions were used: (1) wastewater containing an average PCB concentration of 4,600 parts per million, and (2) waste oil containing an average PCB concentration of 24.5 percent. Both feeds were tested in triplicate. The demonstration of the Eco Logic process yielded the following results:

- At least 99.99 percent destruction and removal efficiency for PCBs during all runs
- A 99.99 percent destruction efficiency for perchloroethylene, a tracer compound, during all runs
- Net destruction of trace feedstock dioxin and furan compounds during all runs

FOR FURTHER INFORMATION:

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EPOC WATER, INC.
(Precipitation, Microfiltration, and Sludge Dewatering)

TECHNOLOGY DESCRIPTION:

The precipitation, microfiltration, and sludge dewatering treatment uses a combination of processes to treat a variety of wastes. In the first step of the process, heavy metals are chemically precipitated. Precipitates and all particles larger than 0.2 micron are filtered through a unique tubular textile crossflow microfilter (EXXFLOW). The concentrate stream is then dewatered in a filter press of the same material.

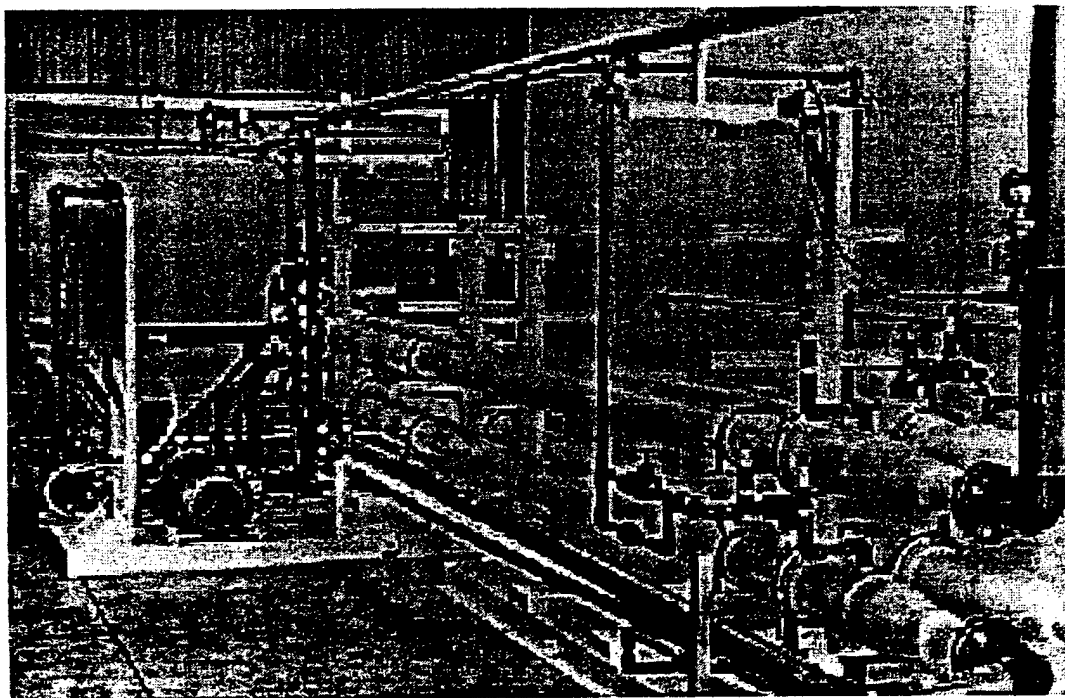
EXXFLOW microfilter modules are fabricated from a proprietary tubular woven polyester. Wastes pumped into the polyester tubes form a dynamic membrane, which produces a high quality filtrate and removes all particle sizes larger than 0.2 micron. The flow velocity continually maintains the membrane, maximizing treatment efficiency.

Metals are removed through precipitation by adjusting the pH in the EXXFLOW feed tank. Metal hydroxides or oxides form a dynamic

membrane with any other suspended solids. The EXXFLOW concentrate stream, which contains up to 5 percent solids, is then dewatered. A semidry cake, up to 0.25 inch thick, is formed inside the tubular filter. When the discharge valve is opened, rollers on the outside of the tubes move to form a venturi within the tubes. The venturi creates an area of high velocity within the tubes, which aggressively cleans the cloth and discharges the cake in chip form onto a wedge wire screen. Discharge water is recycled to the feed tank. Filter cakes are typically 40 to 60 percent solids by weight.

Constituents other than metals can be removed using seeded slurry methods in EXXFLOW. Hardness can be removed by using lime. Oil and grease can be removed by adding adsorbents. Nonvolatile organics and solvents can be removed using adsorbents, activated carbon, or powdered ion-exchange resins.

The EXXFLOW demonstration unit (see photograph below) is transportable and is



EXXFLOW Demonstration Unit

mounted on skids. The unit is designed to process approximately 30 pounds of solids per hour and 10 gallons of wastewater per minute.

WASTE APPLICABILITY:

When flocculation and precipitation techniques are used at close to stoichiometric dosing rates, the EXXFLOW technology removes mixed metals, oil and grease, and suspended solids sized at 0.10 micron.

When the EXXFLOW technology operates with finely divided adsorbent powders, it removes contaminants such as isophthalic acid, acetic acid, methyl ethyl ketone, fluorides, and phosphates from effluents generated by semiconductor manufacture. Treated effluents can then be reclaimed for reuse.

STATUS:

This technology was accepted into the SITE Demonstration Program in 1989. Bench-scale tests were conducted in 1990. The SITE demonstration was conducted during May and June 1992 on highly acidic mine drainage from the Old Number 8 mine seep at the Iron Mountain Superfund site in Redding, California. The Demonstration Bulletin (EPA/540/MR-93/513) and the Applications Analysis Report (EPA/540/AR-93/513) are available from EPA.

This technology was commercialized in 1988. Treatment systems have since been installed at over 45 sites worldwide. System capacities range from 1 gallon per minute to over 2 million gallons per day.

DEMONSTRATION RESULTS:

During the SITE Demonstration, developer claims for metal removal efficiencies on acid mine drainage, when neutralizing with sodium hydroxide (NaOH) and calcium hydroxide $[\text{Ca}(\text{OH})_2]$, were generally met or exceeded except for aluminum. This was most likely due to excessive alkalinity (high pH) produced by the added NaOH and $\text{Ca}(\text{OH})_2$, which redissolved the aluminum. The claims for all metals, including aluminum, were exceeded when magnesium oxide (MgO) was used as the neutralizing agent. In most cases, no detectable concentrations of heavy metals were present in the permeate samples.

Filter cake produced from the demonstration test contained approximately 12 percent, 31 percent, and 30 percent solids when NaOH, $\text{Ca}(\text{OH})_2$, and MgO, respectively, were used as the treatment chemicals. Toxicity characteristic leaching procedure (TCLP) tests performed on the filter cake showed that leachable levels of TCLP metals were below regulatory limits for each treatment chemical tested.

FOR FURTHER INFORMATION:

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FILTER FLOW TECHNOLOGY, INC.
(Colloid Polishing Filter Method®)

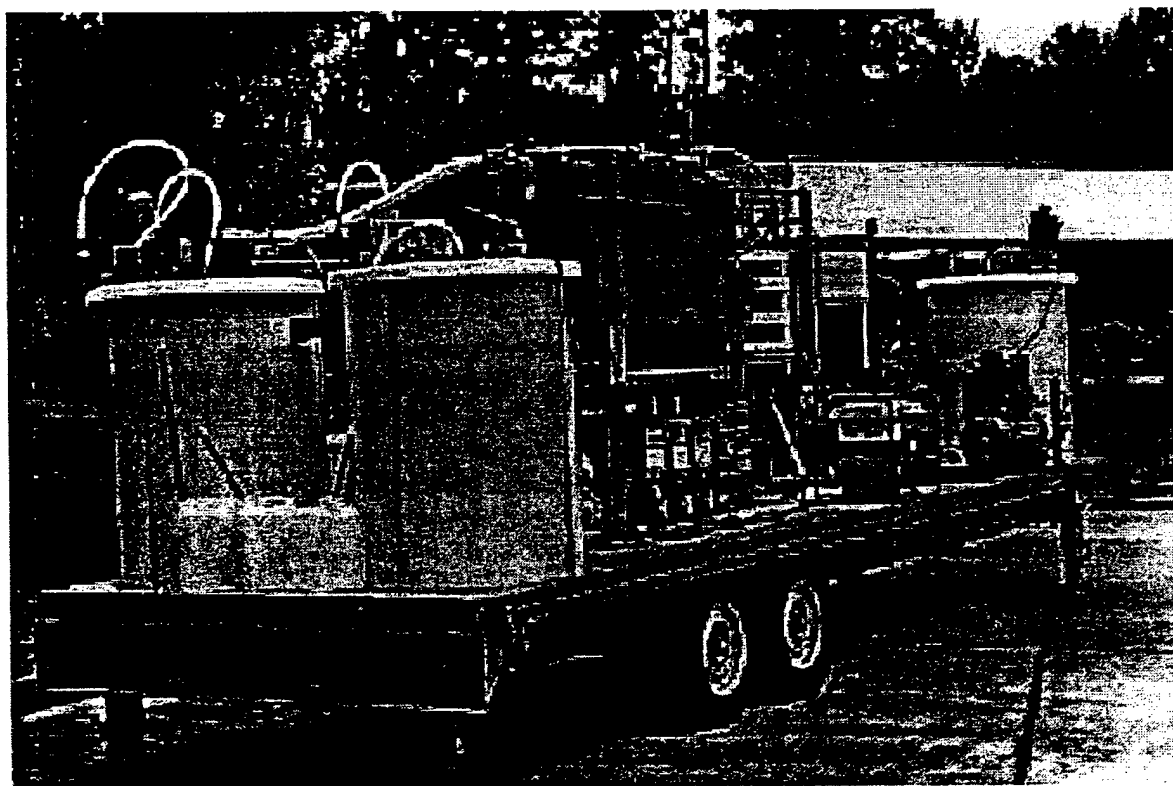
TECHNOLOGY DESCRIPTION:

The Colloid Polishing Filter Method® (CPFM®) uses inorganic, oxide-based sorption particles (FF-1000®) and optimized fluidics control to remove ionic, colloidal heavy metals and nontritium radionuclides from water. Beta- and alpha-emitting radionuclides can be treated selectively by modifying the bed formulation. The methodology efficiently removes inorganics from groundwater, pond water, or wastewater based on sorption, chemical and physical properties of the pollutant species, and filtration. The CPFM® is also an efficient heavy metals and radionuclide polishing filter for groundwater and wastewater. Excess solids and total dissolved solids must be removed first, since they overload the beds, resulting in frequent bed backwashing and regeneration cycles and shorter bed lifetimes.

Three different types of CPFM® equipment have been designed and successfully tested: (1) vertical plate design beds with FF-1000® sorption bed particles packaged in polymesh bags or filter packs for field applications; (2) small, filter-housing units for processing less than 1,000 gallons of contaminated water; and (3) deep-bed, epoxy-coated, stainless steel and carbon steel tanks equipped with special fluidics controls and bed sluicing ports for continuous processing. The photograph below shows a mobile CPFM® unit.

WASTE APPLICABILITY:

The CPFM® efficiently removes heavy metals and nontritium radionuclides from water to parts per million or parts per billion levels. This simple methodology can be used separately to treat water



Mobile CPFM® Unit, Including Mixing Tanks,
Pumps, Filter Apparatus, and Other Equipment

with low total suspended solids; in a treatment train downstream from other technologies such as soil washing or organic oxidation; or as a conventional wastewater treatment that uses flocculation and solids removal.

The CPFM®'s major advantages are its high performance; alpha and beta emitter efficiency; and its application to monovalent, divalent, multivalent, and high valence forms existing as colloids, and ionic, chelated, and complexed forms. The same equipment can treat water at different sites, but the preconditioning chemistry and pH must be optimized for each site through bench-scale and field testing.

STATUS:

This technology was accepted into the SITE Demonstration Program in July 1991. EPA and the U.S. Department of Energy (DOE) cosponsored the technology evaluation. The SITE demonstration occurred in September 1993 at DOE's Rocky Flats Plant (RFP) in Denver, Colorado. The Demonstration Bulletin (EPA/540/MR-94/501), Technology Capsule (EPA/540/R-94/501a), and Innovative Technology Evaluation Report (EPA/540/R-94/501) are available from EPA.

The CPFM has been demonstrated independent of the SITE Program at two locations at DOE's Hanford facility, where it removed Strontium-90, Cesium-137, Plutonium-239, and Americium-241 from water at K-Basin and Strontium-90 from groundwater at Site 100N Area (N-Spring). A report detailing the results is available from DOE (DOE/RL-95-110).

DEMONSTRATION RESULTS:

During the SITE demonstration, the CPFM® treated about 10,000 gallons of water that contained about 100 micrograms per liter of uranium and 100 picoCuries per liter of gross alpha contamination. The demonstration consisted of three tests. The first test consisted of three 4-hour runs, at a flow rate of about 5 gallons per minute (gpm). For the second test, also run for 4 hours at 5 gpm, the influent water was pretreated with sodium sulfide. The third test

was a 15-hour run designed to determine the amount of contamination each filter pack could treat.

The CPFM® system removed up to 95 percent uranium and 94 percent gross alpha contamination. However, due to the significant variation in removal efficiencies between runs, average removal efficiencies were significantly less: 80 percent for uranium and 72 percent for gross alpha. Though removal is largely attributable to the colloid filter pack, uranium was significantly removed in runs one and four before colloid filter treatment. Significant gross alpha was also removed before colloid filter treatment in runs one and three. At less than the maximum removal efficiency, effluent from the CPFM® system did not meet the Colorado Water Quality Control Commission standards for discharge of waters from RFP.

FOR FURTHER INFORMATION:

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GENERAL ENVIRONMENTAL CORPORATION
(formerly HYDROLOGICS, INC.)
(CURE®-Electrocoagulation Wastewater Treatment System)

TECHNOLOGY DESCRIPTION:

The CURE®-Electrocoagulation (CURE®) system is designed to remove ionic metal species and other charged particles from water (see figure below). Because many toxic metal ions such as nickel, lead, and chromates are held in solution by electrical charges, they will precipitate out of solution if they are neutralized with oppositely charged ions. The CURE® system is effective at breaking oily emulsions and removing suspended solids. The system improves on previous electrocoagulation methods through a unique geometrical configuration.

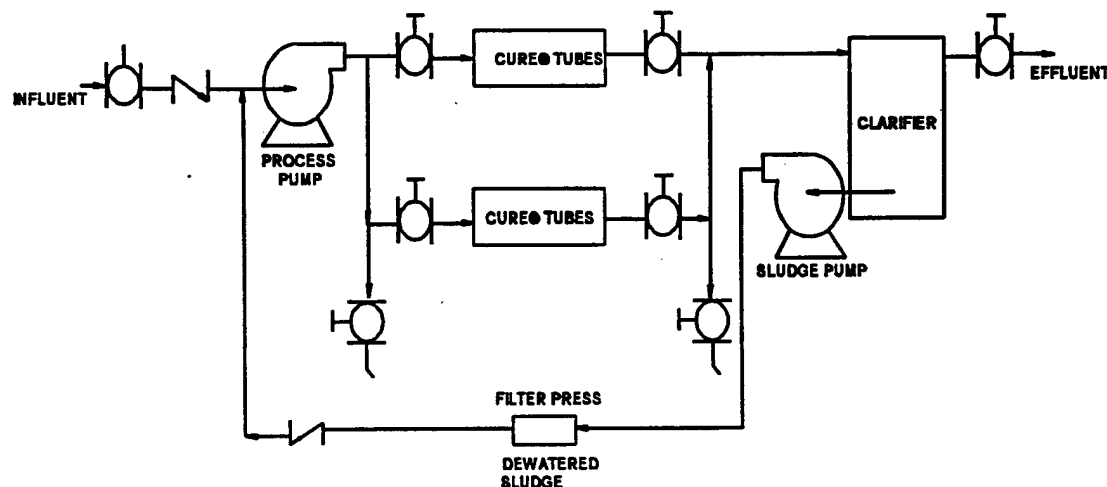
The CURE® system's patented geometry maximizes liquid surface contact between the anode and concentric cathode electrocoagulation tubes, thus minimizing the power requirements for efficient operation. The CURE® system allows the contaminated water to flow continuously through the cathode tube, enabling a direct current to pass uniformly through a water stream. The contaminated water then passes through the annular space between

the cathode and anode tubes and is exposed to sequential positive and negative electrical fields. Typical retention time is less than 20 seconds. Water characteristics such as pH, oxidation-reduction potential, and conductivity can be adjusted to achieve maximum removal efficiencies for specific contaminants.

After the treated water exits the electrocoagulation tubes, the destabilized colloids are allowed to flocculate and are then separated with an integrated clarifier system. Polymers can be added to enhance flocculation, but in most cases they are not required. The sludge produced by this process is usually very stable and acid-resistant. Tests have shown that sludges produced by the CURE® system pass the toxicity characteristic leaching procedure (TCLP) and are often disposed of as nonhazardous waste.

WASTE APPLICABILITY:

The CURE® system can treat a broad range of dissolved metals, including aluminum, arsenic, barium,



CURE®-Electrocoagulation System

cadmium, chromium, cyanide, iron, lead, nickel, uranium, and zinc. The system can also treat contaminants such as emulsified oils, suspended solids, paints, and dyes. Radionuclides were removed by the system at the Rocky Flats Environmental Technology Site (RFETS).

Because this system treats a wide range of contaminants, it is suited for industries and utilities such as plating, mining, electronics, industrial wastewater, as well as remediation projects.

STATUS:

This technology was accepted into the SITE Demonstration Program in 1993. A bench-scale test of the technology was conducted in April 1995 to determine the ability of the system to remove radionuclides from solar evaporation water at RFETS. The system removed over 90 percent of uranium and plutonium from the test water. The technology was demonstrated during August and September 1995 at RFETS under a joint agreement between the Department of Energy, the State of Colorado, and EPA.

The technology has also been demonstrated at several private industrial facilities and is currently being used to remove metals and oily wastes from the following: plating wastewater at a jewelry manufacturing facility, industrial wastewaters from an engine manufacturing facility, cooling tower water at an industrial facility, and for several other industrial applications in the U.S. and internationally. Full- or pilot-scale units are available from General Environmental Corporation.

DEMONSTRATION RESULTS:

During the SITE demonstration, four 3-hour test runs were conducted at RFETS over a 2-week period. Prior to the demonstration, operating parameters were adjusted during several optimization runs.

The demonstration showed that the system removed 30 to 50 percent of uranium and 60 to 99 percent of plutonium from the solar pond water at RFETS. The radionuclide and metal content of the dewatered sludge indicated that these contaminants were highly concentrated in the sludge. Uranium and plutonium were only slightly leachable by TCLP and no metals

were leachable by TCLP. These results suggest that the sludge is very stable and resistant to breakdown.

The Demonstration Bulletin (EPA/540/MR-96/502), Technology Capsule (EPA/540/R-92/502a), and Innovative Technology Evaluation Report (EPA/540/R-96/502) are available from EPA.

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GRUPPO ITALIMPRESSE
(developed by SHIRCO INFRARED SYSTEMS, INC.)
(Infrared Thermal Destruction)

TECHNOLOGY DESCRIPTION:

The infrared thermal destruction technology is a mobile thermal processing system that uses electrically powered silicon carbide rods to heat organic wastes to combustion temperatures. Any remaining combustibles are incinerated in an afterburner. One configuration for this mobile system (see figure below) consists of four components: (1) an electric-powered infrared primary chamber; (2) a gas-fired secondary combustion chamber; (3) an emissions control system; and (4) a control center.

Waste is fed into the primary chamber and exposed to infrared radiant heat (up to 1,850 °F) provided by silicon carbide rods above the conveyor belt. A blower delivers air to selected locations along the belt to control the oxidation rate of the waste feed.

The ash material in the primary chamber is quenched with scrubber water effluent. The ash is then conveyed to an ash hopper, where it is removed to a holding area and analyzed for organic contaminants such as polychlorinated biphenyls (PCB).

Volatile gases from the primary chamber flow into the secondary chamber, which uses higher temperatures, greater residence time, turbulence, and

supplemental energy (if required) to destroy these gases. Gases from the secondary chamber are ducted through the emissions control system. In the emissions control system, the particulates are removed in a venturi scrubber. Acid vapor is neutralized in a packed tower scrubber. An induced draft blower draws the cleaned gases from the scrubber into the free-standing exhaust stack. The scrubber liquid effluent flows into a clarifier, where scrubber sludge settles and is removed for disposal. The liquid then flows through an activated carbon filter for reuse or to a publicly owned treatment works for disposal.

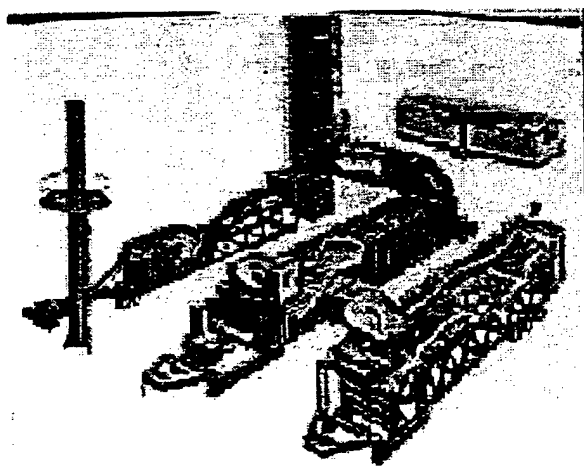
WASTE APPLICABILITY:

This technology is suitable for soils or sediments with organic contaminants. Liquid organic wastes can be treated after mixing with sand or soil. Optimal waste characteristics are as follows:

- Particle size, 5 microns to 2 inches
- Moisture content, up to 50 percent by weight
- Density, 30 to 130 pounds per cubic foot
- Heating value, up to 10,000 British thermal units per pound
- Chlorine content, up to 5 percent by weight
- Sulfur content, up to 5 percent by weight
- Phosphorus, 0 to 300 parts per million (ppm)
- pH, 5 to 9
- Alkali metals, up to 1 percent by weight

STATUS:

EPA conducted two evaluations of the infrared thermal destruction technology. A full-scale unit was evaluated during August 1987 at the Peak Oil Superfund site in Brandon, Florida. The system treated nearly 7,000 cubic yards of waste oil sludge containing PCBs and lead. A pilot-scale demonstration took place at the Rose Township-Demod Road Superfund site in Michigan during November 1987. Organics, PCBs, and metals in soil were the target waste compounds. Two



Mobile Thermal Processing System

Applications Analysis Reports
(EPA/540/A5-89/010 and EPA/540/A5-89/007)
and two Technology Evaluation Reports
(EPA/540/5-88/002a and EPA/540/5-89/007a) are
available from EPA. In addition, the technology has
been used to remediate PCB contamination at the
Florida Steel Corporation and the LaSalle Electric
Superfund sites.

This technology is no longer available through
vendors in the United States. For further
information about the technology, contact the EPA
Project Manager.

DEMONSTRATION RESULTS:

The results from the two SITE demonstrations are
summarized below.

- PCBs were reduced to less than 1 ppm in the ash, with a destruction removal efficiency (DRE) for air emissions greater than 99.99 percent (based on detection limits).
- In the pilot-scale demonstration, the Resource Conservation and Recovery Act standard for particulate emissions (0.08 gram per dry standard cubic foot) was achieved. In the full-scale demonstration, however, this standard was not met in all runs because of scrubber inefficiencies.
- Lead was not immobilized; however, it remained in the ash. Significant amounts were not transferred to the scrubber water or emitted to the atmosphere.

- The pilot-scale unit demonstrated satisfactory performance with high feed rate and reduced power consumption when fuel oil was added to the waste feed and the primary chamber temperature was reduced.
- Economic analysis suggests an overall waste remediation cost of less than \$800 per ton.

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HIGH VOLTAGE ENVIRONMENTAL APPLICATIONS, INC.
(formerly ELECTRON BEAM RESEARCH FACILITY, FLORIDA
INTERNATIONAL UNIVERSITY, and UNIVERSITY OF MIAMI)
(High-Energy Electron Irradiation)

TECHNOLOGY DESCRIPTION:

High-voltage electron irradiation of water produces a large number of very reactive chemical species, including the aqueous electron (e^-_{aq}), the hydrogen radical ($H\cdot$), and the hydroxyl radical ($OH\cdot$). These short-lived intermediates break down organic contaminants in aqueous wastes.

In the principal reaction, the aqueous electron transfers to halogen-containing compounds, breaking the halogen-carbon bond and liberating halogen anions such as chloride (Cl^-) or bromide (Br^-). The hydroxyl radical can undergo addition or hydrogen abstraction reactions, producing organic free radicals that decompose in the presence of other hydroxyl radicals and water. In most cases, organics are converted to carbon dioxide, water, and salts. Lower molecular weight aldehydes, haloacetic acids, and carboxylic acids form at low concentrations in some cases.

During the high-voltage electron irradiation process,

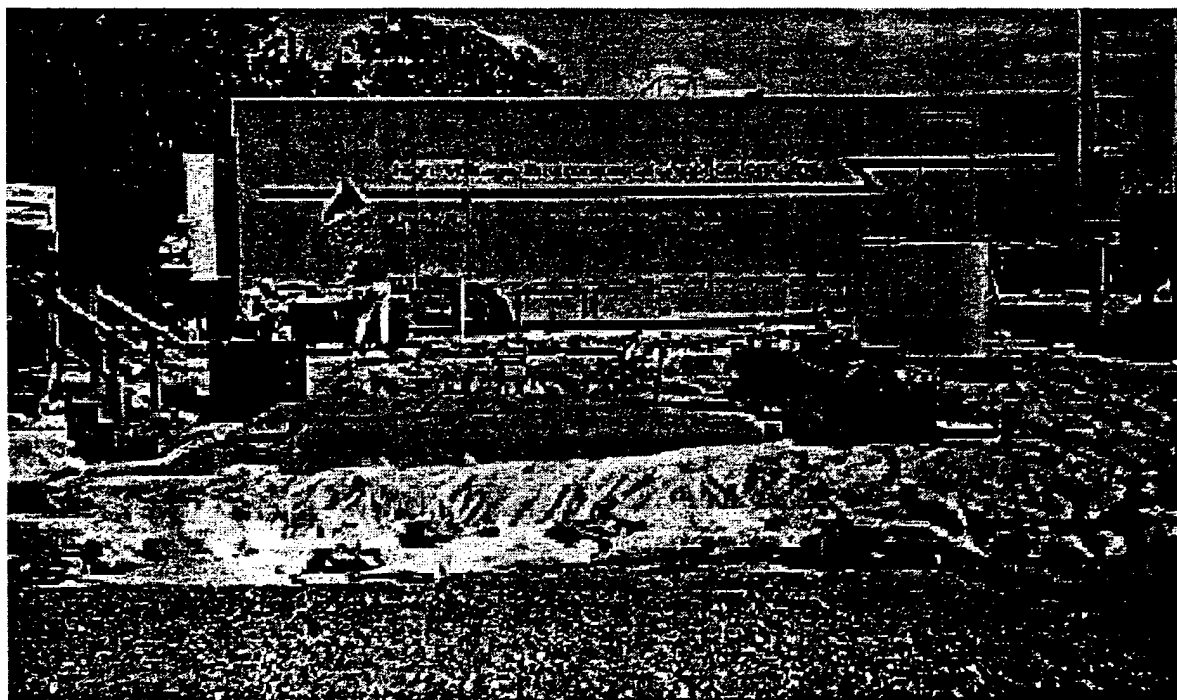
electricity generates high energy electrons. The electrons are accelerated by the voltage to approximately 95 percent of the speed of light. They are then directed into a thin stream of water or sludge. All reactions are complete in less than 0.1 second. The electron beam and waste flow are adjusted to deliver the necessary dose of electrons. Although this is a form of ionizing radiation, there is no residual radioactivity.

High Voltage Environmental Applications, Inc. (High Voltage), has developed a mobile facility to demonstrate the treatment process (see photograph below).

WASTE APPLICABILITY:

This treatment process can effectively treat more than 100 common organic compounds. These compounds include the following:

- Trihalomethanes (such as chloroform), which



The Mobile Electron Beam Hazardous Waste Treatment System

- are found in chlorinated drinking water
- Chlorinated solvents, including carbon tetrachloride, trichloroethane, tetrachloroethene (PCE), trichloroethene (TCE), ethylene dibromide, dibromochloropropane, hexachlorobutadiene, and hexachloroethane
- Aromatics found in gasoline, including benzene, toluene, ethylbenzene, and xylene (BTEX)
- Chlorobenzene and dichlorobenzenes
- Phenol
- Dieldrin, a persistent pesticide
- Polychlorinated biphenyls
- A variety of other organic compounds

The treatment process is appropriate for removing various hazardous organic compounds from aqueous waste streams and sludges.

STATUS:

The high-energy electron irradiation process was accepted into the SITE Emerging Technology Program (ETP) in June 1990. For further information on the pilot-scale facility evaluated under the ETP, refer to the Emerging Technology Bulletins (EPA/540/F-93/502, EPA/540/F-92/009, and EPA/540/F-93/509), which are available from EPA. Based on results from ETP, the process was invited to participate in the Demonstration Program.

The ability of the technology to treat contaminated soils, sediments, or sludges is also being evaluated under the ETP. For further information on this evaluation, refer to the the High Voltage profile in the ETP section (ongoing projects).

The treatment process was demonstrated at the U.S. Department of Energy's Savannah River site in Aiken, South Carolina during two different periods totaling 3 weeks in September and November 1994. The demonstration of a trailer-mounted treatment system took place on a portion of the Savannah River site known as M-Area.

DEMONSTRATION RESULTS:

During the demonstration, the system treated about 70,000 gallons of M-Area groundwater contaminated with volatile organic compounds (VOC). The principal groundwater contaminants were TCE and PCE, which were present at concentrations of about 27,000 and 11,000 micrograms per liter ($\mu\text{g/L}$), respectively. The groundwater also contained low levels of cis-1,2-dichloroethene (40 $\mu\text{g/L}$). The following compounds were also spiked into the influent stream at approximately 500 $\mu\text{g/L}$: 1,2-dichloroethane, carbon tetrachloride, 1,1,1-trichloroethane, chloroform, and BTEX.

The highest VOC removal efficiencies were observed for TCE (99.5 percent), PCE (99.0 percent), and dichloroethene (greater than 99 percent). Removal efficiencies for chlorinated spiking compounds ranged from 68 to 98 percent, and removal efficiencies for BTEX ranged from 88 to 99.5 percent.

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MAGNUM WATER TECHNOLOGY (CAV-OX® Process)

TECHNOLOGY DESCRIPTION:

The CAV-OX® process uses a combination of hydrodynamic cavitation and ultraviolet (UV) radiation to oxidize contaminants in water. The process (see figure below) is designed to remove organic contaminants from wastewater and groundwater without releasing volatile organic compounds into the atmosphere.

The process generates free radicals to degrade organic contaminants. The cavitation process alone has been demonstrated to achieve trichloroethene (TCE) reductions of up to 65 percent. UV excitation and, where necessary, addition of hydrogen peroxide and metal catalysts, provide synergism to achieve overall reductions of over 99 percent. Neither the cavitation chamber nor the UV lamp or hydrogen peroxide reaction generates toxic by-products or air emissions.

Magnum Water Technology (Magnum) estimates the cost of using the CAV-OX® process to be about half the cost of other advanced UV oxidation systems and substantially less than carbon adsorption. Because the process equipment has one moving part, maintenance costs are minimal. According to Magnum, the CAV-OX® process does not exhibit the quartz tube scaling common with other UV equipment.

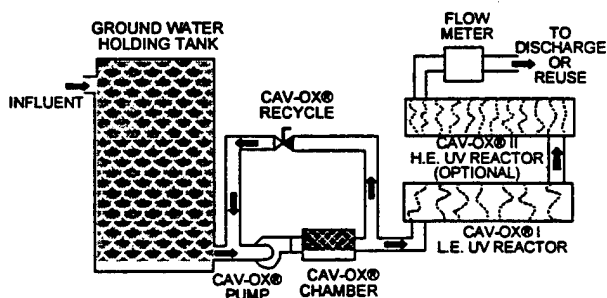
WASTE APPLICABILITY:

The process is designed to treat groundwater or wastewater contaminated with organic compounds. Contaminants such as halogenated solvents; phenol; pentachlorophenol (PCP); pesticides; polychlorinated biphenyls; explosives; benzene, toluene, ethylbenzene, and xylenes; methyl tertiary butyl ether; other organic compounds; and cyanide are suitable for this treatment process. Bacteria and virus strains are also eliminated.

STATUS:

This technology was accepted into the SITE Demonstration Program in summer 1992 and was demonstrated for 4 weeks in March 1993 at Edwards Air Force Base (AFB) Site 16 in California. The Applications Analysis Report (EPA/540/AR-93/520), Technology Evaluation Report (EPA/540/R-93/520), and a videotape are available from EPA.

Magnum reports that improvements in UV lamp and reactor technologies have improved the efficiency of the CAV-OX® process three- to five-fold, compared with the pilot-scale unit tested at Edwards AFB under the SITE Program.



The CAV-OX® Process

CAV-OX® recently (1996) has proven very effective in potentiating ozone concentrations in water reclamation applications. Ozone gas (O₃) is relatively insoluble in water. However, hydrodynamic cavitation used in the CAV-OX® process continuously develops micro bubbles which enhances the dispersion of ozone in water. Three O₃ techniques are available to Magnum: corona discharge with air feed, electrochemical 'water splitting' method, and electrochemical anodic oxidation.

The CAV-OX® process has been tested at several public and private sites. At a Superfund site, the process treated leachate containing 15 different contaminants. PCP, one of the major contaminants, was reduced by 96 percent in one test series. The process has also been used to remediate former gasoline station sites and successfully reduced contaminants in process streams at chemical and pharmaceutical plants.

The CAV-OX® unit is part of an ongoing evaluation at the U.S. Army Aberdeen Proving Ground. Features of the unit to be tested include remote monitoring and control systems for pH; flow; H₂O₂ flow rate, storage level, and pump rate; UV lamp, main power, and CAV-OX® pump function; and system shutdown control.

DEMONSTRATION RESULTS:

The CAV-OX® process achieved removal efficiencies of greater than 99.9 percent for TCE, benzene, toluene, ethylbenzene, and xylenes. SITE demonstration results for the CAV-OX® process are shown in the table below. Results are presented for both the CAV-OX® I (cavitation chamber by itself) and CAV-OX® II (cavitation chamber combined with ultraviolet radiation) demonstrations.

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H ₂ O ₂ ¹ Concentrations (mg/L) ²	Flow (gpm) ³	CAV-OX® I Removal Efficiencies (%)				Flow (gpm)	TCE		CAV-OX® II Removal Efficiencies (%)				Xylene	5-kW	10-kW
		TCE	Benzene	Toluene	Xylene		5-kW	10-kW	Benzene	Toluene	Xylene	5-kW	10-kW		
33.1	0.5	99.9	>99.9	99.4	92.9	1.5	99.6	99.2	99.4	98.8	>99.9	98.6	>99.9	>99.9	>99.9
23.4	0.6	99.9	>99.9	>99.9	>99.9	2.0	99.7	99.7	99.5	99.6	>99.9	>99.9	>99.9	>99.9	>99.9
4.9	1.5	71.4	88.6	87.4	65.6	4.0	87.7	98.1	89.7	98.7	88.8	97.1	78.7	87.2	87.2
48.3	0.6	99.7	>99.9	>99.9	>99.9	1.4	99.8	99.7	99.8	99.8	>99.9	>99.9	98.7	>99.9	>99.9
6.0	0.7	87.8	96.9	94.5	92.1	1.9	98.4	99.3	98.8	99.3	96.9	98.6	93.6	97.0	97.0
4.9	1.5	61.7	81.6	83.8	80.2	3.9	85.1	97.1	89.5	97.8	91.8	97.9	90.4	96.0	96.0
5.9	0.5	96.4	99.4	99.8	98.9	1.4	99.6	99.4	99.6	99.6	99.8	99.8	99.5	99.5	99.5
5.9	0.7	87.1	96.5	97.6	98.1	1.9	97.8	99.2	99.4	99.5	99.5	99.7	99.2	99.7	99.7
6.1	1.5	60.6	86.1	87.3	>99.9	4.0	86.3	98.9	93.5	99.5	94.5	99.6	95.4	>99.9	>99.9
0	-	-	-	-	-	1.6	94.1	99.2	49.1	68.1	20.7	54.7	43.3	46.7	46.7
0	-	-	-	-	-	1.8	80.6	97.6	38.5	60.5	48.6	75.2	56.9	83.8	83.8

¹ hydrogen peroxide ² milligrams per liter ³ gallons per minute ⁴ kilowatts

CAV-OX® Process Demonstration Results

MATRIX PHOTOCATALYTIC INC.

(Photocatalytic Water Treatment)

TECHNOLOGY DESCRIPTION:

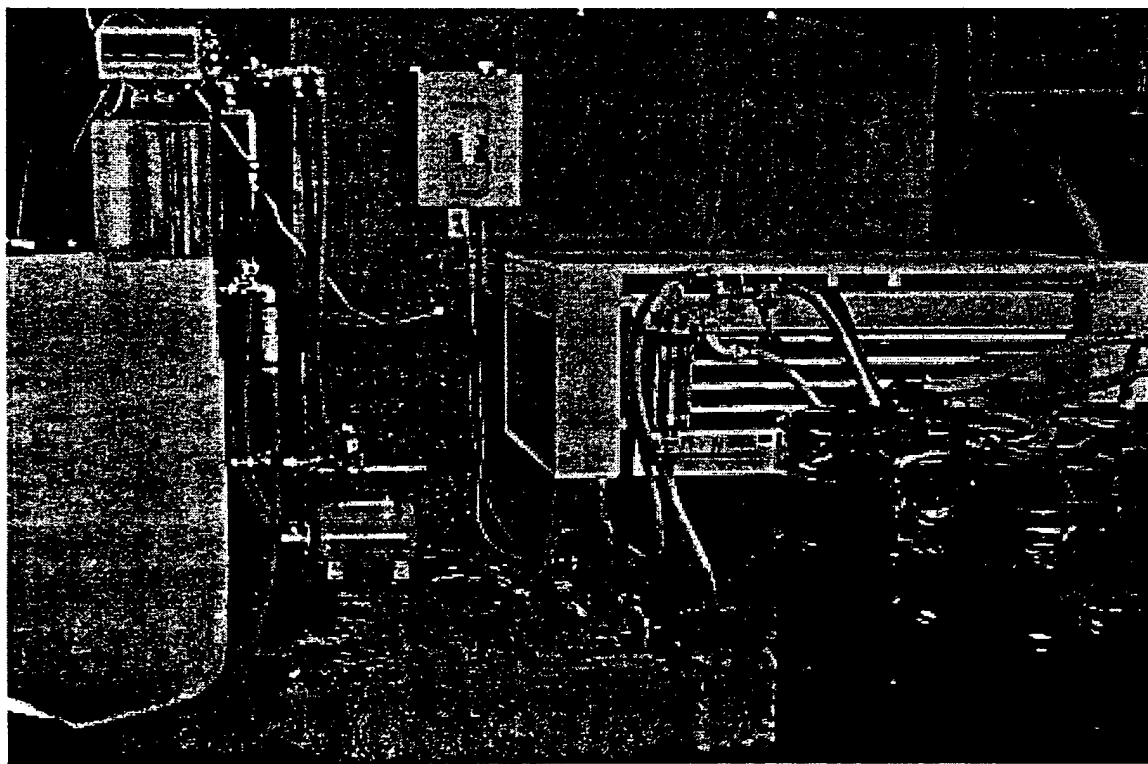
The Matrix Photocatalytic Inc. (Matrix), photocatalytic oxidation system, shown in the photograph below, removes dissolved organic contaminants from water and destroys them in a continuous flow process at ambient temperatures. When excited by light, the titanium dioxide (TiO₂) semiconductor catalyst generates hydroxyl radicals that oxidatively break the carbon bonds of hazardous organic compounds.

The Matrix system converts organics such as polychlorinated biphenyls (PCB); phenols; benzene, toluene, ethylbenzene, and xylene (BTEX); and others to carbon dioxide, halides, and water. Typically, efficient destruction occurs between 30 seconds and 2 minutes actual exposure time. Total organic carbon removal takes longer, depending on the other organic molecules and their molecular weights.

The Matrix system was initially designed to destroy organic pollutants or to remove total organic carbon in drinking water, groundwater, and plant process water. The Matrix system also destroys organic pollutants such as PCBs, polychlorinated dibenzodioxins, polychlorinated dibenzofurans, chlorinated alkenes, chlorinated phenols, chlorinated benzenes, alcohols, ketones, aldehydes, and amines. Inorganic pollutants such as cyanide, sulphite, and nitrite ions can be oxidized to cyanate ion, sulphate ion, and nitrate ion, respectively.

WASTE APPLICABILITY:

The Matrix system can treat a wide range of concentrations of organic pollutants in industrial wastewater and can be applied to the ultrapure water industry and the drinking water industry. The Matrix system can also remediate groundwater.



10 Gallon-Per-Minute TiO₂ Photocatalytic System Treating BTEX in Water

STATUS:

The system was accepted into the SITE Emerging Technology Program (ETP) in May 1991. Results from the ETP evaluation were published in a journal article (EPA/540/F-94/503) available from EPA. Based on results from the ETP, Matrix was invited to participate in the Demonstration Program.

During August and September 1995, the Matrix system was demonstrated at the Department of Energy's Oak Ridge Reservation in Oak Ridge, Tennessee at the K-25 site. Reports detailing the results from the demonstration will be available in 1997.

DEMONSTRATION RESULTS:

Results from the demonstration are detailed below:

- In general, high percent removals (up to 99.9 percent) were observed for both aromatic volatile organic compounds (VOCs) and unsaturated VOCs. However, the percent removals for saturated VOCs were low (between 40 and 21 percent).
- The percent removals for all VOCs increased with increasing number of path lengths and oxidant doses. At equivalent contact times, changing the flow rate did not appear to impact the treatment system performance for all aromatic VOCs and most unsaturated VOCs (except 1,1-dichloroethene [DCE]). Changing the flow rate appeared to impact the system performance for saturated VOCs.
- The effluent met the Solid Waste Disposal Act maximum contaminant levels (MCL) for benzene; cis-1,2-DCE; and 1,1-DCE at a significant level of 0.05. However, the effluent did not meet the MCLs for tetrachloroethene (PCE); trichloroethane (TCE); 1,1-dichloroethane (DCA); and 1,1,1-trichloroethane (TCA) at a significant level of 0.05. The influent concentration for toluene and total xylenes was below the MCLs.
- In tests performed to evaluate the effluent's acute toxicity to water fleas and fathead minnows, more than 50 percent of the organisms died. Treatment by the Matrix system did not reduce the groundwater toxicity for the test organisms at a significant level of 0.05.
- In general, the percent removals were reproducible for aromatic and unsaturated VOCs when the Matrix system was operated under identical conditions. However, the percent removals were not reproducible for saturated VOCs. The Matrix system's performance was generally reproducible in (1) meeting the target effluent levels for benzene; cis-1,2-DCE; and 1,1-DCE and (2) not meeting the target effluent levels for PCE; TCE; 1,1-DCA; and 1,1,1-trichloroethane.
- Purgable organic compounds and total organic halides results indicated that some VOCs were mineralized in the Matrix system. However, formulation of aldehydes, haloacetic acids, and several tentatively identified compounds indicated that not all VOCs were completely mineralized.
- FOR FURTHER INFORMATION:

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NORTH AMERICAN TECHNOLOGIES GROUP, INC.
(Oleophilic Amine-Coated Ceramic Chip)

TECHNOLOGY DESCRIPTION:

This hydrocarbon recovery technology is based on an oleophilic, amine-coated ceramic chip that separates suspended and dissolved hydrocarbons, as well as most mechanical and some chemical emulsions, from aqueous solutions. The oleophilic chip is manufactured by grafting a hydrophobic amine to a mineral support, in this case a ceramic substrate. Each granule is 0.6 to 1 millimeter in diameter, but is very porous and thus has a large surface area. The hydrophobic property of the amine coating makes each granule more effective for microfiltration of hydrocarbons in an unstable emulsion.

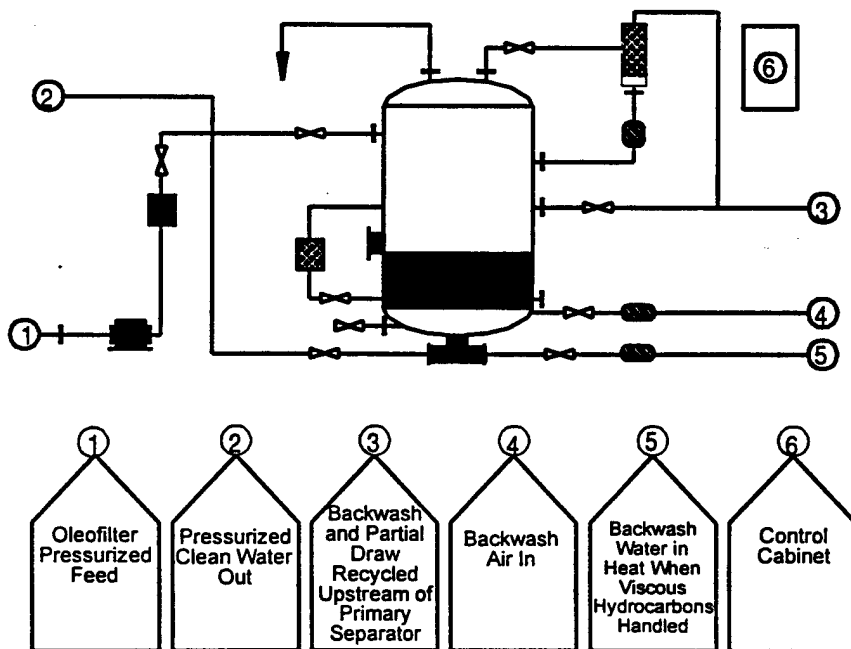
The figure below illustrates the process; the separator, filter, and coalescer unit is shown on the next page. The pressure-sensitive filtering bed is regenerated by automatic backflushing. This automatic regeneration eliminates the expense associated with regeneration of carbon and similar filtration media. Recovered hydrocarbons coalesce and can thus be removed by simple gravity separation.

This technology provides cost-effective oil and water separation, removes free and emulsified hydrocarbon contaminants, and significantly reduces hydrocarbon loading to air strippers and carbon systems. The technology can achieve a concentration of less than 7 parts per million oil and grease in the treated effluent.

WASTE APPLICABILITY:

The amine-coated granules have proven effective on a wide variety of hydrocarbons, including gasoline; crude oil; diesel fuel; benzene, toluene, ethylbenzene and xylene mixtures; and polynuclear aromatic hydrocarbons. The unit also removes hydrophobic chlorinated hydrocarbons such as pentachlorophenol, polychlorinated biphenyls, and trichloroethene, as well as vegetable and animal oils.

Treatment systems incorporating this technology have been designed for various applications, including (1) contaminated groundwater pump-and-treat systems; (2) in-process oil and water separation; (3) filtration systems; (4) combined oil and water separator-filter-coalescer systems for on-



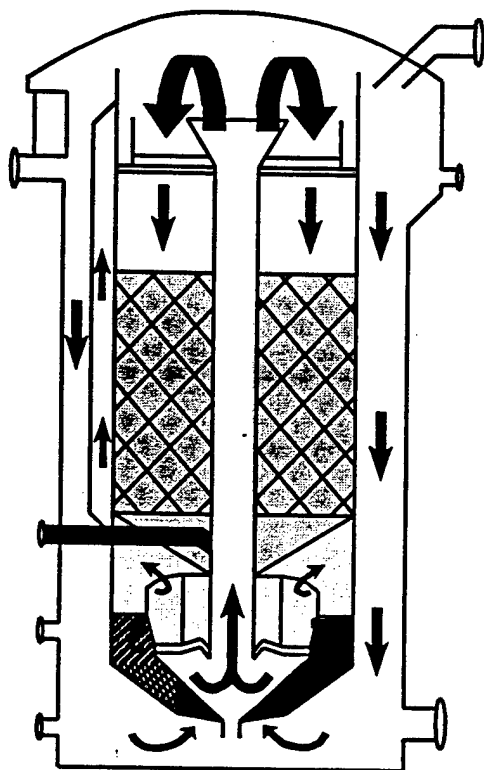
Schematic Diagram of the Oleofilter Technology

site waste reduction and material recovery; and (5) treatment of marine wastes (bilge and ballast waters).

STATUS:

This technology was accepted into the SITE Demonstration Program in December 1992. The SITE demonstration was completed in June 1994 at the Petroleum Products Corporation site in Fort Lauderdale, Florida. The site is a former oil recycling facility where groundwater has been contaminated with a variety of organic and inorganic constituents. The Demonstration Bulletin (EPA/540/MR-94/525) and Innovative Technology Evaluation Report (EPA/540/R-94/525) are available from EPA.

The technology has been used for several full-scale projects. Several separator-filter-coalescers (see figure below) are in use treating industrial process waters and oily wash waters.



Separator, Filter, and Coalescer

DEMONSTRATION RESULTS:

For the demonstration, five separate evaluation periods (runs) were initiated. Each run used the same feed oil, except run four. The oil for run four was a 3:1 mixture of oil to kerosene. The average total recoverable petroleum hydrocarbon (TRPH) concentrations for the feed streams ranged from 422 to 2,267 milligrams per liter (mg/L). Preliminary data indicate that the system removed at least 90 percent of the TRPH from the emulsified oil and water feed stream.

For the runs where the system operated within normal design parameters, TRPH concentrations in the treated water effluent were reduced to 15 mg/L or less. The oleophilic granules achieved a 95 percent reduction of TRPH concentration for the runs with similar feed oil.

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ROCHEM SEPARATION SYSTEMS, INC. (Rochem Disc Tube™ Module System)

TECHNOLOGY DESCRIPTION:

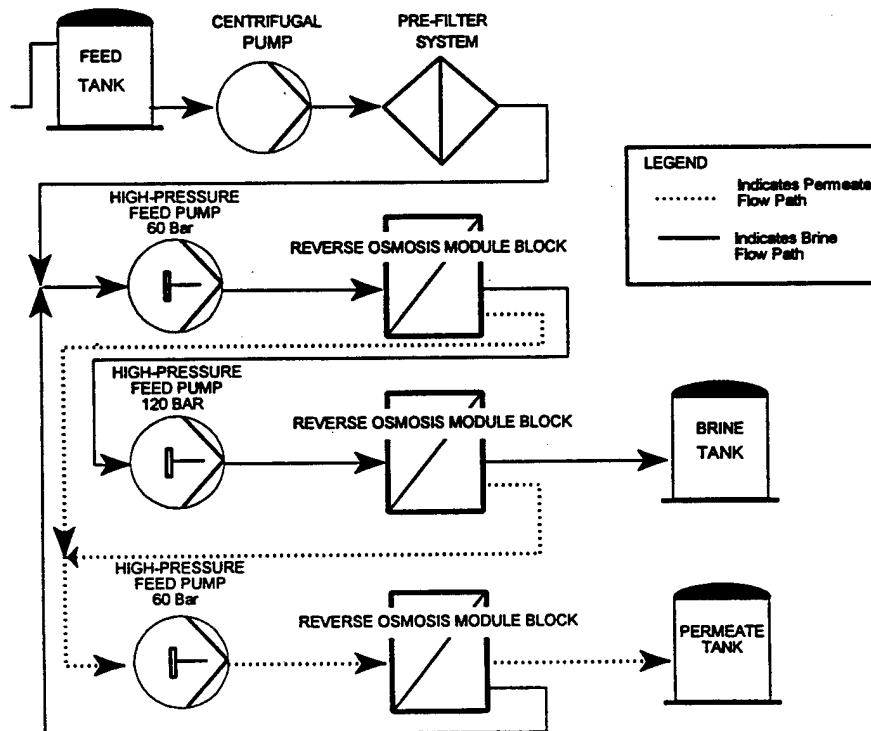
The Rochem Disc Tube™ Module System uses membrane separation to treat aqueous solutions ranging from seawater to leachate contaminated with organic solvents. The system uses osmosis through a semipermeable membrane to separate pure water from contaminated liquids.

Osmotic theory implies that a saline solution may be separated from pure water by a semipermeable membrane. The higher osmotic pressure of the salt solution causes the water (and other compounds having high diffusion rates through the selected membrane) to diffuse through the membrane into the salt water. Water will continue to permeate the salt solution until the osmotic pressure of the salt solution equals the osmotic pressure of the pure water. At this point, the salt concentrations of the two solutions are equal, eliminating any additional driving force for mass transfer across the membrane.

However, if external pressure is exerted on the salt solution, water will flow in the reverse direction from the salt solution into the pure water.

This phenomenon, known as reverse osmosis (RO), can separate pure water from contaminated matrices. RO can treat hazardous wastes by concentrating the hazardous chemical constituents in an aqueous brine, while recovering pure water on the other side of the membrane.

Fluid dynamics and system construction result in an open-channel, fully turbulent feed and water-flow system. This configuration prevents accumulation of suspended solids on the separation membranes, ensuring high efficiency filtration for water and contaminants. Also, the design of the disc tubes allows easy cleaning of the filtration medium, providing a long service life for the membranes.



Three-Stage, Reverse Osmosis Flow Path

A general flow path for the Rochem Disc Tube™ Module System as applied at the SITE demonstration is shown on the previous page. Waste feed, process permeate, and rinse water are potential feed materials to the RO modules. The modules are skid-mounted and consist of a tank and a high-pressure feed system. The high-pressure feed system consists of a centrifugal feed pump, a prefilter cartridge housing, and a triplex plunger pump to feed the RO modules. The processing units are self-contained and require electrical and interconnection process piping before operation.

WASTE APPLICABILITY:

Many types of waste material can be treated with this system, including sanitary and hazardous landfill leachate containing both organic and inorganic chemical species.

STATUS:

This technology was accepted into the SITE Demonstration Program in July 1991. The demonstration was conducted in August 1994 at the Central Landfill Superfund site in Johnston, Rhode Island. The system was used to treat landfill leachate from a hazardous waste landfill. During the demonstration, approximately 4 gallons per minute of contaminated waste was processed over a 3-week period. All feed and residual effluent streams were sampled to evaluate the performance of this technology. The Innovative Technology Evaluation Report (EPA/540/R-96/507), the Technology Capsule (EPA/540/R-96/507a), and the Demonstration Bulletin (EPA/540/MR-96/507) are available from EPA.

DEMONSTRATION RESULTS:

Preliminary results from the demonstration suggest the following:

- Over 99 percent of total dissolved solids, over 96 percent of total organic carbon, and 99 percent of all target metals were removed. In addition, the average percent rejection for volatile organic compounds was greater than the test criteria of 90 percent.
- The average water recovery rate for the Rochem Disc Tube™ Module System during the demonstration was approximately 75 percent. The test criterion was 75 percent treated water recovery rate.
- The Rochem Disc Tube™ Module System operated for 19 days at up to 8 hours per day. Daily operation hours were not as long as planned due to weather and field operational difficulties. However, the system operated long enough to evaluate the technology's performance.

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SBP TECHNOLOGIES, INC.
(Membrane Filtration and Bioremediation)

TECHNOLOGY DESCRIPTION:

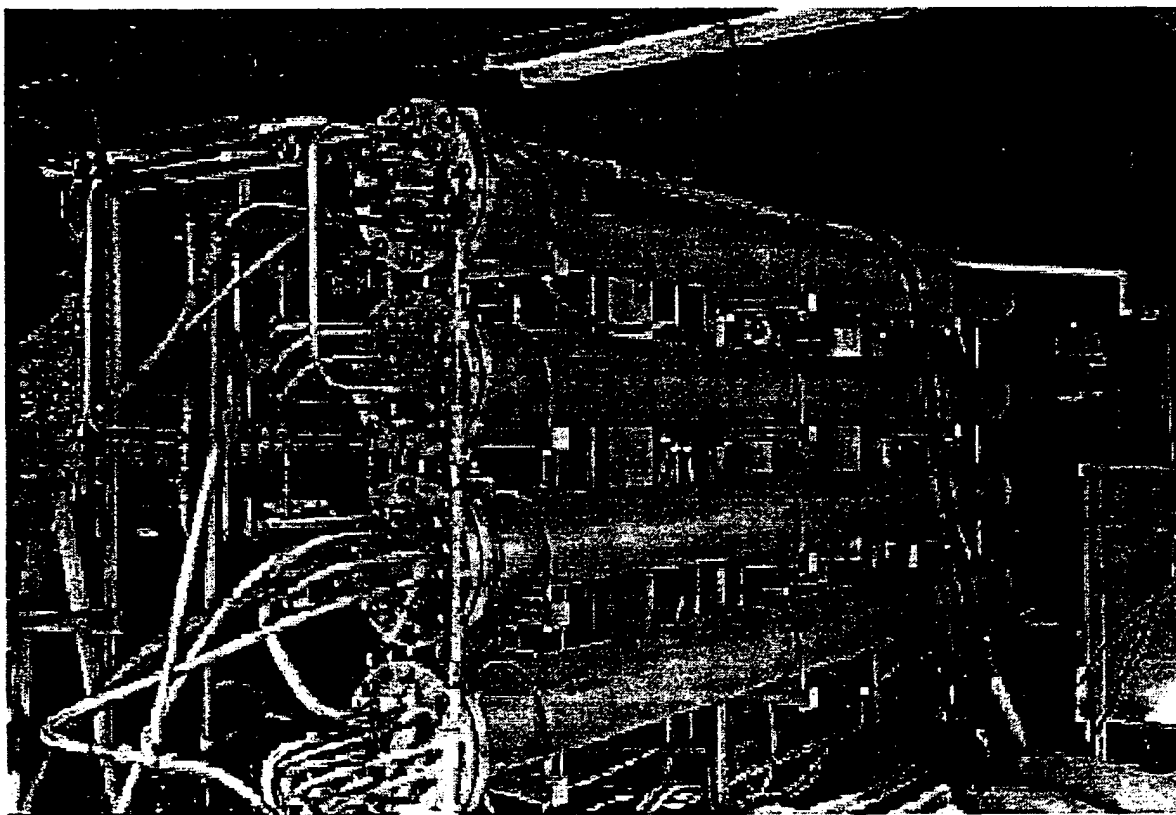
SBP Technologies, Inc. (SBP), has developed a hazardous waste treatment system consisting of (1) a membrane filtration system that extracts and concentrates contaminants from groundwater, surface water, wash water, or slurries; and (2) a bioremediation system that treats concentrated groundwater, wash water, and soil slurries (see photograph below). These two systems treat a wide range of waste materials separately or as parts of an integrated waste handling system.

The membrane filtration system removes and concentrates contaminants by pumping contaminated liquids through porous stainless steel tubes coated with specifically formulated membranes. Contaminants are collected inside the tube membrane, while "clean" water permeates the

membrane and tubes. Depending on local requirements and regulations, the clean permeate can be discharged to the sanitary sewer for further treatment at a publicly owned treatment works (POTW). The concentrated contaminants are collected in a holding tank and fed to the bioremediation system.

Contaminated water or slurry can also flow directly into the bioremediation system and be polished in the membrane filtration system. The bioremediation system consists of one or more bioreactors that are inoculated with specially selected, usually indigenous microorganisms to produce effluent with low to nondetectable contaminant levels. Integrating the two systems allows removal and destruction of many contaminants.

WASTE APPLICABILITY:



Membrane Filtration and Bioremediation

The membrane filtration system concentrates contaminants and reduces the volume of contaminated materials from a number of waste streams, including contaminated groundwater, surface water, storm water, landfill leachates, and industrial process wastewater.

The bioremediation system can treat a wide range of organic contamination, especially wood-preserving wastes and solvents. A modified version can also treat polynuclear aromatic hydrocarbons (PAH) such as creosote and coal tar; pentachlorophenol; petroleum hydrocarbons; and chlorinated aliphatics, such as trichloroethene.

The two technologies can be used separately or combined, depending on site characteristics and waste treatment needs. For example, for wastewaters or slurries contaminated with inorganics or materials not easily bioremediated, the membrane filtration system can separate the material for treatment by another process. Both the membrane filtration system and the bioremediation system can be used as part of a soil cleaning system to handle residuals and contaminated liquids.

STATUS:

The membrane filtration system, accepted into the SITE Program in 1990, was demonstrated in October 1991 at the American Creosote Works in Pensacola, Florida. The Demonstration Bulletin (EPA/540/MR-92/014) and Applications Analysis Report (EPA/540/AR-92/014) are available from EPA. A full-scale SITE Program demonstration of the bioremediation system was canceled. However, a smaller-scale field study was conducted at the site; results are available through the developer.

SBP is marketing its bioremediation and membrane filtration systems to industrial and governmental clients for on-site treatment of contaminated soil, sludge, and water.

DEMONSTRATION RESULTS:

Results from the SITE demonstration are summarized as follows:

- The system effectively concentrated the PAHs into a smaller volume.
- The process removed 95 percent of the PAHs found in creosote from the feed and produced a permeate stream that was acceptable for discharge to a POTW.
- The membrane removed 25 to 35 percent of smaller phenolic compounds.
- The system removed an average of about 80 percent of the total concentrations of creosote constituents (phenolics and PAHs) in the feedwater and permeate.

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U.S. FILTER/ZIMPRO, INC.
(formerly ULTROX, A DIVISION OF ZIMPRO ENVIRONMENTAL, INC.)
(Ultraviolet Radiation and Oxidation)

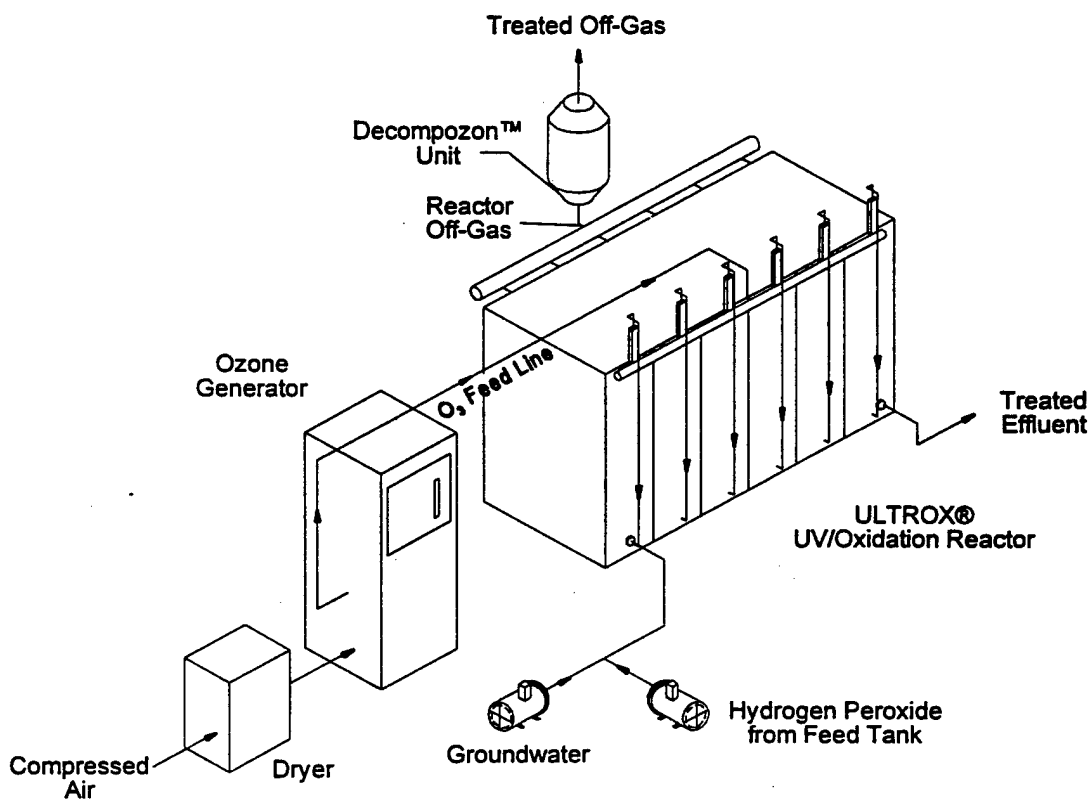
TECHNOLOGY DESCRIPTION:

This ultraviolet (UV) radiation and oxidation technology uses UV radiation, ozone, and hydrogen peroxide to destroy toxic organic compounds, particularly chlorinated hydrocarbons, in water. The technology oxidizes compounds that are toxic or refractory (resistant to biological oxidation) to parts per million (ppm) or parts per billion (ppb) levels.

The UV radiation and oxidation system consists of the UV-oxidation reactor, an air compressor and ozone generator module, and a hydrogen peroxide feed system (see figure below). The system is skid-mounted and portable, and permits on-site treatment

of a wide variety of liquid wastes. Reactor size is determined by the expected wastewater flow rate and the necessary hydraulic retention time needed to treat the contaminated water. The approximate UV intensity, and ozone and hydrogen peroxide doses, are determined from pilot-scale studies.

Reactor influent is simultaneously exposed to UV radiation, ozone, and hydrogen peroxide to oxidize the organic compounds. Off-gas from the reactor passes through a catalytic ozone destruction Decompozon™ unit, which reduces ozone levels before air venting. The Decompozon™ unit also destroys volatile organic compounds (VOC) stripped off in the reactor. Effluent from the reactor



UV Radiation and Oxidation System (Isometric View)

is tested and analyzed before disposal.

WASTE APPLICABILITY:

The UV radiation and oxidation system treats contaminated groundwater, industrial wastewaters, and leachates containing halogenated solvents, phenol, pentachlorophenol, pesticides, polychlorinated biphenyls, explosives, benzene, toluene, ethylbenzene, xylene, methyl tertiary butyl ether, and other organic compounds. The system also treats low-level total organic carbon and reduces chemical oxygen demand and biological oxygen demand.

STATUS:

This technology was accepted into the SITE Demonstration Program in 1989. A field-scale demonstration of the system was completed in March 1989 at the Lorentz Barrel and Drum Company site in San Jose, California. The testing program was designed to evaluate system performance while varying five operating parameters: (1) influent pH, (2) retention time, (3) ozone dose, (4) hydrogen peroxide dose, and (5) UV radiation intensity. The Demonstration Bulletin (EPA/540/M5-89/012), Technology Demonstration Summary (EPA/540/S5-89/012), Applications Analysis Report (EPA/540/A5-89/012), and Technology Evaluation Report (EPA/540/5-89/012) are available from EPA.

The technology is fully commercial, with over 30 systems installed. Units with flow rates ranging from 5 gallons per minute (gpm) to 1,050 gpm are in use at various industries and site remediations, including aerospace, U.S. Department of Energy, U.S. Department of Defense, petroleum, pharmaceutical, automotive, woodtreating, and municipal facilities.

UV radiation and oxidation technology has been included in records of decision for several Superfund sites where groundwater pump-and-treat remediation methods will be used.

DEMONSTRATION RESULTS:

Contaminated groundwater treated by the system during the SITE demonstration met regulatory standards at the appropriate parameter levels. Out of 44 VOCs in the wastewater, trichloroethene, 1,1-dichloroethane, and 1,1,1-trichloroethane were chosen as indicator parameters. All three are relatively refractory to conventional oxidation.

The Decompozon™ unit reduced ozone to less than 0.1 ppm, with efficiencies greater than 99.99 percent. VOCs present in the air within the treatment system were not detected after passing through the Decompozon™ unit. The system produced no harmful air emissions. Total organic carbon removal was low, implying partial oxidation of organics without complete conversion to carbon dioxide and water.

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WHEELABRATOR CLEAN AIR SYSTEMS, INC.
(formerly CHEMICAL WASTE MANAGEMENT, INC.)
(PO*WW*ER™ Technology)

TECHNOLOGY DESCRIPTION:

The PO*WW*ER™ technology is used to treat and reduce complex industrial and hazardous wastewaters containing mixtures of inorganic salts, metals, volatile and nonvolatile organics, volatile inorganics, and radionuclides. The proprietary technology combines evaporation with catalytic oxidation to concentrate and destroy contaminants, producing a high-quality product condensate.

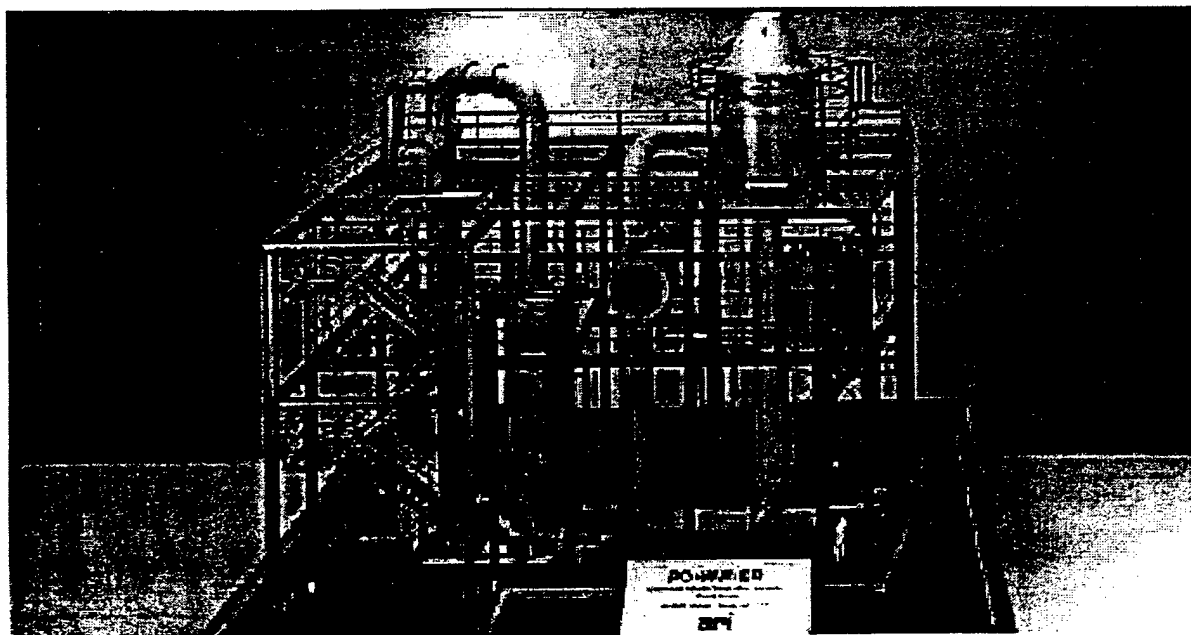
Wastewater is first pumped into an evaporator, where most of the water and contaminants are vaporized and removed, concentrating the contaminants into a small volume for further treatment or disposal. The contaminant vapors then pass over a bed of proprietary robust catalyst, where the pollutants are oxidized and destroyed. Depending on the contaminant vapor composition, effluent vapors from the oxidizer may be treated in a scrubber. The vapors are then condensed to produce water (condensate) that can be used as either boiler or cooling tower

makeup water, if appropriate. Hazardous wastewater can thus be separated into a small contaminant stream (brine) and a large clean water stream without using expensive reagents or increasing the volume of the total stream. The photograph below illustrates a PO*WW*ER™ - based wastewater treatment plant.

WASTE APPLICABILITY:

The PO*WW*ER™ technology can treat wastewaters containing a mixture of the following contaminants:

Organic	Inorganic	Radioactive
• Halogenated volatiles • Halogenated semivolatiles • Nonhalogenated volatiles • Nonhalogenated semivolatiles • Organic pesticides/herbicides • Solvents • Benzene, toluene, ethylbenzene, and xylene • Organic cyanides • Nonvolatile organics	• Heavy metals • Nonmetallic toxic elements • Cyanides • Ammonia • Nitrates • Salts	• Plutonium • Americium • Uranium • Technetium • Thorium • Radium • Barium



PO*WW*ER™-Based Wastewater Treatment Plant

Suitable wastewaters for treatment by the PO*WW*ER™ technology include landfill leachates, contaminated groundwaters, process wastewaters, and low-level radioactive mixed wastes.

STATUS:

The technology was accepted into the SITE Demonstration Program in 1991. The demonstration took place in September 1992 at the Chemical Waste Management, Inc., Lake Charles, Louisiana facility. Landfill leachate, an F039 hazardous waste, was treated in a pilot-scale unit. The Applications Analysis Report (EPA/540/AR-93/506) and Technology Evaluation Report (EPA/540/R93/506) are available from EPA.

A commercial system with a capacity of 50 gallons per minute is in operation at Ysing Yi Island, Hong Kong. A pilot-scale unit, with a capacity of 1 to 1.5 gallons per minute, is available and can treat radioactive, hazardous, and mixed waste streams.

DEMONSTRATION RESULTS:

The ability of the PO*WW*ER™ system to concentrate aqueous wastes was evaluated by measuring the volume reduction and concentration ratio achieved. The volume of brine produced during each 9-hour test period was about 5 percent of the feed waste volume processed in the same period. The concentration ratio, defined as the ratio of total solids (TS) concentration in the brine to the TS concentration in the feed waste, was about 32 to 1.

The feed waste contained concentrations of volatile organic compounds (VOC) ranging from 320 to 110,000 micrograms per liter ($\mu\text{g/L}$); semivolatile organic compounds (SVOC) ranging from 5,300 to 24,000 $\mu\text{g/L}$; ammonia ranging from 140 to 160 milligrams per liter (mg/L); and cyanide ranging from 24 to 36 mg/L. No VOCs, SVOCs, ammonia, or cyanide were detected in the product condensate.

The PO*WW*ER™ system removed sources of feed waste toxicity. The feed waste was acutely toxic with median lethal concentrations (LC_{50}) consistently below 10 percent. The product condensate was nontoxic with LC_{50} values consistently greater than 100 percent, but only after the product condensate was cooled and its pH, dissolved oxygen level, and hardness or salinity were increased.

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ZENON ENVIRONMENTAL INC.
(ZenoGem™ Process)

TECHNOLOGY DESCRIPTION:

ZENON Environmental Inc.'s, ZenoGem™ Process integrates biological treatment with membrane-based ultrafiltration (see figure below). This innovative system treats high strength wastes at long sludge retention time but short hydraulic residence time. As a result, the bioreactor's size is significantly reduced. Membrane filtration reduces the turbidity of the treated wastewater to less than 1 nephelometric turbidity unit.

In the ZenoGem™ Process, wastewater contaminated with organic compounds first enters the bioreactor, where contaminants are biologically degraded. Next, the process pump circulates the biomass through the ultrafiltration membrane system, or ultrafilter. The ultrafilter separates treated water from biological solids and soluble materials with higher molecular weights, including emulsified oil. The solids and soluble materials are then recycled to the bioreactor. The ZenoGem™

Process captures higher molecular weight materials that would otherwise pass through conventional clarifiers and filters. The ZenoGem™ Process pilot-scale system is mounted on a 48-foot trailer and consists of the following six major components:

- Polyethylene equalization/holding tank: reduces the normal flow concentration fluctuations in the system
- Polyethylene bioreactor tank: contains the bacterial culture that degrades organic contaminants
- Process and feed pumps: ensures proper flow and pressure for optimum system performance
- Ultrafiltration module: contains rugged, clog-free, tubular membranes that remove solids from treated water
- Clean-in-place tank: includes all the necessary valves, instrumentation, and controls to clean the membrane filters
- Control panel and computer: monitors



ZenoGem™ Process

system performance

The treatment capacity of the pilot-scale, trailer-mounted system is about 500 to 1,000 gallons of wastewater per day; however, a full-scale system can treat much larger quantities of wastewater. The trailer is also equipped with a laboratory that enables field personnel to conduct tests to evaluate system performance. The system is computer-controlled and equipped with alarms to notify the operator of mechanical and operational problems.

WASTE APPLICABILITY:

The ZenoGem™ Process is designed to remove biodegradable materials, including most organic contaminants, from wastewater to produce a high quality effluent. The process consistently nitrifies organics and can denitrify organics with the addition of an anoxic bioreactor. The process is limited to aqueous media and may be used to treat high strength leachates, contaminated groundwater, and soil washing effluent.

STATUS:

The ZenoGem™ Process was accepted into the SITE Demonstration Program in summer 1992. The ZenoGem™ Process was demonstrated at the Nascolite Superfund site in Millville, New Jersey from September through November 1994. Groundwater at this 17.5-acre site is contaminated with methyl methacrylate (MMA) and other volatile organic compounds from manufacturing polymethyl methacrylate plastic sheets, commonly known as Plexiglas. The Demonstration Bulletin (EPA/540/MR-95/503) and Technology Capsule (EPA/540/R-95/503a) are available from EPA. The Innovative Technology Evaluation Report will be available in 1997.

Since the development of the ZenoGem™ technology in 1987, ZENON has performed pilot tests for government and private clients on several different types of wastewater, including oily wastewater, metal finishing wastes, cleaning solutions containing detergents, alcohol-based cleaning solutions, landfill leachate, aqueous paint-stripping wastes, and deicing fluids. Information

about the two demonstrations conducted in Canada and the United States is available from ZENON.

DEMONSTRATION RESULTS:

During the 3-month demonstration, sampling results showed that the system achieved average removal efficiencies of greater than 99.9 percent for MMA and 97.9 percent for chemical oxygen demand. MMA concentrations measured in the off-gas emission stream indicated insignificant volatilization. The ultrafiltration system effectively dewatered the process sludge, which yielded a smaller waste volume for off-site disposal. Sludge dewatering resulted in an approximate volume reduction of 60 percent and a solids increase from 1.6 to 3.6 percent. The process effluent was clear and odorless, and accepted for discharge by the local publicly owned treatment works. During the demonstration, the system was left unattended at night and on weekends, demonstrating that computer control is practical for extended operating periods.

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**LOCKHEED MARTIN MISSILES AND SPACE CO.
and GEOKINETICS INTERNATIONAL, INC.**
(Electrokinetic Remediation Process)

TECHNOLOGY DESCRIPTION:

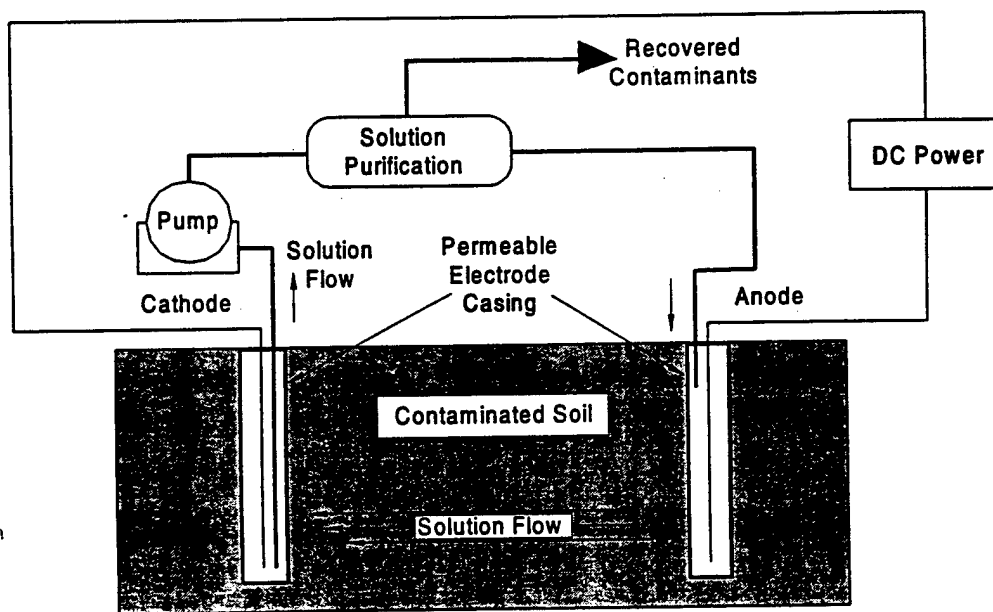
The Electrokinetic Remediation (ER) process removes metals and organic contaminants from soil, mud, sludge, and marine dredgings. ER uses electrochemical and electrokinetic processes to desorb and remove metals and polar organics. The technology may be applied in situ or in the batch mode.

The figure below is a flow diagram of the batch reactor. Waste material is placed into the batch reactor, between Ebonex® ceramic electrodes that are divided into a cathode array and an anode array. A direct current is then applied, causing ions and water to move toward the electrodes. Metal ions, ammonium ions, and positively charged organic compounds move toward the cathode. Anions such as chloride, cyanide, fluoride, nitrate, and negatively charged organic compounds move toward the anode. Two primary mechanisms transport contaminants through the soil: electromigration and electroosmosis. In electromigration, charged particles are transported through the substrate. In

contrast, electroosmosis is the movement of a liquid containing ions relative to a stationary charged surface. Of the two, electromigration is much faster and it is the principle mechanism for the ER process.

The electrodes are positioned inside permeable casings that are inserted into the waste material. After the annulus of each casing is filled with water, the current is turned on. The water passes from the anode casing into the waste and toward the cathode. This procedure (1) supports electrokinetic movement of the contaminants through the soil; (2) helps maintain soil moisture, thereby sustaining the electric field; and (3) enables various chemicals that enhance contaminant removal to be added as required.

As the water accumulates in the annulus of the cathode casing, it is pumped out for processing. Processing involves removal of contaminants by electrochemical means, producing a concentrated contaminant brine that can be either further processed or disposed of as hazardous waste. The



Flow Diagram of the Electrokinetic Remediation Process

water is then returned to the annulus of the anode casing.

WASTE APPLICABILITY:

ER is designed to remove heavy metals, anions, and polar organics from soil, mud, sludge, and dredgings. Treatable concentrations range from a few parts per million (ppm) to tens of thousands ppm. The batch technology is most appropriate for sites with contaminated estuarine and river muds and dredgings, sewage processing sludges, and fines remaining after soil washing. The process can be used with virtually any substrate. ER's effectiveness is sharply reduced for wastes with a moisture content of less than 10 percent.

STATUS:

This technology was accepted into the SITE Demonstration Program in 1994. A demonstration of the process will be conducted at the Alameda Naval Air Station in California.

The ER process has been used successfully at several European sites (see table below) on soils contaminated with metals.

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Site Description	Site Dimensions (in meters [m])	Contaminants	Initial Concentration	Final Concentration
Former paint factory (limited duration field trial)	70 m x 3 m	Copper Lead	> 5,000 ppm 500-1,000 ppm	1,000 ppm 150-300 ppm
Galvanizing plant (limited duration field trial)	15 m x 6 m	Zinc	2,400 ppm average	1,680 ppm average
Former timer impregnation plant	25 m x 15 m	Arsenic	115 ppm average	10 ppm average
Temporary landfill	70 m x 40 m	Cadmium	250 ppm average	< 20 ppm
Soil deposit on military airbase	90 m x 20 m	Cadmium Chromium Copper Lead Nickel Zinc	2,600 ppm 770 ppm 730 ppm 660 ppm 7,300 ppm 860 ppm	150 ppm 10-20 ppm 10-20 ppm 10-20 ppm 10-20 ppm 10-20 ppm

Performance Summary of In Situ Electrokinetic Remediation Process
Applied at Five Field Sites in Europe

MATRIX PHOTOCATALYTIC INC.
(Photocatalytic Air Treatment)

TECHNOLOGY DESCRIPTION:

Matrix Photocatalytic Inc. is developing a titanium dioxide (TiO_2) photocatalytic air treatment technology that destroys volatile organic compounds (VOC) and semivolatile organic compounds in air streams. During treatment, contaminated air at ambient temperatures flows through a fixed TiO_2 catalyst bed activated by ultraviolet (UV) light. Typically, organic contaminants are destroyed in fractions of a second.

Technology advantages include the following:

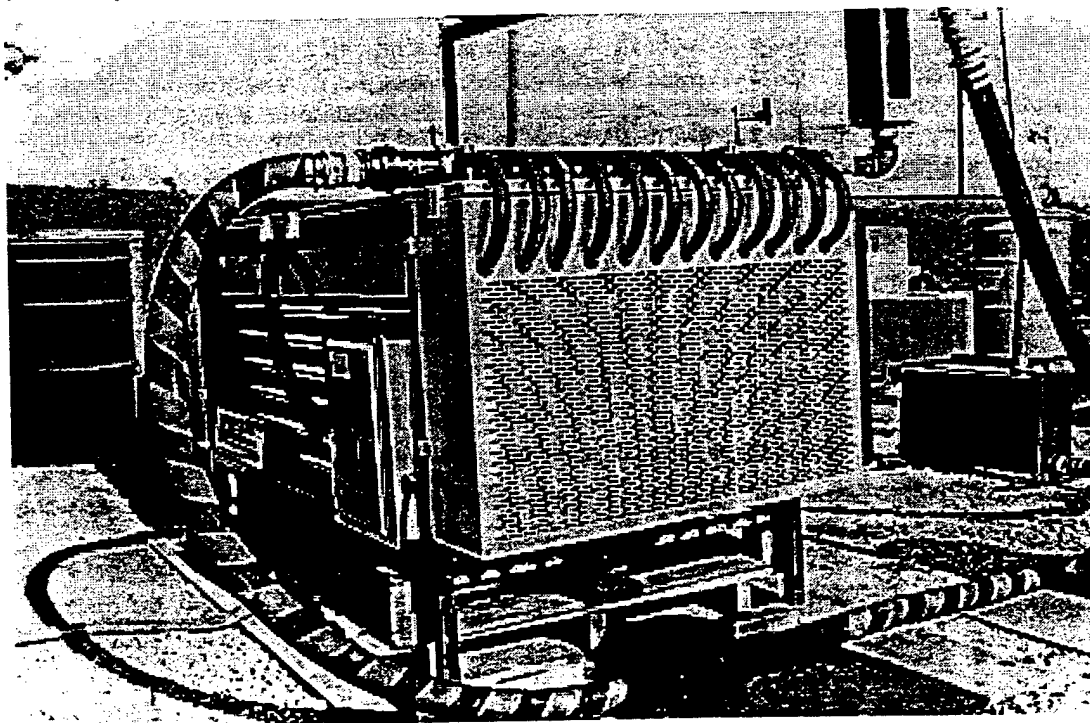
- Robust equipment
- No residual toxins
- No ignition source
- Unattended operation
- Low direct treatment cost

The technology has been tested on benzene, toluene, ethylbenzene, and xylene;

trichloroethene; tetrachloroethane; isopropyl alcohol; acetone; chloroform; methanol; and methyl ethyl ketone. A field-scale system is shown in the photograph on the next page.

WASTE APPLICABILITY:

The TiO_2 photocatalytic air treatment technology can effectively treat dry or moist air. The technology has been demonstrated to purify contaminant steam directly, thus eliminating the need to condense. Systems of 100 cubic feet per minute have been successfully tested on vapor extraction operations, air stripper emissions, steam from desorption processes, and VOC emissions from manufacturing facilities. Other potential applications include odor removal, stack gas treatment, soil venting, and manufacturing ultra-pure air for residential, automotive, instrument, and medical needs. Systems of up to about 1,000 cubic feet per minute can be cost-competitive with thermal destruction systems.



Full-Scale Photocatalytic Air Treatment System

STATUS:

The TiO₂ photocatalytic air treatment technology was accepted into SITE Emerging Technology Program (ETP) in October 1992; the evaluation was completed in 1993. Based on results from the ETP, this technology was invited to participate in the SITE Demonstration Program. For further information about the evaluation under the ETP, refer to the journal article (EPA/600/A-93/282), which is available from EPA. A suitable demonstration site is being sought.

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ALUMINUM COMPANY OF AMERICA
(formerly ALCOA SEPARATION TECHNOLOGY, INC.)
(Bioscrubber)

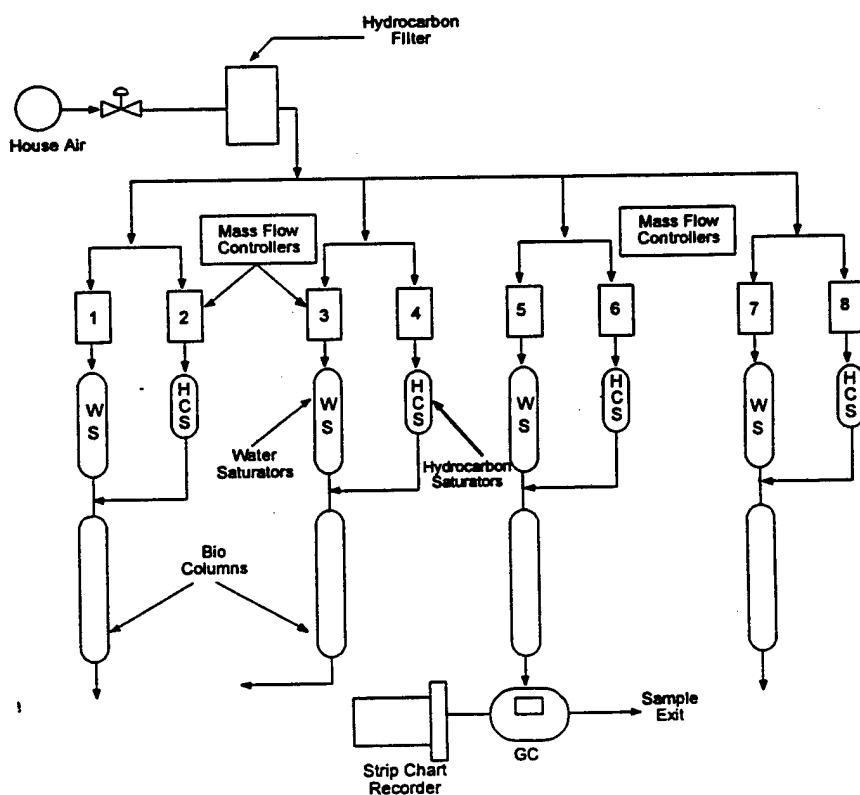
TECHNOLOGY DESCRIPTION:

This bioscrubber technology digests hazardous organic emissions generated by soil, water, and air decontamination processes. The bioscrubber consists of a filter with an activated carbon medium that supports microbial growth. This unique medium, with increased microbial population and enhanced bioactivity, converts diluted organics into carbon dioxide, water, and other nonhazardous compounds. The filter removes biomass, supplies nutrients, and adds moisture. A pilot-scale unit with a 4-cubic-foot-per-minute capacity is being field-tested (see figure below).

In addition to efficient degradation, the bioscrubber provides an effective sink to mitigate feed fluctuations. During an 11-month bench-scale test, the bioscrubber consistently removed contaminants

such as petroleum hydrocarbons, alcohols, ketones, and amines from the waste feed at levels ranging from less than 5 to 40 parts per million (ppm).

The bioscrubber provides several advantages over conventional activated carbon adsorbers. First, bioregeneration keeps the maximum adsorption capacity constantly available; thus, the mass transfer zone remains stationary and relatively short. The carbon does not require refrigeration, and the required bed length is greatly reduced, reducing capital and operating expenses. Finally, the chromatographic effect (premature desorption) common in an adsorber is eliminated because the maximum capacity is available constantly. The bioscrubber's advantages are fully exploited when the off-gas contains weakly adsorbed contaminants, such as methylene chloride, or adsorbates competing with moisture in the stream. The bioscrubber may replace



Bioscrubber Pilot-Scale Unit

activated carbon in some applications.

WASTE APPLICABILITY:

The bioscrubber technology removes organic contaminants in air streams from soil, water, or air decontamination processes. The technology is especially suited to treat streams containing aromatic solvents, such as benzene, toluene, and xylene, as well as alcohols, ketones, hydrocarbons, and others. The technology has several applications to Superfund sites, including (1) organic emission control for groundwater decontamination using air strippers, (2) emission control for biological treatment of ground and surface water, and (3) emission control for soil decontamination. These primary treatment processes have not been designed to prevent volatile organic compound discharges into the atmosphere. The bioscrubber is an ideal posttreatment for these processes because it handles trace organic volatiles economically and effectively.

STATUS:

This technology was accepted into the SITE Emerging Technology Program in July 1990. Bench-scale bioscrubbers operated continuously for more than 11 months to treat an air stream with trace concentrations of toluene at about 10 to 20 ppm. The bioscrubbers accomplished a removal efficiency of greater than 95 percent. The filter had a biodegradation efficiency 40 to 80 times greater than existing filters. The project was completed in June 1993. Based on results from the Emerging Technology Program, the bioscrubber technology was invited to participate in the SITE Demonstration Program.

Evaluation results have been published in the report "Bioscrubber for Removing Hazardous Organic Emissions from Soil, Water and Air Decontamination Processes" (EPA/540/R-93/521). This report is available from the National Technical Information Service. The Emerging Technology Bulletin (EPA/540/F-93/507) and the Emerging Technology Summary (EPA/540/SR-93/521) are available from EPA. An article was also published in the *Journal of Air and Waste Management*, Volume 44, March 1994, pp. 299-303.

The pilot-scale unit has also been tested on discharge from an air stripping tower at a flow rate of 2 standard cubic feet per minute. The discharge contained from less than 10 ppm up to 200 ppm toluene. The unit demonstrated the effectiveness, efficiency, and reliability of its design. Additional tests are underway to confirm results at higher flow rates and with other contaminants.

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ATOMIC ENERGY OF CANADA, LIMITED (Chemical Treatment and Ultrafiltration)

TECHNOLOGY DESCRIPTION:

The Atomic Energy of Canada, Limited (AECL), process uses chemical pretreatment and ultrafiltration to remove trace concentrations of dissolved metals from wastewater, contaminated groundwater, and leachate. The process selectively removes metal contaminants and produces a volume-reduced water stream for further treatment and disposal.

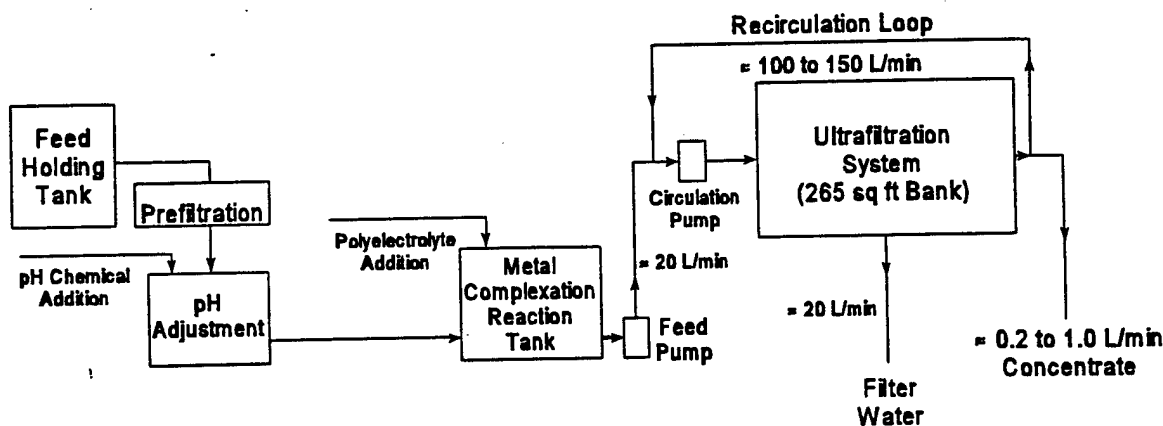
The installed unit's overall dimensions are 5 feet wide by 7 feet long by 6 feet high. The skid-mounted unit consists of (1) a bank of 5-micron cartridge prefilters, (2) a feed conditioning system with polyelectrolytes and chemicals for pH adjustment, (3) two banks of hollow-fiber ultrafilters, (4) a backflush system for cleaning the membrane unit, and (5) associated tanks and instrumentation.

The figure below illustrates the process. Wastewater enters the prefilter through the feed holding tank, where suspended particles are removed from the feed. The filtered waste stream is then routed to conditioning tanks where the solution pH is adjusted. Water-soluble

macromolecular compounds are then added to the wastewater to form complexes with heavy metal ions. Next, a relatively high molecular weight polymer, generally a commercially available polyelectrolyte, is added to the wastewater to form selective metal-polymer complexes at the desired pH and temperature. The polyelectrolyte quantities depend on the metal ion concentration.

The wastewater then passes through a cross-flow ultrafiltration membrane system by way of a recirculation loop. The ultrafiltration system provides a total membrane surface area of 265 square feet and a flow rate of about 6 gallons per minute (gpm). The membranes retain the metal complexes (concentrate), while allowing uncomplexed ions to pass through the membrane with the filtered water. The filtered water (permeate) is continuously withdrawn, while the concentrate stream, containing most of the contaminants, is recycled through the recirculation loop until it meets the target concentration. After reaching the target concentration, the concentrate stream is withdrawn for further treatment, such as solidification. It can then be safely disposed of, while the clean filtered water is discharged.

WASTE APPLICABILITY:



Single-Stage Chemical Treatment and Ultrafiltration Process

The AECL process treats groundwater, leachate, and surface runoff contaminated with trace levels of toxic heavy metals. The process also treats effluents from (1) industrial processes, (2) production and processing of base metals, (3) smelters, (4) electrolysis operations, and (5) battery manufacturing. Potential applications include removal of metals such as cadmium, lead, mercury, uranium, manganese, nickel, chromium, and silver.

The process can treat influent with dissolved metal concentrations from several parts per million (ppm) up to about 100 ppm. In addition, the process removes other inorganic and organic materials present as suspended or colloidal solids. The sole residue is the ultrafiltration concentrate, which generally constitutes 5 to 20 percent of the feed volume.

STATUS:

The AECL process was accepted into the SITE Emerging Technology Program in 1988. During initial bench-scale and pilot-scale tests, the AECL process successfully removed cadmium, lead, and mercury. These results were used to help designers construct the mobile unit.

The mobile unit has been tested at Chalk River Laboratories and a uranium mine tailings site in Ontario, Canada. The field evaluation indicated that process water characteristics needed further study; pretreatment schemes are being evaluated. The mobile unit, which is capable of treating influent flows ranging from 1,000 to 5,000 gallons per day, is available for treatability tests and on-site applications. An Emerging Technology Bulletin (EPA/540/F-92/002) is available from EPA.

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INSTITUTE OF GAS TECHNOLOGY (Chemical and Biological Treatment)

TECHNOLOGY DESCRIPTION:

The Institute of Gas Technology (IGT) chemical and biological treatment (CBT) process remediates sludges, soils, groundwater, and surface water contaminated with organic pollutants, such as polynuclear aromatic hydrocarbons (PAH) and polychlorinated biphenyls (see photograph below). The treatment system combines two remedial techniques: (1) chemical oxidation as pretreatment, and (2) biological treatment using aerobic and anaerobic biosystems in sequence or alone, depending on the waste. The CBT process uses mild chemical treatment to produce intermediates that are biologically degraded, reducing the cost and risk associated with a more severe treatment process such as incineration.

During the pretreatment stage, the contaminated material is treated with a chemical reagent that degrades the organics to carbon dioxide, water, and partially oxidized intermediates. In the second stage

of the CBT process, biological systems degrade the hazardous residual materials and the partially oxidized intermediates from the first stage. Chemically treated wastes are subjected to cycles of aerobic and anaerobic degradation if aerobic or anaerobic treatment alone is not sufficient. Several cycles of chemical and biological treatment are also used for extremely recalcitrant contaminants.

WASTE APPLICABILITY:

The CBT process can be applied to soils, sludges, groundwater, and surface water containing (1) high waste concentrations that would typically inhibit bioremediation, or (2) low waste concentrations for which bioremediation alone is too slow. The process is not adversely affected by radionuclides or heavy metals. Depending on the types of heavy metals present, these metals will bioaccumulate in the biomass, complex with organic or inorganic material in the soil slurries, or solubilize in the recycled water.



Chemical and Biological Treatment Process

The CBT process can be applied to a wide range of organic pollutants, including alkenes, chlorinated alkenes, aromatics, substituted aromatics, and complex aromatics.

STATUS:

IGT evaluated the CBT process for 2 years under the SITE Emerging Technology Program. The Emerging Technology Bulletin (EPA/540/F-94/540), which details results from the evaluation, is available from EPA. Based on results from the Emerging Technology Program, this technology was invited to participate in the SITE Demonstration Program.

Under the SITE Demonstration Program, IGT plans to conduct a full-scale demonstration of the CBT process on sediments containing PAHs. Different operating scenarios will be used to demonstrate how effectively the CBT process treats sediments in a bioslurry reactor. Several sites are being considered for the demonstration.

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INSTITUTE OF GAS TECHNOLOGY (Fluid Extraction-Biological Degradation Process)

TECHNOLOGY DESCRIPTION:

The three-step fluid extraction-biological degradation (FEBD) process removes organic contaminants from soil (see figure below). The process combines three distinct technologies: (1) fluid extraction, which removes the organics from contaminated solids; (2) separation, which transfers the pollutants from the extract to a biologically compatible solvent or activated carbon carrier; and (3) biological degradation, which destroys the pollutants and leaves innocuous end-products.

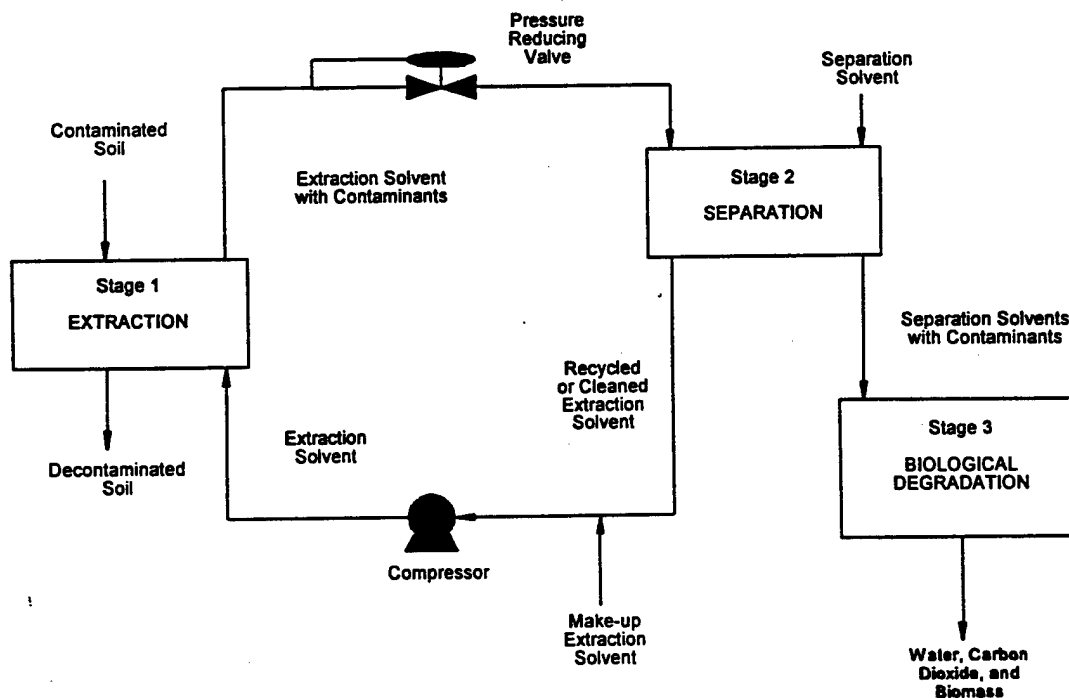
In the fluid extraction step, excavated soils are placed in a pressure vessel and extracted with a recirculated stream of supercritical or near-supercritical carbon dioxide. An extraction cosolvent may be added to enhance the removal of additional contaminants.

During separation, organic contaminants are transferred to a biologically compatible separation solvent such as water or a water-methanol mixture.

The separation solvent is then sent to the final stage of the process, where bacteria degrade the waste to carbon dioxide and water. Clean extraction solvent is then recycled for use in the extraction stage.

Organic contaminants are biodegraded in aboveground aerobic bioreactors, using mixtures of bacterial cultures capable of degrading the contaminants. Selection of cultures is based on site contaminant characteristics. For example, if a site is mainly contaminated with polynuclear aromatic hydrocarbons (PAH), cultures able to metabolize or cometabolize these hydrocarbons are used. The bioreactors can be configured to enhance the rate and extent of biodegradation.

Research continues on using bound activated carbon in a carrier system during the separation step. Bound activated carbon should allow high-pressure conditions to be maintained in the fluid extraction step, enhancing extraction efficiency and decreasing extraction time. Bound activated carbon should also limit the loss of carbon dioxide, thereby decreasing costs. The activated carbon containing the bound



Fluid Extraction-Biological Degradation Process

PAHs could then be treated in the biodegradation step by converting the carrier system to a biofilm reactor. These activated carbon carrier systems could then be recycled into the high-pressure system of the extraction and separation steps.

WASTE APPLICABILITY:

This technology removes organic compounds from contaminated solids. It is more effective on some classes of organics, such as hydrocarbons (for example, gasoline and fuel oils) than on others, such as halogenated solvents and polychlorinated biphenyls. The process has also been effective in treating nonhalogenated aliphatic hydrocarbons and PAHs.

STATUS:

This technology was accepted into the SITE Emerging Technology Program in June 1990. The Institute of Gas Technology has evaluated all three stages of the technology with soils from a Superfund site and from three town gas sites. These soils exhibited a variety of physical and chemical characteristics. Approximately 85 to 99 percent of detectable PAHs, including two- to six-ring compounds, were removed from the soils.

The measurable PAHs were biologically converted in both batch-fed and continuously fed, constantly stirred tank reactors. The conversion rate and removal efficiency were high in all systems. The PAHs were biologically removed or transformed at short hydraulic retention times. All PAHs, including four- to six-ring compounds, were susceptible to biological removal.

Results from this project were published in the *Emerging Technology Bulletin* (EPA/540/F-94/501), which is available from EPA. An article was submitted to the *Journal of Air and Waste Management*.

Potential users of this technology have expressed interest in continuing research. This technology has been invited to participate in the SITE Demonstration Program. The technology would be able to remediate town gas sites, wood treatment sites, and other contaminated soils and sediments.

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**LEWIS ENVIRONMENTAL SERVICES, INC./
HICKSON CORPORATION**
(Chromated Copper Arsenate Soil Leaching Process)

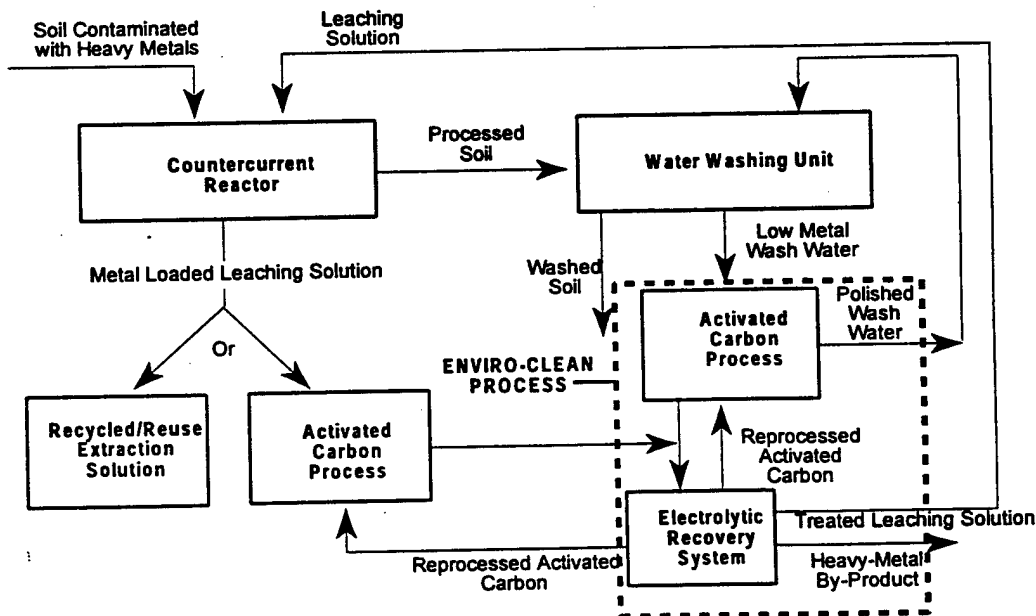
TECHNOLOGY DESCRIPTION:

Lewis Environmental Services, Inc. (Lewis), has developed a soil leaching process to remediate soils contaminated with inorganics and heavy metals including chromium, copper, cadmium, mercury, arsenic, and lead.

The soil leaching process consists of leaching contaminated soil in a countercurrent stirred reactor system (see figure below). A screw feeder delivers the soil into the reactor, where it is leached with sulfuric acid for 30 to 60 minutes. The sulfuric acid solubilizes the inorganics and heavy metals into the leaching solution. Any organic contaminants are separated and decanted from the leaching solution, using strong acid leachate, space separation, and skimming. The processed soil is then washed with water and air-dried.

The wash water is then treated with Lewis' ENVIRO-CLEAN PROCESS, which consists of a granulated activated carbon system followed by an electrolytic recovery system. The ENVIRO-CLEAN PROCESS recovers the heavy metals from the leaching solution and wash water and produces an effluent that meets EPA discharge limits for heavy metals. The treated wash water can then be reused in the soil washing step. The leaching solution can be returned directly to the stirred reactor system, depending on its metals concentration.

Contaminated soil must be properly sized and screened to facilitate leaching in the stirred reactor system. Large pieces of debris such as rocks, wood, and bricks must be removed before treatment. Standard screening and classification equipment, such as that used in municipal waste treatment plants, is suitable for this purpose.



Chromated Copper Arsenate Soil Leaching Process

The soil leaching process does not generate appreciable quantities of treatment by-products or waste streams containing heavy metals. The treated soil meets toxicity characteristic leaching procedure (TCLP) criteria and can be either returned to the site or disposed of at a nonhazardous landfill. The granular activated carbon requires disposal after about 20 to 30 treatment cycles and should also meet TCLP criteria. Heavy metals recovered by the ENVIRO-CLEAN process can be reused by industry.

WASTE APPLICABILITY:

The soil leaching process can treat wastes generated by the wood preserving and metal plating industries, battery waste sites, and urban lead sites.

STATUS:

The soil leaching process was accepted into the Emerging Technology Program in 1993. Laboratory-scale tests have shown that the process successfully treats soil contaminated with chromated copper arsenate (CCA). The evaluation of the technology under the SITE Program was completed in September 1996. Results from the evaluation will be available in 1997.

In 1992, Lewis treated a 5-gallon sample of CCA-contaminated soil from Hickson Corporation (Hickson), a major CCA chemical manufacturer. The treated soil met TCLP criteria, with chromium and arsenic, the two main leaching solution constituents, averaging 0.8 milligram per kilogram (mg/kg) and 0.9 mg/kg, respectively.

Analysis also revealed 3,330 milligrams per liter (mg/L) of chromium, 13,300 mg/L of copper, and 22,990 mg/L of iron in the leaching solution. In addition, analysis indicated 41.4 mg/L of chromium, 94.8 mg/L of copper, and 3.0 mg/L of arsenic present in the wash water. After treatment, the wash water contained metals levels below 0.01 mg/L for copper and chromium and 0.3 mg/L for arsenic.

Lewis plans further laboratory-scale testing at its Pittsburgh, Pennsylvania facility, followed by bench- or pilot-scale testing at Hickson's facility in Conley, Georgia.

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NEW JERSEY INSTITUTE OF TECHNOLOGY
(GHEA Associates Process)

TECHNOLOGY DESCRIPTION:

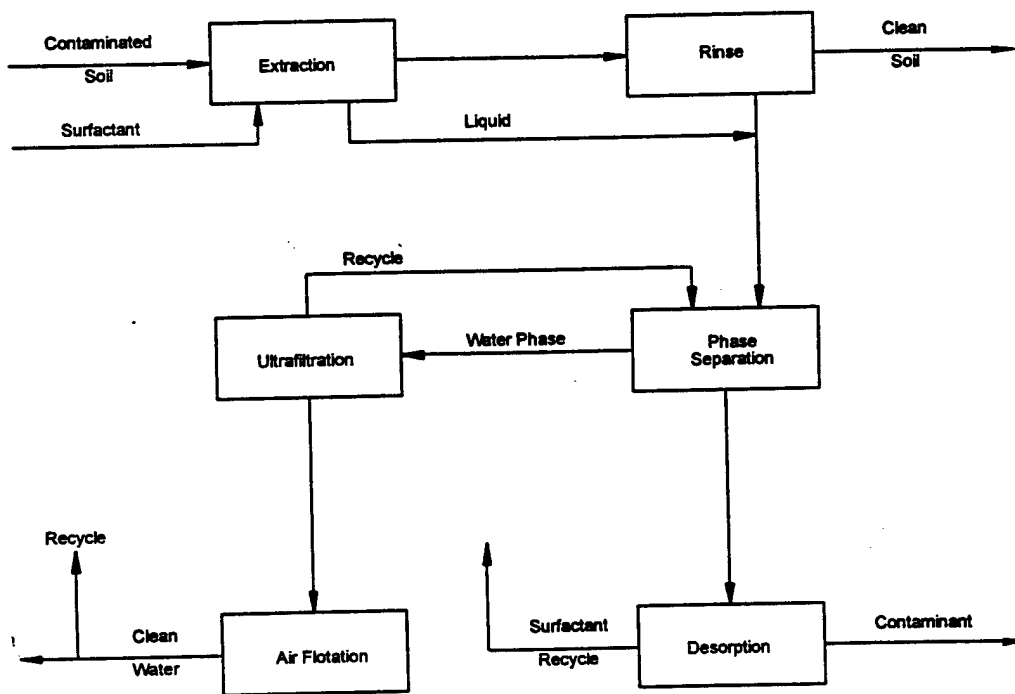
The GHEA Associates process applies surfactants and additives to soil washing and wastewater treatment to make organic and metal contaminants soluble. In soil washing, soil is first excavated, washed, and rinsed to produce clean soil. Wash and rinse liquids are then combined and treated to separate surfactants and contaminants from the water. Next, contaminants are separated from the surfactants by desorption and isolated as a concentrate. Desorption regenerates the surfactants for repeated use in the process.

The liquid treatment consists of a sequence of steps involving phase separation, ultrafiltration, and air flotation (see figure below). The treated water meets all National Pollutant Discharge Elimination System groundwater discharge criteria, allowing it to be (1) discharged without further treatment, and (2) reused in the process itself or reused as a source of high quality water for other users.

In wastewater treatment applications, surfactants added to the wastewater adsorb contaminants. The mixture is then treated in the same manner as described above for (1) water purification, (2) separation of the contaminants, and (3) recovery of the surfactants. The treatment process yields clean soil, clean water, and a highly concentrated fraction of contaminants. No other residues, effluents, or emissions are produced. The figure below illustrates the GHEA process.

WASTE APPLICABILITY:

This technology can be applied to soil, sludges, sediments, slurries, groundwater, surface water, end-of-pipe industrial effluents, and in situ soil flushing. Contaminants that can be treated include both organics and heavy metals, nonvolatile and volatile organic compounds, and highly toxic refractory compounds.



GHEA Process for Soil Washing

STATUS:

The technology was accepted into the SITE Emerging Technology Program in June 1990. Treatability tests were conducted on various matrices, including soils with high clay contents, industrial oily sludges, industrial wastewater effluents, and contaminated groundwater (see table below). In situ soil flushing tests have shown a 20-fold enhancement of contaminant removal rates. Tests using a 25-gallon pilot-scale plant have also been conducted. The Emerging Technology Bulletin (EPA/540/F-94/509), which details evaluation results, is available from EPA. Costs for treatment range from \$50 to \$80 per ton.

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SUMMARY OF TREATABILITY TEST RESULTS			
MATRIX	UNTREATED SAMPLE	TREATED SAMPLE	PERCENT REMOVAL
Volatile Organic Compounds (VOC): Trichloroethene; 1,2-Dichloroethene; Benzene; Toluene Soil, parts per million (ppm) Water, parts per billion (ppb)	20.13 109.0	0.05 2.5	99.7% 97.8%
Total Petroleum Hydrocarbons (TPH): Soil, ppm	13,600	80	99.4%
Polychlorinated Biphenyls (PCB): Soil, ppm Water, ppb	380.00 6,000.0	0.57 <0.1	99.8% >99.9%
Trinitrotoluene in Water, ppm	180.0	<0.08	>99.5%
Coal Tar Contaminated Soil (ppm): Benzo[a]pyrene Benzo[k]fluoranthene Chrysene Benzanthracene Pyrene Anthracene Phenanthrene Fluorene Dibenzofuran 1-Methylnaphthalene 2-Methylnaphthalene	28.8 24.1 48.6 37.6 124.2 83.6 207.8 92.7 58.3 88.3 147.3	<0.1 4.4 <0.1 <0.1 <0.1 <0.1 <0.1 <0.1 <0.1 1.3 <0.1	>99.7% 81.2% >99.8% >99.7% >99.9% >99.8% >99.9% >99.9% >99.8% >99.8% >99.9%
Heavy Metals In Soil: Chromium, ppm	21,000	640	96.8%
Iron (III) in Water, ppm:	30.8	0.3	99.0%

PULSE SCIENCES, INC.
(X-Ray Treatment of Aqueous Solutions)

TECHNOLOGY DESCRIPTION:

X-ray treatment of organically contaminated aqueous solutions is based on the in-depth deposition of ionizing radiation. X-rays collide with matter, generating a shower of lower energy secondary electrons within the contaminated waste material. The secondary electrons ionize and excite the atomic electrons, break up the complex contaminant molecules, and form highly reactive radicals. These radicals react with the volatile organic compounds (VOC) and semivolatile organic compounds (SVOC) to form nontoxic by-products such as water, carbon dioxide, and oxygen.

An efficient, high-power, high-energy, linear induction accelerator (LIA) plus X-ray converter generates the X-rays used in the treatment process. The LIA energy, which must be small enough to avoid nuclear activation and as large as possible to increase the bremsstrahlung conversion efficiency, will most likely be in the range of 8 to 10 million electron volts (MeV). A repetitive pulse of electrons 50 to 100 nanoseconds long is directed onto a cooled converter of a high atomic number metal to efficiently generate X-rays. The X-rays then penetrate the container and treat the waste materials contained within.

Based on coupled electron/photon Monte Carlo transport code calculations, the effective penetration depth of X-rays produced by converting 10-MeV electrons is 32 centimeters in water after passing through the side of a standard 55-gallon drum. Large contaminant volumes can be easily treated without absorbing a significant fraction of the ionizing radiation in the container walls. Either flowing waste or contaminated waste in stationary or rotating containers can be treated. No additives are required for the process, and in situ treatment is feasible. The cost of high throughput X-ray processing is estimated to be competitive with alternative processes which decompose the contaminants.

WASTE APPLICABILITY:

X-ray processing can treat a large number of organic contaminants in aqueous solutions (groundwater, liquids, leachates, or wastewater) without expensive waste extraction or preparation. The technology has successfully treated 17 organic contaminants, listed in the table on the next page. No hazardous by-products are predicted to form or have been observed in the experiments.

STATUS:

This technology was accepted into the SITE Emerging Technology Program in May 1991 and was completed in April 1994. A 1.2-MeV, 800-ampere, 55-nanosecond LIA gave a dose rate of 5 to 10 rads per second. Twelve different VOCs and SVOCs found in Superfund sites were irradiated in 21 aqueous matrices prepared with a neat solution of the contaminant in reagent grade water. The amount of X-ray dose (1 rad = 10^5 Joules per gram) required to decompose a particular contaminant was a function of its chemical bond structure and its reaction rate with the hydroxyl radical. When carbonate and bicarbonate ions (hydroxyl radical scavengers) were present in contaminated well water samples, approximately five times the X-ray dose was required to decompose contaminants that react strongly with the hydroxyl radical. The remediation rate of carbon tetrachloride, which does not react with hydroxyl radicals, was not affected.

An X-ray dose of 150 kilorads (krad) reduced the moderate contamination levels in a well water sample from a Superfund site at Lawrence Livermore National Laboratory (LLNL) to less than those set by the California Primary Drinking Water Standards. For a more highly contaminated LLNL well water sample, experimental data suggested a 500-krad dose was needed to reduce the contamination levels to drinking water standards. In principle, the rate coefficients determined from the data can be used to estimate the dose level required to destroy mixtures of multiple VOC contaminants and OH- radical scavengers. However, these estimates should be applied judiciously. Only the experimentally determined

destruction curves, based on the remediation of test samples of the actual mixture, can be used with confidence at the present. The table below summarizes the X-ray treatment results from the SITE evaluation.

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CONTAMINANTS	MATRIX	INITIAL CONCENTRATION (ppb)	FINAL CONCENTRATION (ppb)	CPDWS ¹ (ppb)	X-RAY DOSE (Krad)
TCE	Deionized Water	9,780	< 0.1	5	50.3
PCE		10,500	< 0.1	5	69.8
Chloroform		2,000	4.4	—	178
Methylene Chloride		270	3.1	5	145.9
Trans-1,2-Dichloroethene		260	0.78	10	10.6
Cis-1,2-Dichloroethene		13	< 0.5	6	10.6
1,1,1-Trichloroethane		590	54	200	207.1
Carbon Tetrachloride (CCl ₄)		180	14	0.5	224
Benzene		240	< 0.5	1	8.8
Toluene		150	< 0.5	150	4.83
Ethylbenzene		890	3.6	680	20.4
Xylene		240	1.2	1,750	5.6
Benzene/CCl ₄	Contaminated Well Water	262/400	< 0.5/196	1/0.5	39.9/93.8
Ethylbenzene/CCl ₄		1,000/430	< 0.5/70.9	680/0.5	33.2/185
Ortho-xylene/CCl ₄		221/430	< 0.5/85	1,750/0.5	20.5/171
TCE	LLNL Well Water Sample #1	3,400	< 0.5	5	99.0
PCE		500	< 0.5	5	99.0
1,1-Dichloroethane		< 10	1	5	145.4
1,1-Dichloroethene		25	< 1	6	49.9
1,1,1-Trichloroethane		13	2.0	200	145.4
Cis-1,2-Dichloroethene		14	< 0.5	6	49.9
TCE	LLNL Well Water Sample #2	5,000	< 1.0	5	291
PCE		490	1.6	5	291
Chloroform		250	81	—	291
CCl ₄		14	4	0.5	291
1,2-Dichloroethane		38	17	5	291
1,1-Dichloroethane		11	6.8	5	291
Freon		71	32	—	291

¹ parts per billion
California Primary Drinking Water Standards

Summary of X-ray Treatment Results

RECRA ENVIRONMENTAL, INC.
(formerly ELECTRO-PURE SYSTEMS, INC.)
(Alternating Current Electrocoagulation Technology)

TECHNOLOGY DESCRIPTION:

The alternating current electrocoagulation (ACE) technology offers an alternative to the use of metal salts or polymers and polyelectrolyte addition for breaking stable emulsions and suspensions. The technology removes metals, colloidal solids and particles, and soluble inorganic pollutants from aqueous media by introducing highly charged polymeric aluminum hydroxide species. These species neutralize the electrostatic charges on suspended solids and oil droplets to facilitate agglomeration or coagulation and resultant separation from the aqueous phase. The treatment prompts the precipitation of certain metals and salts.

The figure below depicts the basic ACE process. Electrocoagulation occurs in either batch mode, allowing recirculation, or continuous (one-pass) mode in an ACE fluidized bed separator. Electrocoagulation is conducted by passing the aqueous medium through the treatment cells in upflow mode. The electrocoagulation cell(s) consist of nonconductive piping equipped with rectilinearly shaped, nonconsumable metal electrodes between which is maintained a turbulent, fluidized bed of aluminum alloy pellets.

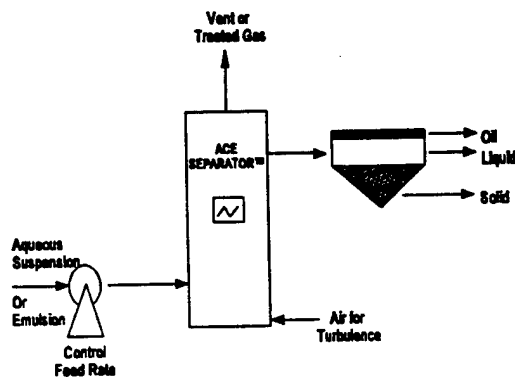
Application of the alternating current electrical charge to the electrodes prompts the dissolution of the fluidized bed and the formation of the polymeric hydroxide species. Charge neutralization is initiated within the electrocoagulation cell(s) and continues

following effluent discharge. Application of the electrical field prompts electrolysis of the water medium and generates minute quantities of hydrogen gas. The coagulated solids will often become entrained in the gas, causing their flotation.

Attrition scrubbing of the fluidized bed pellets within the cell inhibits the buildup of scale or coating on the aluminum pellets and the face of the electrodes. Coagulation and flocculation occur simultaneously within the ACE cells as the effluent is exposed to the electric field and the aluminum dissolves from the fluidized bed.

The working volume of the fluidized bed cell, excluding external plumbing, is 5 liters. The ACE systems have few moving parts and can easily be integrated into a process treatment train for effluent, pretreatment, or polishing treatment. The ACE technology has been designed into water treatment systems which include membrane separation, reverse osmosis, electrofiltration, sludge dewatering, and thermo-oxidation technologies.

System operating conditions depend on the chemistry of the aqueous medium, particularly the conductivity and chloride concentration. Treatment generally requires application of low voltage (<135 VAC) and operating currents of less than 20 amperes. The flow rate of the aqueous medium through the treatment cell(s) depends on the solution chemistry, the nature of the entrained suspension or emulsion, and the treatment



Alternating Current Electrocoagulation (ACE)

objectives.

Product separation occurs in conventional gravity separation devices or filtering systems. Each phase is removed for reuse, recycling, additional treatment, or disposal.

Current systems are designed to treat waste streams of between 10 and 100 gallons per minute (gpm). RECRA Environmental, Inc., maintains a bench-scale unit (1 to 3 gpm) at its Amherst Laboratory for use in conducting treatability testing.

WASTE APPLICABILITY:

The ACE technology treats aqueous-based suspensions and emulsions such as contaminated groundwater, surface water runoff, landfill and industrial leachate, wash and rinse waters, and various solutions and effluents. The suspensions can include solids such as inorganic and organic pigments, clays, metallic powders, metal ores, and colloidal materials. Treatable emulsions include a variety of solid and liquid contaminants, including petroleum-based by-products.

The ACE technology has demonstrated reductions of clay, latex, and various hydroxide loadings by over 90 percent. Chemical oxygen demand and total organic carbon content of spiked slurries have been reduced by over 80 percent. The technology has removed heavy metals at between 55 and 99 percent efficiency. Fluoride and phosphate have been removed at greater than 95 percent efficiency. The system has been used to recover fine-grained products which would otherwise have been discharged.

STATUS:

The ACE technology was accepted into the SITE Emerging Technology Program in July 1988. The laboratory-scale testing was completed in June 1992. The Emerging Technology Bulletin (EPA/540/F-92/011) and Emerging Technology Summary (EPA/540/S-93/504) are available from EPA. The research results are described in the *Journal of Air and Waste Management*, Volume 43, May 1993, pp. 784-789, "Alternating Current Electrocoagulation for Superfund Site Remediation."

Experiments on metals and complex synthetic slurries have defined major operating parameters for broad classes of waste streams. The technology has been modified to minimize electrical power consumption and maximize effluent throughput rates.

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RESOURCE MANAGEMENT & RECOVERY
(formerly BIO-RECOVERY SYSTEMS, INC.)
(AlgaSORB® Biological Sorption)

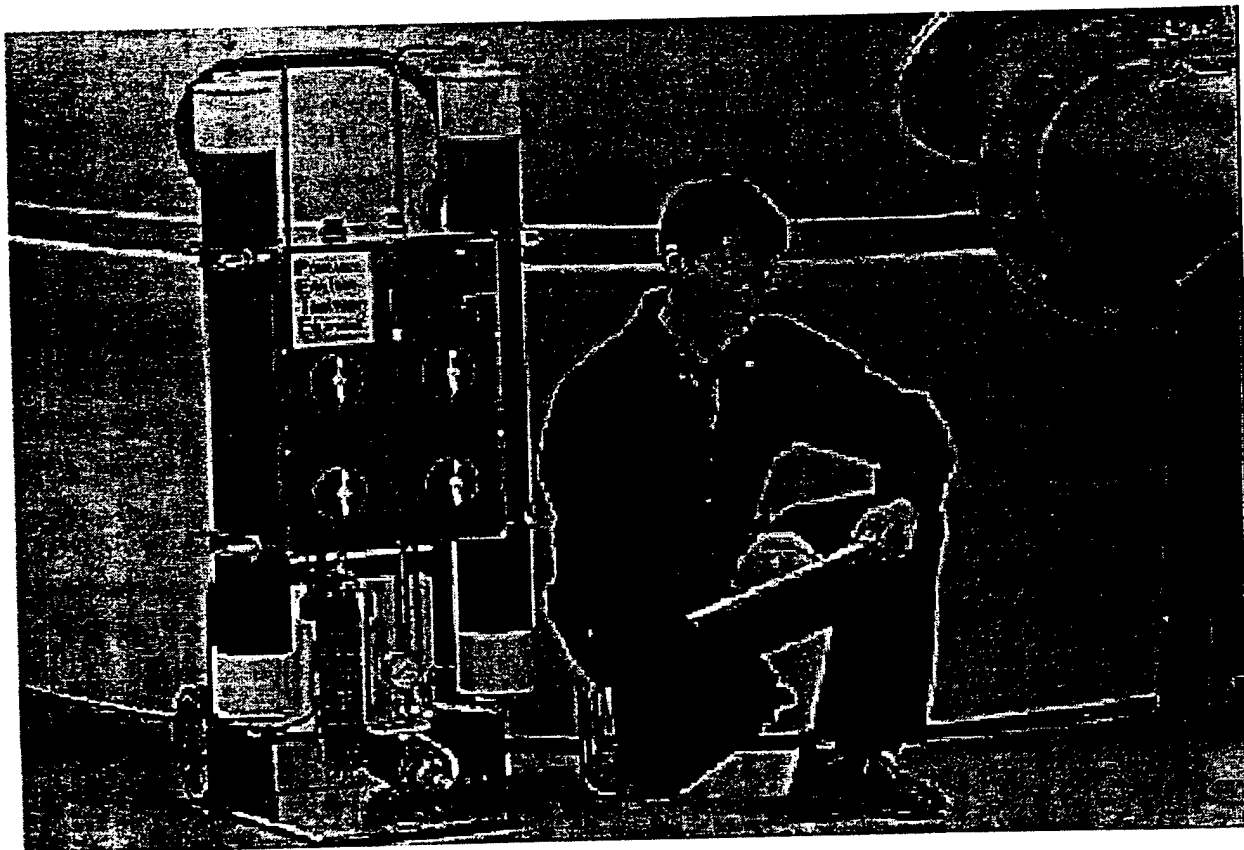
TECHNOLOGY DESCRIPTION:

The AlgaSORB® sorption process uses algae to remove heavy metal ions from aqueous solutions. The process takes advantage of the natural affinity for heavy metal ions exhibited by algal cell structures.

The photograph below shows a portable effluent treatment equipment (PETE) unit, consisting of two columns operating either in series or in parallel. Each column contains 0.25 cubic foot of AlgaSORB®, the treatment medium. The PETE unit shown below can treat waste at a flow rate of approximately 1 gallon per minute (gpm). Larger systems have been designed and manufactured to treat waste at flow rates greater than 100 gpm. The AlgaSORB® medium consists of dead algal

cells immobilized in a silica gel polymer. This immobilization serves two purposes: (1) it protects the algal cells from decomposition by other microorganisms, and (2) it produces a hard material that can be packed into columns that, when pressurized, still exhibit good flow characteristics.

The AlgaSORB® medium functions as a biological ion-exchange resin to bind both metallic cations (positively charged ions, such as mercury [Hg^{+2}]) and metallic oxoanions (negatively charged, large, complex, oxygen-containing ions, such as selenate [SeO_4^{-2}]). Anions such as chlorides or sulfates are only weakly bound or not bound at all. In contrast to current ion-exchange technology, divalent cations typical of hard water, such as calcium (Ca^{+2}) and magnesium (Mg^{+2}), or monovalent cations, such as sodium (Na^+) and potassium (K^+) do not



Portable Effluent Treatment Equipment (PETE) Unit

significantly interfere with the binding of toxic heavy metal ions to the algae-silica matrix.

Like ion-exchange resins, AlgaSORB® can be regenerated. After the AlgaSORB® medium is saturated, the metals are removed from the algae with acids, bases, or other suitable reagents. This regeneration process generates a small volume of solution containing highly concentrated metals. This solution must undergo treatment prior to disposal.

WASTE APPLICABILITY:

This technology can remove heavy metal ions from groundwater or surface leachates that are "hard" or that contain high levels of dissolved solids. The process can also treat rinse waters from electroplating, metal finishing, and printed circuit board manufacturing operations. Metals removed by the technology include aluminum, cadmium, chromium, cobalt, copper, gold, iron, lead, manganese, mercury, molybdenum, nickel, platinum, selenium, silver, uranium, vanadium, and zinc.

STATUS:

This technology was accepted into the Emerging Technology Program in 1988; the evaluation was completed in 1990. Under the Emerging Technology Program, the AlgaSORB® sorption process was tested on mercury-contaminated groundwater at a hazardous waste site in Oakland, California. Testing was designed to determine optimum flow rates, binding capacities, and the efficiency of stripping agents. The Emerging Technology Report (EPA/540/5-90/005a&b), Emerging Technology Summary (EPA/540/S5-90/005), and Emerging Technology Bulletin (EPA/540/F-92/003) are available from EPA. An article was also published in the *Journal of Air and Waste Management*, Volume 41, No. 10, October 1991.

Based on results from the Emerging Technology Program, Resource Management & Recovery was invited to participate in the SITE Demonstration Program.

The process is being commercialized for groundwater treatment and industrial point source treatment.

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UNIVERSITY OF WASHINGTON (Adsorptive Filtration)

TECHNOLOGY DESCRIPTION:

Adsorptive filtration removes inorganic contaminants (metals) from aqueous waste streams. An adsorbent ferrihydrite is applied to the surface of an inert substrate such as sand, which is then placed in one of three vertical columns (see figure below). The contaminated waste stream is adjusted to a pH of 9 to 10 and passed through the column. The iron-coated sand grains in the column act simultaneously as a filter and adsorbent. When the column's filtration capacity is reached (indicated by particulate breakthrough or column blockage), the column is backwashed. When the adsorptive capacity of the column is reached (indicated by break-through of soluble metals), the metals are removed and concentrated for subsequent recovery with a pH-induced desorption process.

Sand can be coated by ferrihydrite formed when either iron nitrate or iron chloride salts react with sodium hydroxide. The resulting ferrihydrite-coated sand is insoluble at a pH greater than 1; thus, acidic solutions can be used in the regeneration step to ensure complete metal recovery. The system does

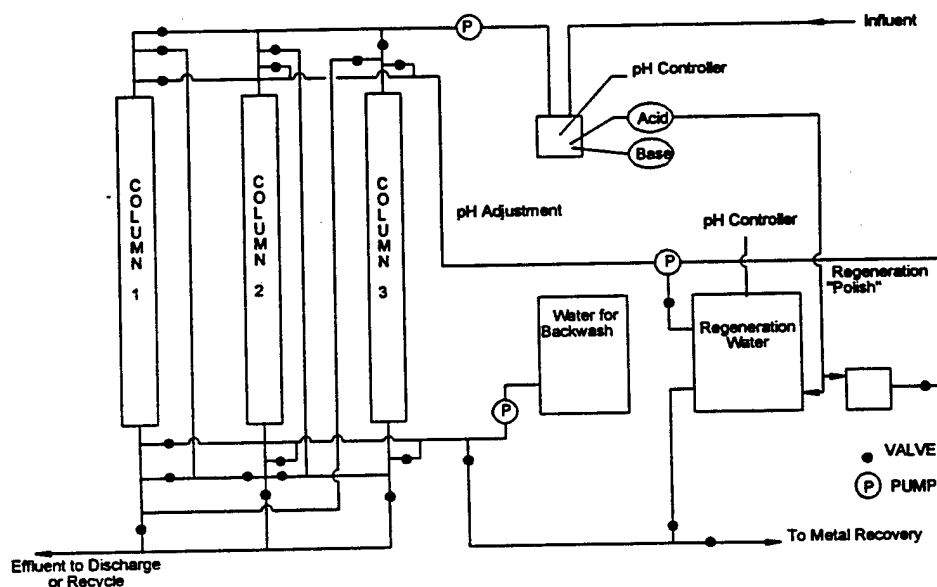
not appear to lose treatment efficiency after numerous regeneration cycles. Anionic metals such as arsenate, chromate, and selenite can be removed from the solution by treating it at a pH near 4 and regenerating it at a high pH. The system has an empty bed retention time of 2 to 5 minutes.

This technology offers several advantages over conventional treatment technologies. These advantages are its ability to (1) remove both dissolved and suspended metals from the waste stream, (2) remove a variety of metal complexes, (3) work in the presence of high concentrations of background ions, and (4) remove anionic metals.

WASTE APPLICABILITY:

This adsorptive filtration process removes inorganic contaminants, consisting mainly of metals, from aqueous waste streams. It can be applied to aqueous waste streams with a wide range of contaminant concentrations and pH values.

STATUS:



Adsorptive Filtration Treatment System

This technology was accepted into the SITE Emerging Technology Program in January 1988; the evaluation was completed in 1992. The Emerging Technology Report (EPA/540/R-93/515), Emerging Technology Summary (EPA/540/SR-93/515), and Emerging Technology Bulletin (EPA/540/F-92/008) are available from EPA.

During the SITE evaluation, synthetic solutions containing cadmium, copper, or lead at concentrations of 0.5 part per million (ppm) were treated in packed columns using 2-minute retention times. After approximately 5,000 bed volumes were treated, effluent concentrations were about 0.025 ppm for each metal, or a 95 percent removal efficiency. The tests were stopped, although the metals were still being removed. In other experiments, the media were used to adsorb copper from wastewater containing about 7,000 milligrams per liter (mg/L) copper.

The first batch of regenerant solutions contained cadmium and lead at concentrations of about 500 ppm. With initial concentrations of 0.5 ppm, this represents a concentration factor of about 1,000 to 1. Data for the copper removal test have not been analyzed. At a flow rate yielding a 2-minute retention time, the test would have taken about 7 days of continuous flow operation to treat 5,000 bed volumes. Regeneration took about 2 hours.

The system has also been tested for treatment of rinse waters from a copper-etching process at a printed circuit board shop. The coated sand was effective in removing mixtures of soluble, complexed, and particulate copper, as well as zinc and lead, from these waters. When two columns were used in series, the treatment system was able to handle fluctuations in influent copper concentration from less than 10 mg/L up to several hundred mg/L.

Groundwater from Western Processing, a Superfund site near Seattle, Washington, was treated to remove both soluble and particulate zinc.

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ROY F. WESTON, INC.
(Ambersorb® 563 Adsorbent)

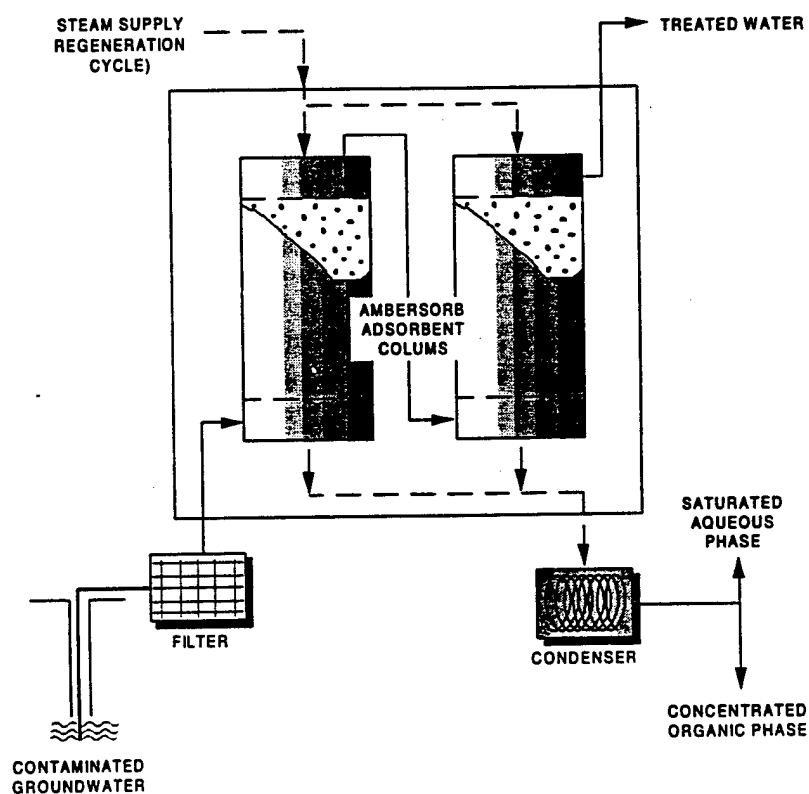
TECHNOLOGY DESCRIPTION:

Ambersorb® 563 adsorbent is a regenerable adsorbent that treats groundwater contaminated with hazardous organics (see figure below). Ambersorb 563 adsorbent has 5 to 10 times the capacity of granular activated carbon (GAC) for low concentrations of volatile organic compounds (VOC).

Current GAC adsorption techniques require either disposal or thermal regeneration of the spent carbon. In these cases, the GAC must be removed from the site and shipped as a hazardous material to the disposal or regeneration facility.

Ambersorb 563 adsorbent has unique properties that provide the following benefits:

- Ambersorb 563 adsorbent can be regenerated on site using steam, thus eliminating the liability and cost of off-site regeneration or disposal associated with GAC treatment. Condensed contaminants are recovered through phase separation.
- Because Ambersorb 563 adsorbent has a much higher capacity than GAC for volatile organics (at low concentrations), the process can operate for significantly longer service cycle times before regeneration is required.



Ambersorb® 563 Adsorbent

- Ambersorb 563 adsorbent can operate at higher flow rate loadings than GAC, which translates into a smaller, more compact system.
- Ambersorb 563 adsorbents are hard, nondusting, spherical beads with excellent physical integrity, eliminating handling problems and attrition losses typically associated with GAC.
- Ambersorb 563 adsorbent is not prone to bacterial fouling.
- Ambersorb 563 adsorbent has extremely low ash levels.

In addition, the Ambersorb 563 carbonaceous adsorbent-based remediation process can eliminate the need to dispose of by-products. Organics can be recovered in a form potentially suitable for immediate reuse. For example, removed organics could be burned for energy in a power plant.

WASTE APPLICABILITY:

Ambersorb 563 adsorbent is applicable to any water stream containing contaminants that can be treated with GAC, such as 1,2-dichloroethane, 1,1,1-trichloroethane, tetrachloroethene, vinyl chloride, xylene, toluene, and other VOCs.

STATUS:

This technology was accepted into the SITE Emerging Technology Program in 1993. The Emerging Technology Bulletin (EPA/540/F-95/500), the Emerging Technology Summary (EPA/540/SR-95/516), and the Emerging Technology Report (EPA/540/R-95/516) are available from EPA.

The Ambersorb 563 technology evaluation was conducted at the former Pease Air Force Base in Newington, New Hampshire. The groundwater

contained vinyl chloride, 1,1-dichloroethene, and trichloroethene. The field study was conducted over a 12-week period. The tests included four service cycles and three steam regenerations. The effluent from the Ambersorb adsorbent system consistently met drinking water standards. On-site steam regeneration demonstrated that the adsorption capacity of the Ambersorb system remained essentially unchanged following regeneration.

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Note: Ambersorb® is a registered trademark of Rohm and Haas Company.

HIGH VOLTAGE ENVIRONMENTAL APPLICATIONS, INC. (High-Energy Electron Beam Irradiation)

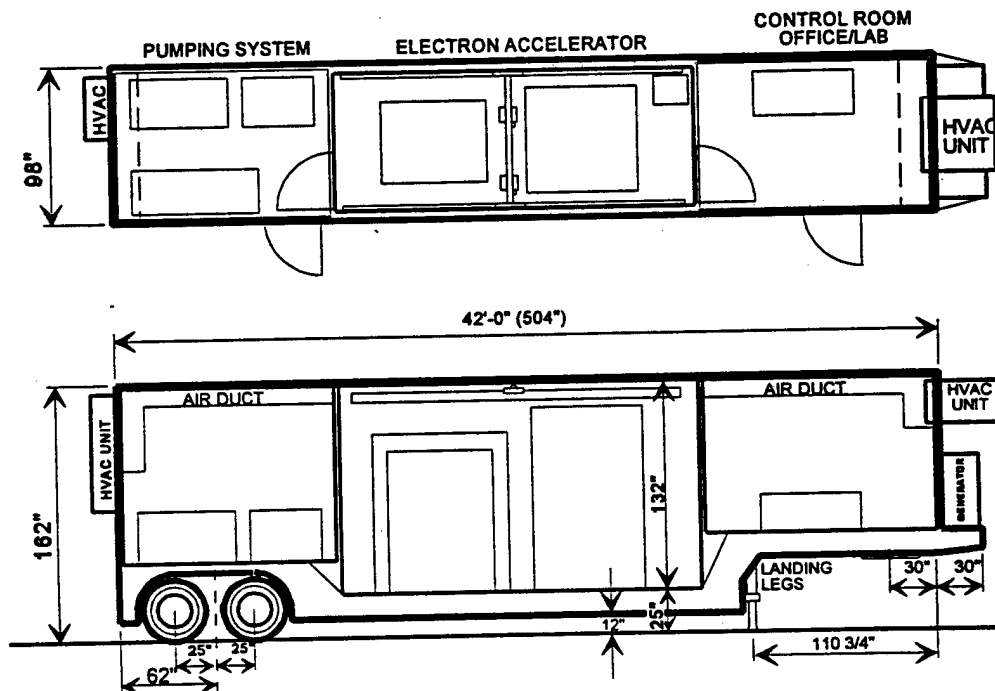
TECHNOLOGY DESCRIPTION:

The high-energy electron beam irradiation technology is a low-temperature method for destroying complex mixtures of hazardous organic chemicals in hazardous wastes. These wastes include slurried soils, river or harbor sediments, and sludges. The technology can also treat contaminated soils and groundwater.

The figure below illustrates the mobile electron beam treatment system. The system consists of a computer-automated, portable electron beam accelerator and a delivery system. The 500-kilovolt electron accelerator produces a continuously variable beam current from 0 to 40 milliamperes. At full power, the system is rated at 20 kilowatts. The waste feed rate and beam current can be varied to obtain doses of up to 2,000 kilorads in a one-pass, flow-through mode.

The system is trailer-mounted and is completely self-contained, including a 100-kilowatt generator for remote locations or line connectors where power is available. The system requires only a mixing tank to slurry the treatable solids. The system also includes all necessary safety checks.

The computerized control system continuously monitors the waste feed rate, absorbed dose, accelerator potential, beam current, and all safety shutdown features. The feed rate is monitored with a calibrated flow valve. The absorbed dose is estimated based on the difference in the temperature of the waste stream before and after irradiation. The system is equipped with monitoring devices that measure the waste stream temperature before and after irradiation. Both the accelerating potential and the beam current are obtained directly from the transformer.



Mobile Electron Beam Treatment System

Except for slurring, this technology does not require pretreatment of wastes.

WASTE APPLICABILITY:

This technology treats a variety of organic compounds, including wood-treating chemicals, pesticides, insecticides, petroleum residues, and polychlorinated biphenyls (PCB) in slurried soils, sediments, and sludges.

STATUS:

High Voltage Environmental Applications, Inc. (HVEA), was accepted into the SITE Emerging Technology Program in 1993. Under this program, HVEA will demonstrate its mobile pilot plant on soils, sediments, or sludges at various hazardous waste sites. Candidate sites are being identified. On-site studies will last up to 2 months.

Initial studies by HVEA have shown that electron beam irradiation effectively removes 2,4,6-trinitrotoluene from soil slurries.

As part of the Emerging Technology Program, HVEA has identified 350 tons of soil contaminated with an average Aroclor 1260 concentration of approximately 1,000 milligrams per kilogram. A small 1-ton feasibility study occurred in August 1995. After results are available from the 1-ton study, HVEA plans to make its mobile unit available for full-scale remediations.

In a recent bench-scale study, a multisource hazardous waste leachate containing 1 percent dense nonaqueous phase liquid was successfully treated. In another bench-scale study, a leachate containing a light nonaqueous phase liquid contaminated with PCBs was treated to F039 standards.

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INSTITUTE OF GAS TECHNOLOGY (Supercritical Extraction/Liquid Phase Oxidation)

TECHNOLOGY DESCRIPTION:

The Institute of Gas Technology's (IGT) Supercritical Extraction/Liquid Phase Oxidation (SELPPhOx) process (see figure below) removes organic contaminants from soils and sludges and destroys them. SELPPhOx combines two processing steps: (1) supercritical extraction (SCE) of organic contaminants in liquids, and (2) wet air oxidation (WAO) destruction of the contaminants. The two-step process, linked by a contaminant collection stage, offers great flexibility for removing and destroying both high and low concentrations of organic contaminants.

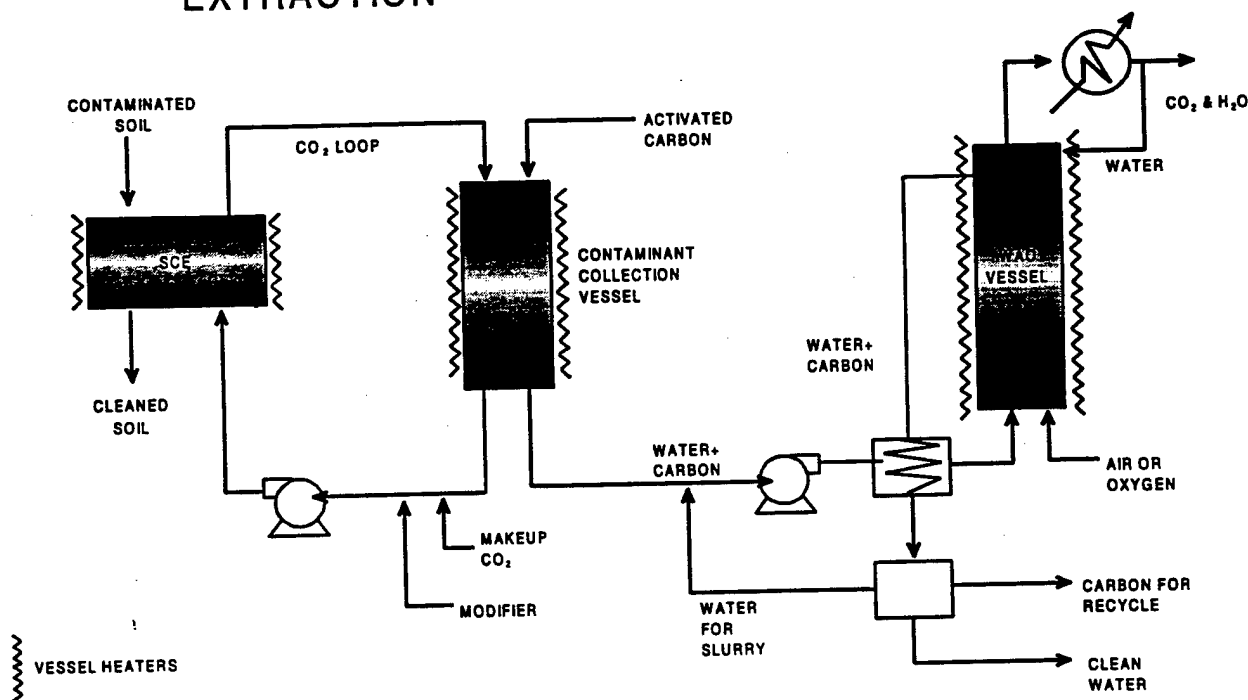
Combining SCE and WAO in a single two-step process allows development of a highly efficient and economical process for remediating contaminated soils. Supercritical extraction with carbon dioxide (CO_2) removes organic contaminants from the soil and transfers them to an aqueous phase while

leaving much of the original soil organic matrix in place. The contaminants are then collected on activated carbon in a contaminant collection vessel. The activated carbon with sorbed contaminants is then transported in an aqueous stream to a WAO reactor for destruction. Concentrating the organic contaminants on activated carbon in water provides a suitable matrix for the WAO feed stream and improves process economics by decreasing WAO reactor size. The activated carbon is regenerated in the WAO reactor with minimal carbon loss and can be recycled to the contaminant collection vessel.

The SELPPhOx process requires only water, air, makeup activated carbon, and the extractant (CO_2). Primary treatment products include cleaned soil, water, nitrogen (from the air fed to the WAO step), and CO_2 . Organic sulfur, nitrogen, and chloride compounds that may be present in the original soil or sludge matrix are transformed to relatively innocuous compounds in the product water. These

EXTRACTION

WET AIR OXIDATION



Supercritical Extraction/Liquid Phase Oxidation (SELPPhOx) Process

compounds include sulfuric acid and hydrogen chloride, or their salts. The treated soil can be returned to the original site, and the water can be safely discharged after thermal energy recovery and minor secondary treatment. The gas can be depressurized by a turbo expander for energy recovery and then vented through a filter.

WASTE APPLICABILITY:

The SELPhOx process removes organic contaminants from soils and sludges, including chlorinated and nonchlorinated polynuclear aromatic hydrocarbons (PAH), polychlorinated biphenyls, and other organic contaminants. The process is targeted toward sites that are contaminated with high levels of these organics (hot spots).

STATUS:

The SELPhOx process was accepted into the SITE Emerging Technology Program in July 1994. The primary objectives of the project are to (1) evaluate SCE's contaminant removal efficiency, (2) determine the potential for CO₂ recovery and reuse, and (3) determine destruction efficiencies of extracted contaminants in the WAO process. Analytical results from the project will provide the necessary information for the full-scale process design.

Laboratory-scale SCE tests have been completed using soils contaminated with PAHs. Operating conditions for the SCE stage and the activated carbon adsorption stage have been selected. A transportable field test unit has been constructed. Testing of this unit with PAH-contaminated soil is underway.

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IT CORPORATION
(Chelation/Electrodeposition of Toxic Metals from Soils)

TECHNOLOGY DESCRIPTION:

IT Corporation has conducted laboratory-scale research on an innovative process that removes heavy metals from contaminated soils and sludges by forming a soluble chelate. The metals and the chelating agent are then separated from the soils and recovered.

The treatment employs two key steps (see figure below): (1) a water-soluble chelating agent, such as ethylenediamine tetra acetic acid, bonds with heavy metals and forms a chelate; and (2) an electromembrane reactor (EMR) recovers the heavy metals from the chelate and regenerates the chelating agent.

Soils are screened before the chelation step to remove large particles such as wood, metal scrap, and large rocks.

The chelate is dewatered to separate the water-soluble chelating agent from the solid phase. The separated chelating agent, which contains heavy metals, is then treated in the EMR. The EMR

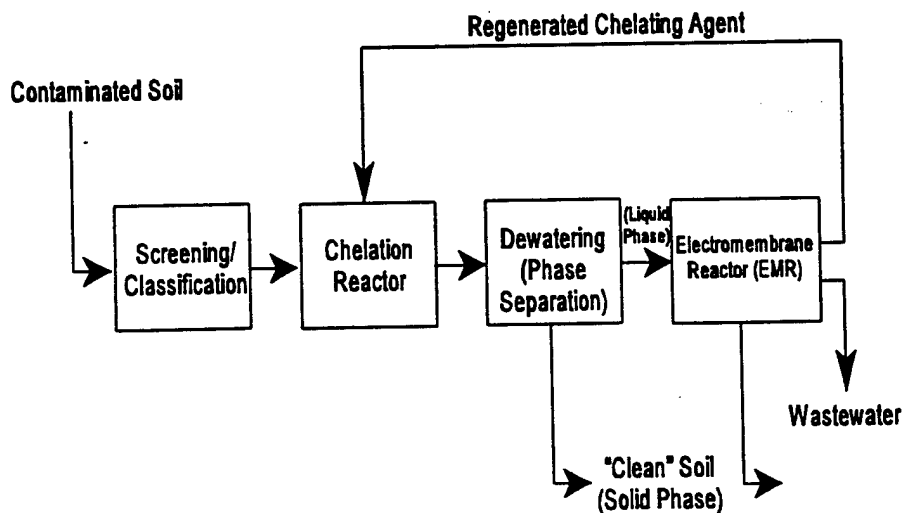
consists of an electrolytic cell with a cation transfer membrane separating the cathode and anode chambers.

WASTE APPLICABILITY:

The technology may be applicable to a wide variety of metal-contaminated hazardous wastes, including soils and sludges. Limited work has also been conducted to determine its effectiveness in removing cadmium from soils and sludges.

STATUS:

This technology was accepted into the SITE Emerging Technology Program in July 1994. The Jack's Creek site, located near Maitland, Pennsylvania, was selected for evaluation of the technology. The site was operated as a precious and nonprecious metal smelting and nonferrous metal recycling operation from 1958 to 1977. A portion of the property is currently operated as a scrap yard. The lead concentration in the contaminated soil used for the evaluation was approximately 2 percent. Toxicity characteristic leaching procedure (TCLP)



Simplified Process Flow Diagram of Treatment Process

analysis on the contaminated soil showed lead levels of 7.7 milligrams per liter (mg/L), which is above the regulatory limit of 5 mg/L. During the project, IT Corporation will establish appropriate conditions for removal of lead from the soil and reduce TCLP concentrations of lead in the soil to below regulatory levels.

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KSE, INC.

(Adsorption-Integrated-Reaction Process)

TECHNOLOGY DESCRIPTION:

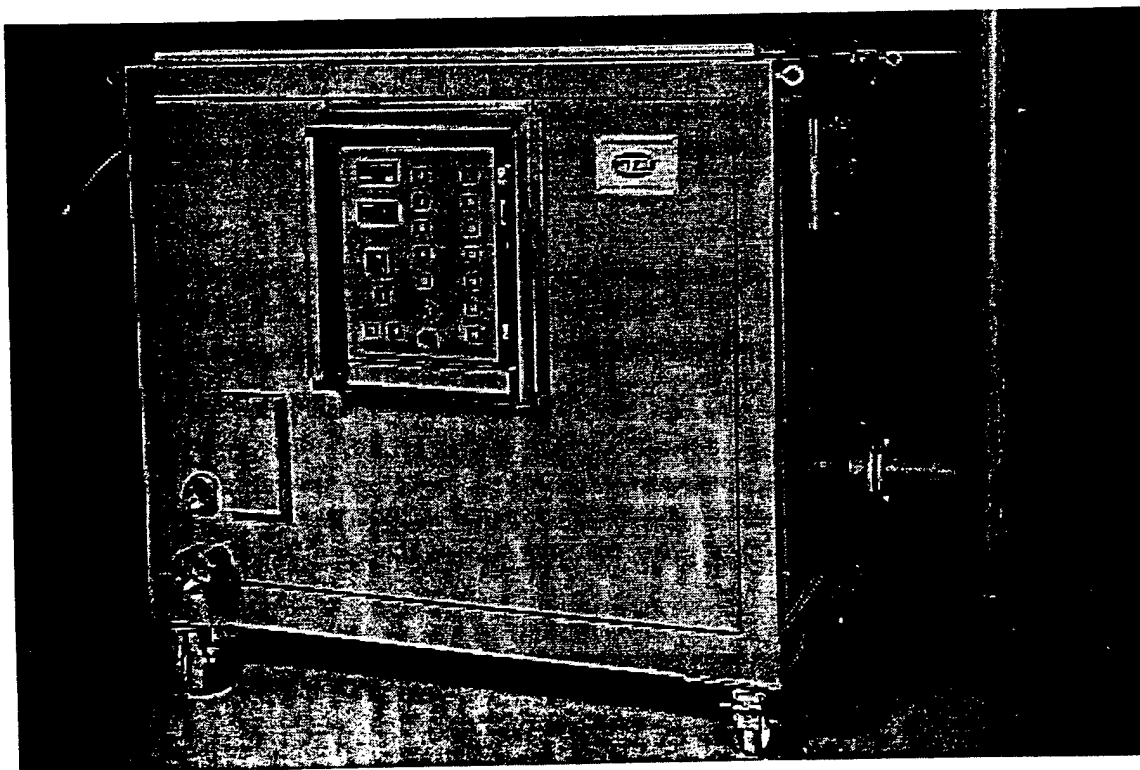
The Adsorption-Integrated-Reaction (AIR-II) process combines two unit operations, adsorption and chemical reaction, to treat air streams containing dilute concentrations of volatile organic compounds (VOC) (see photograph below).

The contaminated air stream containing dilute concentrations of VOCs flows into a photocatalytic reactor, where chlorinated and nonchlorinated VOCs are destroyed. The VOCs are trapped on the surface of a proprietary catalytic adsorbent. This catalytic adsorbent is continuously illuminated with ultraviolet light, destroying the trapped, concentrated VOCs through enhanced photocatalytic oxidation. This system design simultaneously destroys VOCs and continuously regenerates the catalytic adsorbent. Only oxygen in the air is needed as a reactant.

The treated effluent air contains carbon dioxide and water, which are carried out in the air stream exiting the reactor. For chlorinated VOCs, the chlorine atoms are converted to hydrogen chloride with some chlorine gas. If needed, these gases can be removed from the air stream with conventional scrubbers and adsorbents.

The AIR-II process offers advantages over other photocatalytic technologies because of the high activity, stability, and selectivity of the photocatalyst. The photocatalyst, which is not primarily titanium dioxide, contains a number of different semiconductors, which allows for rapid and economical treatment of VOCs in air. Previous results indicate that the photocatalyst is highly resistant to deactivation, even after thousands of hours of operation in the field.

The photocatalyst is particulate-based, which allows for more freedom in reactor design and more economical scale-up than reactors with a



Air-II Process Unit

catalyst film coated on a support medium. Packed beds, annular reactors, and monolithic reactors are all feasible reactor designs. Because the catalytic adsorbent is continuously regenerated, it does not require disposal or removal from treatment for regeneration, as does traditional carbon adsorption. The AIR-II process produces no residual wastes or by-products needing further treatment or disposal as hazardous waste. The treatment system is self-contained and mobile, requires a small amount of space, and requires less energy than thermal incineration or catalytic oxidation. In addition, it has lower total system costs than these traditional technologies.

WASTE APPLICABILITY:

The AIR-II process is designed to treat a wide range of VOCs in air, present at low concentrations from less than 1 part per million (ppm) to thousands of ppm. The process can destroy the following VOCs: chlorinated hydrocarbons, aromatic and aliphatic hydrocarbons, alcohols, ethers, ketones, and aldehydes.

The AIR-II process can be integrated with existing technologies, such as thermal desorption, air stripping, or soil vapor extraction, to treat additional media, including soils, sludges, and groundwater.

STATUS:

The AIR-II process was accepted into the SITE Emerging Technology Program in 1995. Studies under the Emerging Technology Program are focusing on (1) developing photocatalysts for a broad range of chlorinated and nonchlorinated VOCs, and (2) designing advanced and cost-

effective photocatalytic reactors for remediation and industrial service.

The AIR-II Process was initially evaluated at full-scale operation for treatment of soil vapor extraction off-gas at Loring Air Force Base (AFB). Destruction efficiency of perchloroethene exceeded 99.8 percent. The performance results were presented at the 1996 World Environmental Congress.

This system's forerunner, the AIR-I process, was tested extensively at the laboratory scale on chlorinated VOCs in air with concentrations ranging from 1 to 3,000 ppm. The AIR-I process was demonstrated as part of a groundwater remediation demonstration project at Dover AFB in Dover, Delaware. The process was used to treat effluent air from a groundwater stripper. Test results showed over 99 percent removal of dichloroethane (DCA) from air initially containing about 1 ppm DCA and saturated with water vapor.

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OHM REMEDIATION SERVICES CORPORATION

(Oxygen Microbubble In Situ Bioremediation)

TECHNOLOGY DESCRIPTION:

The use of in situ bioremediation on contaminated soils and groundwater is becoming more widespread and accepted; however, one of the difficulties with in situ bioremediation is the limitations of oxygen delivery to the microflora for the degradation of the target contaminant. Oxygen microbubble technology may be effective in overcoming this limitation.

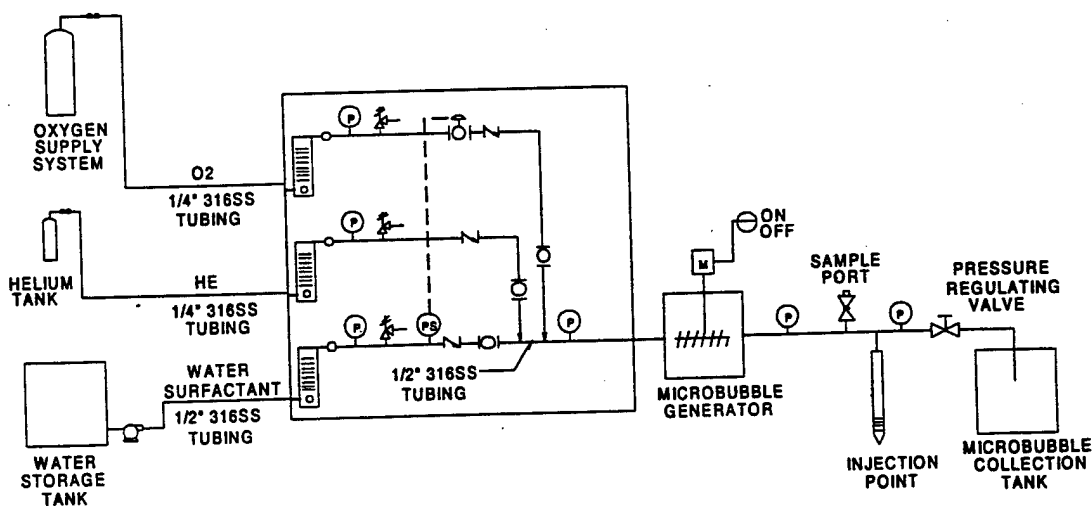
The oxygen microbubble technology (see figure below) uses a continuously generated stream of oxygen and water solution containing low concentrations of a surfactant. A water stream containing about 200 milligrams per liter of surfactant is mixed with oxygen under pressure. The resulting oxygen and water mixture is pumped through a microbubble generator that produces a

zone of high-energy mixing. The result is a 60 to 80 percent by volume dispersion of bubbles with a typical bubble diameter ranging from 50 to 100 microns. The microbubble dispersion is then pumped through an injection well into the treatment zone. The microbubbles deliver oxygen into the contaminated groundwater, providing an oxygen source for the biodegradation of the contaminant by the indigenous microflora.

WASTE APPLICABILITY:

The process has successfully treated groundwater contaminated with a number of organic compounds including volatile organic compounds, semivolatile organic compounds, and petroleum hydrocarbons.

STATUS:



LEGEND

	PRESSURE SWITCH		SAMPLE PORT
	CHECK VALVE		SOLENOID VALVE (NORMALLY CLOSED)
	PRESSURE RELIEF VALVE		BALL/SHUT OFF VALVE

Oxygen Microbubble In Situ Bioremediation of Groundwater

The Oxygen Microbubble In Situ Bioremediation process was accepted into the Emerging Technology Program in summer 1992. This process is being evaluated at a jet fuel spill site at Tyndall Air Force Base in Panama City, Florida.

The overall objective of this project is to evaluate the in situ application of the oxygen microbubble technology for bioremediation. The goals are to determine the subsurface oxygen transfer to the groundwater, retention of the microbubble in the soil matrix, and the biodegradation of the petroleum hydrocarbons present in the soil and groundwater.

A pilot test was performed at the site in 1995. The objective of this test was to determine the rate at which generated microbubbles could be injected into the surficial aquifer at the site. In addition, changes that occurred in the microbubbles and the aquifer during injection were monitored. Parameters that were monitored included the following:

- Microbubble quality, quantity, and stability
- Microbubble injection rate and pressure
- Lateral migration rates of microbubbles
- Lateral extent of migration of surfactant in the aquifer
- Lateral changes in dissolved oxygen concentration in the aquifer
- Rate of migration of tracer gas (helium) in the vadose zone
- Oxygen in the vadose zone

The pilot test verified that microbubbles can be injected into a shallow aquifer consisting of unconsolidated, fine-grained sediments. The study also verified that aquifer characteristics allowed the injection of the microbubble foam at rates of at least 1 gallon per minute (foam). Continued injection of foam after about 45 minutes resulted in coalescence of the foam based on pressure measurements. The microbubble foam was observed to be persistent in the aquifer for long periods of time. This testing supported the use of oxygen microbubbles as an oxygen delivery system for in situ bioremediation.

The next testing phase at the site began in fall 1996. During this test, multiple injection points will be used to determine the maximum rate of foam

injection while maintaining foam stability. Oxygen will be used as the gas for microbubble production. The retention of oxygen microbubbles will be compared to sparged air to determine oxygen delivery efficiency.

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UNIVERSITY OF WISCONSIN-MADISON
(Photoelectrocatalytic Degradation and Removal)

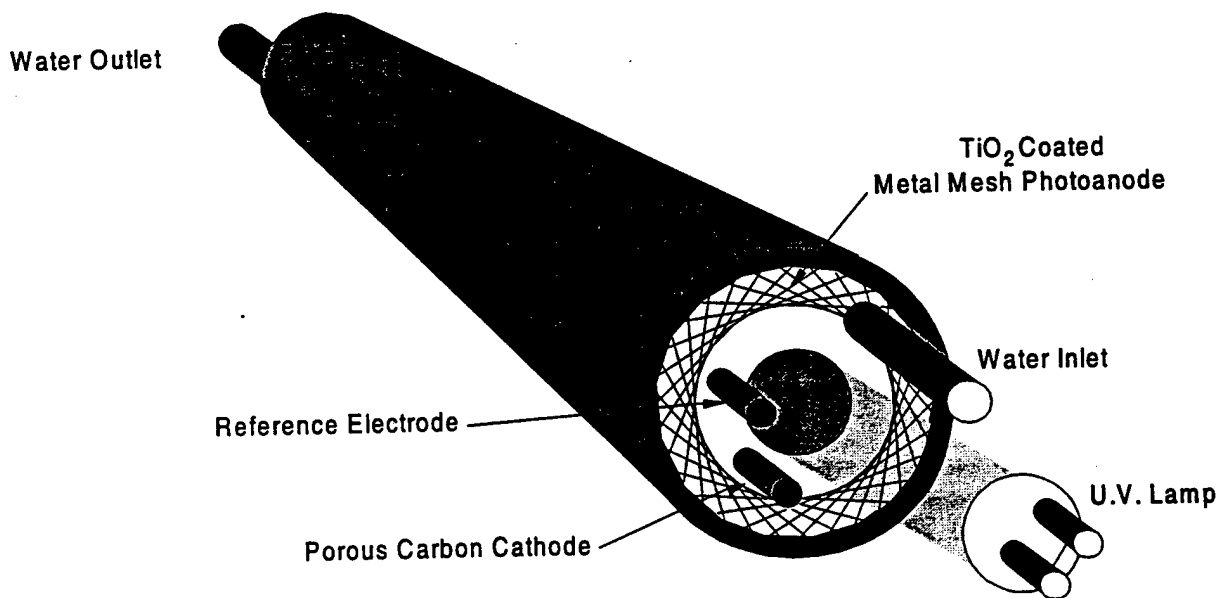
TECHNOLOGY DESCRIPTION:

The University of Wisconsin-Madison (UW-Madison) is developing a photocatalytic technology that uses titanium dioxide (TiO_2) suspensions to coat various supporting materials used in treatment applications. For this application, the suspensions are used to coat a conductive metallic or carbon mesh. Coating the mesh with a suitable thickness of TiO_2 catalyst provides the basis for a photoreactor that uses most of the available ultraviolet (UV) radiation. An electrical field can also be applied across the catalyst to improve its performance.

The figure below shows a possible photoreactor design that uses a ceramic film. In this design, the TiO_2 coating on the porous metal acts as a photoanode. An electric potential can then be placed across the coating to direct the flow of electrons to a porous carbon counter-electrode that

has a high surface area and would collect any heavy metal ions present in the liquid. In addition, an applied electric potential can improve the destruction efficiency of organic contaminants by reducing electron-hole recombination on the catalyst surface. This recombination is seen as a primary reason for the observed inefficiency of other UV/ TiO_2 systems when treating organics in groundwater. Lastly, the electric potential has been shown to reduce the interference of electrolytes on the oxidation process. Electrolytes such as the bicarbonate ion are known hydroxyl radical scavengers and can be problematic in the UV/ TiO_2 treatment of contaminated groundwater.

This technology improves on liquid-phase photocatalytic technologies by distributing radiation uniformly throughout the reactor. Also, the technology does not require additional oxidants, such as peroxide or ozone, to cause complete mineralization or to improve reaction rates. In



Photoreactor Design using Ceramic Film

addition, it eliminates the need for an additional unit to separate and recover the catalyst from the purified water after the reaction is complete.

WASTE APPLICABILITY:

This particular technology is designed to treat groundwater and dilute aqueous waste streams contaminated with organics and heavy metals. Organics are completely oxidized to carbon dioxide, water, and halide ions. Heavy metals are subsequently stripped from the cathode and recovered.

STATUS:

The UW-Madison photocatalytic technology was accepted into the SITE Emerging Technology Program in 1995. The overall objective of the Emerging Technology Program study is to refine the reactor design, enabling it to treat heavy metals as well as organic contaminants. Testing of a bench-scale unit is currently underway.

UW-Madison has tested its photocatalytic reactor at the laboratory scale on aqueous solutions of several organic contaminants, including polychlorinated biphenyls, chlorosalicylic acid, salicylic acid, and ethylenediamine tetraacetate. UW-Madison has also used similar reactors to remove volatile organic compounds, such as trichloroethene, tetrachloroethene, benzene, and ethylene from air streams. Photooxidation of trichloroethene and tetrachloroethene has been successfully field-tested at low flow rates (<0.1 standard cubic feet per minute).

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APPENDIX B

SERDP Projects Potentially Applicable to Incidental Shipboard Liquid Wastes

APPENDIX B

The Strategic Environmental Research and Development Program (SERDP) was established by Congress to address environmental matters of concern to the Department of Defense (DoD) and the Department of Energy (DoE). It is a DoD program, planned, managed, and executed in full partnership with the DoE and the Environmental Protection Agency, with participation by numerous other Federal and non-Federal organizations. SERDP thrust areas are Cleanup, Compliance, Pollution Prevention, and Conservation.

SERDP research projects were reviewed, and those technologies that could be applied to incidental Navy shipboard liquid wastes were identified and included in this appendix.

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PROJECT SUMMARY

PROJECT TITLE & ID: Thermal Actively Controlled Sludge Treatment; CP-1132

RESEARCH CATEGORY: 6.3 Advanced Research

LEAD ORGANIZATION: U.S. Navy

LAB: Naval Air Warfare Center Weapons Division, China Lake

PRINCIPAL INVESTIGATOR: Dr. Klaus C. Schadow, Naval Air Warfare Center Weapons Division

FY 1999 FUNDS: \$500K

OBJECTIVE: This project proposes a system that addresses the sludge disposal problem onboard ships by using a unique, highly compact and high performance combustion process. The project's objective is to develop a two-stage incineration process comprising: (1) a primary vortex containment combustion (VCC) process, which also separates and retains particulates; (2) a self-propagating, high-temperature synthesis (SHS) thermal processing and encapsulation process for treatment of resultant ash; and (3) an actively controlled and monitored after-burner (AB) process for emissions reduction. The process can be automated and integrated into a comprehensive, continuously operated, oily water treatment system.

BENEFITS: The DoD currently makes wide use of oil/water separators (OWS) to remove oil from a variety of aqueous waste streams prior to discharge. On-site or shipboard methods to treat or reduce the volume of accumulated sludges generated by these OWSs are required to eliminate sludge transportation costs for offsite disposal, to reduce downtime for maintenance, and to increase separator efficiency. The Navy is spending about \$24M per year to treat 1 billion gallons of bilge oil per year. This treatment includes storage, off-loading, on-shore treatment, transportation, and off-site disposal. This technology could significantly reduce cost by on-site disposal, either on shore facilities or, for larger vessels, on-board ship. Other advantages of on-site disposal include increasing costs of off-site disposal, reducing assumed liability of third party disposal, eliminating waste handling and transportation, and avoiding costs for improper field disposal.

TECHNICAL APPROACH AND RISKS: The technical approach builds on the compact, closed-loop-controlled waste incinerator for blackwater successfully developed in previous SERDP projects CP-034 and CP-887. It consists of six development phases: (1) fundamental laboratory-scale studies (injection, swirl design, flame stability, laser diagnostics, modeling, ash treatment) on surrogate sludge waste mixtures; (2) VCC and AB integration schemes; (3) conceptual design; (4) scale-up and testing of practical embodiments under full-scale conditions; (5) integration of monitoring and automatic active control schemes; and (6) testing requirements definition for future transition to a demonstration/validation program.

ACCOMPLISHMENTS: This is a FY 1999 New Start.

TRANSITION: The user community will be involved throughout the development of the proposed work. There have been discussions with Navy organizations, and the Army and Air Force have also expressed interest in the new sludge treatment system for potential application to a Deployable Waste Disposal System.

PROJECT SUMMARY

PROJECT TITLE & ID: Electrochemical Advanced Oxidation Process for Shipboard Final Purification of Filtered Black Water, Gray Water, and Bilge Water; CP-1107

RESEARCH CATEGORY: 6.2 Applied Research

LEAD ORGANIZATION: U.S. Navy

LAB: Naval Surface Warfare Center

PRINCIPAL INVESTIGATOR: Dr. Oleh Weres - Sonoma Research Company

FY 1999 FUNDS: \$202K

OBJECTIVE: The overall objective of this project is to advance development of an electrochemical Advanced Oxidation Process (AOP) which will be used as a final polishing step following membrane filtration of shipboard wastewater. To comply with International Maritime Organizations Marine Pollution Convention (MARPOL) Annex V and other environmental regulations, U.S. Navy vessels require compact, energy efficient water purification technology which will allow most of the wastewaters produced on board (bilge, gray, black, etc.) to be discharged overboard following purification. In addition, military bases and private industry generate wastewater in machine shops, which must be purified before discharge to sewers. Membrane filtration does not achieve the degree of purification required, and a final "polishing" process is needed prior to discharge overboard. The specific objectives include producing AOP electrodes with improved service life and improved performance at low substrate concentrations, developing methods for reprocessing the electrodes, and identifying optimal operating conditions for the AOP.

BENEFITS: Once the practical feasibility of this technology has been demonstrated, the U.S. Navy will be able to decide what combination of shipboard wastewater treatment technologies to plan for. In combination with improved membrane filtration technology, electrochemical AOP will allow existing ships to be retrofitted for compliance with MARPOL Annex V and other regulations. Estimated cost savings over 20 years are \$1.49 billion (estimate of cost to off-load untreated wastewaters). Electrochemical AOP will find broad military and industrial applications, wherever moderate concentrations of contaminants need to be removed from water at moderate cost.

TECHNICAL APPROACH AND RISKS: Existing equipment for producing small test electrodes in the laboratory will be upgraded. An apparatus permitting long-term testing of the electrodes will be developed, and a correlation of service life vs. current density will be determined. Tests will be developed to evaluate the kinetics of different oxidation mechanisms for several substrates. X-ray diffraction, scanning electron microscopy, and specialized surface analyses will be used to characterize the crystal structure, surface morphology, and surface composition of the electrodes.

Fiber made of the alloy Ti-6Al-4V (aerospace titanium) will be procured and evaluated for service as an electrode substrate. This alloy is expected to decrease the brittleness of the porous anodes produced, and

thereby allow reprocessing of used-up electrodes at a fraction of replacement cost. A standardized test of brittleness of the coated Ti-fibers will be developed.

The precoating process, which is necessary to provide a useful electrode service life, will be optimized to eliminate the use of flammable organic solvents, and to decrease seepage of the precoating material into the electrocatalytic oxide coat. Also, the method of application of the oxide coat will be optimized to provide better surface coverage and better block access of electrolyte (that is, the water being treated) to the precoat and underlying metal, thereby improving the efficiency of the electrode and increasing its service life.

ACCOMPLISHMENTS: In FY98, values of current yield in the 30-55% range using precoated anodes were achieved. The improved production method and sealing coat that allowed this breakthrough also eliminated the need for high temperature annealing of the electrodes, thereby simplifying and accelerating the production of test and full-sized electrodes. Mini-plate test anodes were developed and put into use. Attempts were made to determine current yield of hydroxyl ion at the anode by measuring the amount of oxygen produced. While this effort has not yet achieved its goal to allow direct and quick measurement of the current yield of the anode without using Chemical Oxygen Demand (COD) tubes, it indicated that the reaction at the cathode and the interaction of anode with cathode have a major effect upon current yield attained.

Experimental observations lead to the hypothesis that the one-electron reduction of oxygen to superoxide at the cathode sets-up a parasitic reaction cycle. The gap between anode and cathode in the optimized electrolytic cells is small and mass transfer is quite good, therefore, the superoxide produced at the cathode is able to reach the anode where it is readily reoxidized to oxygen. In effect, a short-circuit exists between cathode and anode, and part of the current flows through the cell producing no net reaction. The realization that processes at the cathode and interaction between cathode and anode can have a large effect upon current yield opens new possibilities for improving overall performance of the electrolytic cell.

The first complete set of sample anodes at various stages of the coating process have been analyzed utilizing X-ray diffraction and several techniques of surface analysis. The results of surface analysis indicate that the morphology and thickness of the resultant precoat vary tremendously from fiber-to-fiber. Bringing this subtle processing variable under control should enable better control the morphology of the anodes produced, thereby allowing improved current yield and service life.

TRANSITION: Interested potential users have been identified, including: the Naval Facilities Engineering Center, the Carderock Naval Surface Warfare Center, Eaton Corporation, and Showa Engineering Co. of Tokyo, Japan. Chemical Engineering magazine twice described this technology, eliciting 130 requests for information. The prototype water treatment unit will very likely be carried forward to eventual commercialization.

PROJECT SUMMARY

PROJECT TITLE & ID: Novel Nonporous Fouling - Resistant Composite Nanofiltration Membranes and Membrane Separation Systems for Wastewater Treatment; CP-1108

RESEARCH CATEGORY: 6.2 Applied Research

LEAD ORGANIZATION: U.S. Navy

LAB: Naval Surface Warfare Center

PRINCIPAL INVESTIGATOR: Dr. Benny Freeman - North Carolina State University

FY 1999 FUNDS: \$490K

OBJECTIVE: Fouling associated with currently available membranes is the principal problem inhibiting widespread adoption of nanofiltration/ultrafiltration to treat shipboard wastewater to allow the Navy to meet current future overboard discharge limits. All current nanofiltration/ultrafiltration membranes are finely porous and are subject to surface or internal fouling by particulates, resulting in a dramatic decline in the water flux. The objective of this project is to develop a shipboard wastewater treatment system based on a novel type of fouling-resistant, composite-membrane module. The composite membrane will consist of an ultrathin (0.2-0.5 micrometer), nonporous, highly water-permeable, rubbery, block copolymer layer coated on to a conventional, microporous ultrafiltration or nanofiltration membrane for support. This coating layer provides fouling resistance without significantly reducing the water flux.

BENEFITS: Novel, low-fouling membranes for graywater and bilgewater treatment would offer longer service life and less frequent cleaning. When housed in high performance modules, these would provide a compact, reliable, economical shipboard wastewater treatment facility to enable the Navy to meet current and anticipated wastewater purification targets. This technology will be widely applicable to Navy and civilian ships and to onshore treatment of highly fouling waters.

TECHNICAL APPROACH AND RISKS: Three candidate materials have been developed under earlier Office of Naval Research grants. In this project, development of these membranes will be completed and a systematic series of new materials will be synthesized and characterized. The properties of these new heterophase block copolymer membrane materials will be tailored to provide better fouling resistance than conventional membranes while maintaining or improving the flux/selectivity combinations relative to currently available materials. These materials will be based on aromatic polyamide hard blocks with either hydrophilic ether groups as the soft, water-permeable block or water-soluble aromatic polyamides as the hydrophilic blocks. This research program will characterize the physical, chemical, and morphological structure of these materials as well as their water permeation, rejection, and fouling properties to develop systematic structure/property relations to guide the preparation of a new generation of advanced high performance materials for shipboard wastewater treatment. The best membrane materials will be selected for scale-up, first to bench-scale and then to industrial-scale membrane modules for evaluation in a pilot-scale system.

The risks associated with this approach include difficulties that might be encountered in the preparation of new materials, the unknown ability of these materials to be formed into thin film composite membranes, the durability of these materials in long term tests, and the ability of the materials to withstand cleaning protocols which might be used to regenerate their properties after extended use.

ACCOMPLISHMENTS: In FY 1998, efforts focused on: (1) optimizing polymerization preparation methods and characterizing new coating materials; (2) developing membrane coating methodology; and (3) developing bench-scale modules. Commercial polymers and previously developed experimental polymers (Pebax, Nafion, and PFOMA-b-PDMAEMA) were characterized for water uptake, permeability, and fouling properties. Three new families of heterophase polymers were also synthesized: poly(ethylene oxide)-b-poly(p-benzamide) block copolymers; random and block copolymers based on the polyisophthalamide of 4,4'-methylenedianiline, (MDA-I) or of 2,5-diaminobenzenesulfonic acid, (PPDS); and poly (sulfo-m-phenyleneisophthalamide)-b-poly(m-phenyleneisophthalamide) block and random copolymers. Interfacial polymerization routes for synthesis of these block copolymers were faster (for screening purposes) than the traditional solution polymerization route due to less stringent monomer purification requirements. High flux, thin- film composite membranes were prepared, which will be tested when fabrication of bench-scale modules is complete.

TRANSITION: Collaboration will occur with Hydranautics Inc., San Diego, CA in the module preparation work in the final phase of the project. Hydranautics is a major producer of membrane water treatment modules in the U.S. and would be a logical commercialization partner to introduce this technology to the water treatment market.

PROJECT SUMMARY

PROJECT TITLE & ID: Environmentally Advantaged Substitutes for Ethylene Glycol for Aircraft Ice Control; PP-1111

RESEARCH CATEGORY: 6.2 Applied Research

LEAD ORGANIZATION: U.S. Air Force

LAB: Air Force Research Laboratory

PRINCIPAL INVESTIGATOR: Ms. Carolyn Westmark - Foster-Miller, Inc.

FY 1999 FUNDS: \$614K

OBJECTIVE: The technical objective of this program is to develop a high performance, environmentally benign aircraft anti-icing fluid which can be safely released to the environment without capture, control, and post-treatment of the runoff. Specific objectives are to: (1) develop a molecular modeling approach which allows for prediction of non-Newtonian viscosity behavior of materials based on their chemical structure; (2) develop a non-toxic, non-Newtonian thickening agent with enhanced performance capabilities for anti-icing fluids, particularly extended holdover times; (3) select low environmental impact additives for performance enhancement; (4) demonstrate that the anti-ice formulations are compatible with military aircraft materials and weapons systems; (5) demonstrate the ability of the anti-icing formulations to prevent ice formation for extended periods of time in simulated adverse weather environments; (6) develop encapsulated enzyme additives which exhibit controlled release properties and actively degrade the anti-ice formulation at reduced temperatures; (7) predict the water quality impact of new anti-ice formulations at actual airfield sites using computer modeling and laboratory analysis of key environmental parameters; (8) determine any potential health/safety risks of anti-icing formulations; and (9) develop cost-effective anti-icing formulations by screening out excessively costly materials throughout the testing program. The most promising freezing point depressants from an earlier Air Force funded Small Business Innovation Research (SBIR) Phase I program will be used as a basis for anti-ice formulations.

BENEFIT: The project benefits include: (1) a drop-in, fully characterized, environmentally advantaged replacement for ethylene and propylene glycol based aircraft deicing materials; (2) elimination of the cost of capture/treatment of effluent from aircraft deicing processes; (3) reduction of material cost for aircraft deicing processes (since high efficiency fluids require less material usage); and (4) increased flight safety and mission readiness. Additionally, this project will provide a model for non-Newtonian viscosity prediction based on the chemical structure of compounds, a self-remediating anti-icing fluid formulation, and a model for predicting the impact of changes in ice control material formulation on runoff water quality at actual airfields.

TECHNICAL APPROACH AND RISKS: The Foster-Miller strategy to develop environmentally advantaged aircraft ice control materials involves three key elements: (1) substitution: identifying ice control material formulations which are inherently less damaging to the environment than currently used

materials; (2) source reduction: developing efficient, high performance fluids which require less material to accomplish the objective of protecting aircraft surfaces from ice accretion; and (3) "in-situ remediation": developing "self-remediating fluids" which degrade to less harmful products prior to entering the ecosystem by means of a triggerable reaction.

Foster-Miller is already pursuing the development of inherently environmentally advantaged freezing point depressants (FPDs) in a U.S. Air Force (Air Force Laboratory) sponsored SBIR program. This SERDP sponsored project focuses on the development of anti-icing fluids, which will incorporate the FPDs developed under the SBIR program. Anti-icing fluids offer source reduction benefits as compared to deicing fluids since less material is wasted on runoff and overspray and the material remains on the aircraft surfaces until takeoff to provide long lasting protection against icing, thus avoiding re-application of fluids. In addition, these anti-icing fluids offer advantages in terms of enhanced flight safety and mission readiness.

In this program, Foster-Miller will develop environmentally advantaged anti-icing fluids using all three elements of this strategy. This will be accomplished by: (1) identifying a wide range of candidate formulations, ranking them based on their predicted performance, environmental impact, and cost using computer model-aided screening, multi-tiered testing, and expert advice from aircraft deicing fluid manufacturers; and (2) developing high performance anti-icing fluids which require less material than current fluids to protect the aircraft from icing. The key to this approach is Foster-Miller's development of a high performance, environmentally benign thixotrope; and development of a gel-encapsulated, FPD-degrading enzyme system which will be incorporated into the anti-icing fluid and released on demand to initiate the degradation of the fluid into harmless byproducts.

During the first year of the program (FY98), Foster-Miller will identify non-Newtonian thixotropic agents and develop a model which predicts non-Newtonian viscosity of a compound based on its chemical structure. This model will be used to identify candidate thixotropic agents and synthesize new thixotropes with enhanced performance compared to currently available materials. Thixotropes will be added to freezing point depressant materials and their rheological behavior will be evaluated. The combination of thixotrope and freezing point depressant will be subjected to the first tier (screening) series of tests of performance, toxicity, materials compatibility, and cost. In addition, development of an enzyme which is active in degrading the FPD will be initiated in FY98.

ACCOMPLISHMENTS: Candidate FPDs identified with ultimate BODs less than propylene glycols. Screening tests completed on three commercially available. One meets most Tier 1 requirements with a 25 percent lower five-day BOD than propylene glycol. In the enzyme development part of the project, *Xanthobacter autotrophicus* shown to degrade PEG and PG at high concentrations (up to 25 percent) at room temperature, and grows on propylene glycol as sole carbon source and at reduced temperatures. Other psychrophiles under investigations. The encapsulation effort work resulted in evaluation of Dextran gel encapsulation, and demonstration of gel encapsulation of hemoglobin. The initial results indicate that the encapsulation concept is biodegradable, nontoxic, has good stability in water/FPD solutions, and is inexpensive.

TRANSITION: All Services and the commercial airline industry will be apprised of initial results. Successful candidates may be further tested by Service programs.

PROJECT SUMMARY

PROJECT TITLE & ID: Recycle and Reuse of Industrial Rags Using Liquid CO₂ and Surfactant Additives as a Cleaning Agent; PP-1112

RESEARCH CATEGORY: 6.2 Applied Research

LEAD AGENCY: Environmental Protection Agency

LAB: National Risk Management Research Laboratory

PRINCIPAL INVESTIGATOR: Mr. Charles H. Darwin

FY 1999 FUNDS: \$307K

OBJECTIVE: The technical objectives of this proposal are to develop, demonstrate, and evaluate a liquid CO₂ (LCO₂) fabric cleaning technology for application to the cleaning of DoD generated hazardous cleaning rags. The most promising candidate technology to accomplish this objective is the use of liquid CO₂ (LCO₂) with surfactant additives. The economics of LCO₂ /surfactants systems will be critically dependent on recovery and separation of surfactants, CO₂, and contaminants. LCO₂ has no associated environmental impacts and few safety concerns: it is non-hazardous, non-flammable, non-ozone-depleting, and non-toxic. Thus, there are none of the concerns which might be found with conventional cleaning technologies using organic solvents or aqueous solutions. Also, a system using liquid phase CO₂ is expected to be less destructive to fabrics. Finally, there is no pollution control process cost associated with achieving environmental compliance using the potential LCO₂ technology.

The initial focus of the program will be using CO₂ in the liquid phase, and not supercritical phase, unless research directions dictate a technical efficiency in the supercritical. Some studies outlined in the references on the use of CO₂ indicate that the use of CO₂ in the liquid phase will present a more efficient system for the cleaning of fabrics. A system operating in the liquid phase will present a more efficient system for the cleaning of fabrics. A system operating in the liquid phase is expected to be less destructive to fabrics and clothing as well as to attachments, such as buttons on work clothing.

BENEFIT: If contaminants contained on the rags can be removed successfully and collected, the rags can be recycled back to the operation and will eliminate rags as a source of hazardous waste pollution from DoD and related facilities.

A 1996 study, conducted for the Chief of Naval Operations, found that a minimum of \$5M in rags are procured each year by the U.S. Navy for U.S. based facilities. This study did not include shipboard or foreign facilities. A major part of these rags is disposed of as hazardous waste at a disposal cost estimated to be in excess of \$7M. This estimate results in an annual rag procurement and disposal cost for the U.S. Navy in excess of \$12M. Rags generated on ships and at foreign facilities are required by many host countries to be transported back to the U.S. for disposal. It is reasonable to assume that an equal amount of rags are procured and disposed of by the remaining military Services. This would result in an additional \$24M in rag procurement and disposal cost for U.S. military services. The estimated cost

savings in rag procurement and disposal for all U.S. military Services is therefore estimated at more than \$360M over a 10-year period.

TECHNICAL APPROACH AND RISKS: The major objective during the FY98 Phase I portion of the program will be to conduct and complete research to design and synthesize LCO₂ compatible amphiphilic surfactants. The proposed surfactants will have a micelle-forming capability to emulsify lipophilic contaminants within a continuous LCO₂ phase. These surfactant systems must be applicable to a broad range of contaminants, which will be defined by the potential users.

The chemical design philosophy of the candidate, micelle-forming surfactants to be synthesized during the Phase I effort is based upon results of surfactant research investigations recently published by Dr. J. DeSimone at the University of North Carolina. To date, two nonionic, amphiphilic copolymers have been synthesized. Accordingly, families of these amphiphilic surfactants will be tailored to meet the specific requirements necessary to emulsify and displace the contaminants typically found in industrial rags.

The use of CO₂ in the supercritical phase is a proven technology for certain applications such as precision metal cleaning and solid waste decontamination, or where the contaminants are primarily light organic compounds and non-particulates. However, LCO₂ has yet to be proven for fabric cleaning, or for military cleaning requirements which contain heavy molecular weight organic compounds, inorganic salts, metal oxides, proteins, and solid matter.

ACCOMPLISHMENTS: A survey was completed in March 1998 by the project team to establish the magnitude of the rag contamination and disposal problem. This assessment concluded that over 7 million pounds of rags are generated each year by the military services. The cost of rag waste disposal is estimated to be more than 24 million dollars. The project team also completed a preliminary rag pollutant identification and characterization assessment. This information is required to assist researchers in developing the correct surfactant formulation to address the cleaning requirements presented by DoD waste products. At the direction of the SERDP Science Advisory Board, a preliminary cost benefits analysis was completed by the project team. This analysis indicated that the 10 year cost savings can be as much as \$360,000,000 in waste disposal savings and decreased purchases.

TRANSITION: The military Services will be apprised of initial results. Success may lead to cooperative Service programs.

PROJECT SUMMARY

PROJECT TITLE & ID: Compact, Closed-Loop-Controlled Waste Incinerator; CP-34

RESEARCH CATEGORY: 6.2 Applied Research

LEAD AGENCY: U.S. Navy

LAB: Naval Air Warfare Center - China Lake, CA

PRINCIPAL INVESTIGATOR: Dr. Klaus Schadow

FY 1998 COMPLETED PROJECT

OBJECTIVE: This project established the Science and Technology (S&T) basis for a compact, closed-loop- controlled waste incinerator using resonant acoustics for enhanced waste pyrolysis and controlled vortex dynamics for enhanced and controlled after-burning. The after-burning process is closed-looped controlled using diode-laser based sensors for real-time and continuous emission monitoring, new types of actuators, and a non-standard controller based on fuzzy logic or neural nets. A second SERDP project, **CP-887 Demonstration of a Compact, Closed-Loop-Controlled Waste Incinerator**, applies this new technology to two Navy incinerator programs.

BENEFIT: Successful demonstration of a compact incinerator with real-time exhaust monitoring for active combustion control represents a significant step towards assured waste incineration and can be the basis for next-generation incinerators. The compact-incinerator technology, specific to shipboard applications, is essential for the development of environmentally sound ships beyond the year 2000. Compact incinerators also are desirable for on-shore use in the government and private sectors. Small, compact incinerators allow on-site waste destruction and avoid waste transportation to large incineration sites. The closed-loop, active control of the incineration process assures proper incineration. For shipboard application this will result in significant cost savings by avoiding costs for waste off-loading and on-shore destruction, particularly in foreign countries.

ACCOMPLISHMENTS: In FY 98, this project focused on two areas: improvement of the after-burner using active combustion control, and improvement of the sludge incinerator using resonant acoustics. Using a 50kW actively controlled after-burner, progress was made in four areas: (1) carbon monoxide and NO_x emissions were reduced using realistic, hot waste gases (115 BTU/ft³) and operating temperature (700F); (2) the after-burner was re-designed for extended duration with hot pyrolysis gases; (3) data acquisition and analysis hardware for the diode-laser sensor system were improved; (4) the fuzzy controller was adapted to the current after-burner geometry and unsteady pyrolysis gas mass flow; and (5) failure modes were determined for incineration in actively established vortices. Additional accomplishments included: (1) the feasibility of using diode-laser based sensors under practical operational conditions was demonstrated for real time monitoring of combustion processes inside the combustor and critical species (CO, C₂H₄, and C₂H₂) in the exhaust; (2) closed-looped active combustion control was achieved based on data from the diode-laser based sensors; and (3) the 1-dimensional

engineering model was applied to the after-burner: good agreement between experimental and predicted values for NO_x and CO was obtained.

TRANSITION: Continuing interaction is taking place with the Navy for multi-functional incinerators (for sludge and oil), demonstrating acoustics retrofits, and developing an after-burner for another DoD facility under a joint development program. Three marine incinerator manufactures interested in collaborating have been identified and a proposal for collaboration with one has been developed. The Principal Investigator is pursuing future DoD funding for a compact, integrated system for hazardous waste incineration at DoD facilities and for 6.4 research funding for shipboard advanced incineration.

PROJECT SUMMARY

PROJECT TITLE & ID: Supercritical Water Oxidation of Organic Wastes; CP-35

LEAD AGENCY: Navy

LAB: Naval Facilities Engineering Service Center (NFESC) and Idaho National Engineering Laboratory (INEL)

PRINCIPLE INVESTIGATORS: Mr. Richard Kirts, NFESC and Mr. John M. Beller, INEL

PROBLEM: The overall goal of this project is to determine if supercritical water oxidation (SCWO) is an effective treatment for certain DOE and DoD organic waste streams.

The DOE has a very large amount of organic wastes, such as cutting oils and solvents, that have been contaminated with radioactive materials. The problem for the DOE is to determine if, through oxidation of the organic portion of the waste into nonhazardous water and carbon dioxide, SCWO can reduce the volume of radioactive material that needs to be stored while separating out the radioactive elements.

The Navy generates about 10,000 tons per year of hazardous organic materials such as waste oils, solvents, cleaners, and paint. It is estimated that Army industrial activities generate about the same amount of organic wastes; Air Force industrial activities generate substantially less. The problem for the DoD is to determine if SCWO is a technically and economically viable method of destroying organic wastes generated by industrial activities. The current disposal cost for these materials ranges from \$15 to \$45 per gallon of waste. The total cost of organic waste disposal for the Navy was \$40 M in 1992. In addition to high disposal costs, the DoD retains legal liability for proper disposal of these wastes.

This effort supports the SERDP goal of effective treatment and disposal of hazardous waste (compliance with the Resource Recovery and Conservation Act).

APPROACH: This project will demonstrate, at pilot scale, the use of supercritical water oxidation as a method of destroying organic hazardous wastes generated by DoD industrial activities. In addition, the project will demonstrate the destruction of organics in simulants of wastes generated by the DOE and gain an understanding of the fate of radionuclides in an SCWO system.

In this project, two existing pilot plants of differing reactor designs will be acquired to demonstrate SCWO technology on actual DoD wastes and simulated DOE wastes. These different reactor designs will provide data on two alternative solutions to technical issues related to SCWO system design and operation. This approach will provide the engineering design data required by both DoD and DOE to support the treatment of RCRA wastes on site. The Navy is planning a 6.3A funded onsite demonstration of SCWO technology. The data produced by tasks 1, 2, and 3 will be used to prepare a detailed specification for the design and demonstration of a SCWO plant to be located at the Naval Public Works Center, San Diego. The tasks comprising the project are:

Task 1: Waste Characterization. Task 1 will produce a detailed survey of the volume, composition, and current disposal costs of organic waste streams managed by PWC San Diego. Estimates of future volume and composition will also be produced. Split samples of characteristic waste streams will be collected for use in tasks 2 and 3.

Task 2: Data Acquisition (Vessel Reactor). An existing cooperative agreement between DOE and a company called MODAR, Inc. will be used to access an SCWO pilot plant having a vessel type reactor. The MODAR SCWO plant will be demonstrated using selected DoD wastes and simulated DOE wastes. Data will be collected on waste destruction performance, reliability, operability, and plant design problems. This information will provide input for establishing the criteria for the next generation of pilot plant designs and demonstrations.

Task 3: Data Acquisition (Tubular Reactor). An agreement will be established between the Navy and a company that has an SCWO plant having a tubular type reactor for the purpose of conducting comparative performance tests between the two reactor types. The same wastes tested in Task 2 will be tested in the tubular reactor in Task 3. The same data set collected in Task 2 will be collected in Task 3 also in order to provide a basis for comparison between the two reactor designs.

The results of tasks 2 and 3 will provide the DoD and DOE with design information to support onsite SCWO demonstrations. In addition, it is anticipated that new information will be available by the end of 1994 from other research projects currently underway. These projects, supported by DoD, DOE, and private industry, will provide additional technical data and engineering solutions to the technical challenges facing SCWO development.

Task 4: Permits, Site Preparation. This effort will gather data on applicable Federal, State, and local health and safety codes, air and water discharge limits, and SCWO operating permit requirements. Site preparation work, such as design of building and utilities modifications, will be initiated.

Task 5: Specification Preparation. This task will develop SCWO performance criteria and prepare contract statements of work for the design, construction, installation, and demonstration of the SCWO plant.

Task 6: Testing of Mineral Acid Forming Wastes. The DOE is designing and fabricating an advanced SCWO reactor that has the potential of eliminating the corrosion problems associated with the processing of halogenated wastes. This task will support testing of halogenated Navy wastes in this advanced reactor.

The critical technical difficulties of SCWO development are associated with materials of construction. More specifically, the major materials problem is the very rapid corrosion of the reaction vessel caused by mixes of strong acids formed when certain types of wastes are oxidized. Also, heating or oxidation of some wastes results in the formation salts and oxides of metals that can adhere to process components and cause plugging of the apparatus. These problems must be solved before an SCWO unit can be designed to heat radioactive materials or industrial wastes such as chlorinated solvents.

This project is directly responsive to DoD and DOE environmental objectives, such as the Army and Navy hazardous waste minimization programs (as expressed in OFNAVINST 50M.1 and similar documents) and DOE's Mixed Waste Integrated Demonstration program.

This project is listed in the Tri-Service Environmental R&D Strategic plan under Pillar 2, Compliance, (Requirement Thrust 2.C.2.a), General Hazardous Waste Management.

This proposed project does not duplicate any current SCWO programs. The Defense Research Projects Agency initiated work in March, 1992 to design, build, test, and evaluate a 1500 gal/day SCWO pilot plant to destroy chemical warfare agents. The Air Force initiated work in August, 1992 to develop a 1200 gal/day SCWO pilot plant to destroy the propellants from the third stage motors of Minuteman ICBMs. This joint DoD/DOE project will not include chemical warfare agents, explosives, propellants, pyrotechnic devices, or radioactive materials.

EXPECTED PAYOFF: It has been demonstrated in a Navy 6.2 project on supercritical water oxidation that SCWO technology can destroy most Navy organic hazardous wastes. Independent economic analyses indicate that the SCWO process will also be economically attractive. Estimated unit disposal cost using SCWO is \$10 per gallon, for a savings of \$5 to \$35 per gallon of waste. The payback period for the capital investment is less than 5 years. There is an estimated DoD market for about 30 SCWO plants of 6000 gal/day total throughput (300 to 900 gal/day of organic material depending on waste composition).

TRANSITION: It is planned to transition the Navy development of SCWO technology to a field demonstration in FY-95 through the Navy 6.3A Program. The 6.3A program will competitively select the best SCWO technology that is presently available and then design, fabricate, test, and evaluate an SCWO plant. It is anticipated that the plant will have the capacity of 3000 to 4000 gallons per day total throughput. The plant will be located at the naval complex in San Diego, probably at Naval Air Station North Island. Public Works Center personnel will be trained to take over operation of the plant after testing is completed. Detailed design of the plant is anticipated to begin in FY95, with construction and startup taking place in PY96.

The user and regulators will be invited to participate at all stages of SCWO pilot plant development to ensure that their concerns regarding safety, cost, compliance, reliability, and other issues are addressed.

PROJECT SUMMARY

PROJECT TITLE & ID: Kinetics of Supercritical Water Oxidation; CP-364

RESEARCH CATEGORY: 6.1 Basic Research

LEAD AGENCY: Department of Energy

LAB: Sandia National Laboratory - Livermore, CA

PRINCIPAL INVESTIGATOR: Dr. Steven F. Rice

FY 1998 COMPLETED PROJECT

OBJECTIVE: The objective of this project was to develop a supercritical water oxidation (SCWO) technology to treat aqueous wastes. SCWO is an emerging technology under development at several laboratories, including Sandia National Laboratory, for the treatment of hazardous wastes such as obsolete chemical munitions, mixed wastes, and naval shipboard excess hazardous materials. Understanding of the rates and mechanisms of reactions in supercritical water was limited to a handful of empirical rate expressions for very simple chemicals. These expressions were of limited use in the formulation of predictive models of SCWO for the design and operation of large-scale waste processing equipment. To be applicable as design tools, the models needed to be based on elementary reaction steps or, at minimum, a detailed quantitative mechanistic description incorporating all the key fundamental reactions. Basic research was needed to improve the ability to predict reaction rates in supercritical water. The project was designed to result in a user-friendly, computer-based model that could predict reaction rates and conversion efficiency for a wide range of waste feeds and reactor conditions.

BENEFIT: The SCWO process, operating at two orders of magnitude greater density than atmospheric gaseous combustion, provides high reaction rates at moderate temperatures. The technical chemical engineering literature contains results of studies of SCWO measuring destruction efficiencies for a variety of waste chemicals and mixtures. Some of these data can be used to generate empirical, global kinetic rate expressions for a select list of simple species. However, the in-situ measurements used in this project, particularly on intermediates, lead to valuable information for predictive model development. The improved understanding of reaction rates and the kinetic models developed by this project have produced advanced strategies for reactor design and improved methods for commercial system optimization.

ACCOMPLISHMENTS: This project has provided oxidation rates for common organic compounds in supercritical water. These data provided the basis to develop a model (combustion-based as opposed to liquid-phase oxidation) to be used as a design engineer's tool for testing the effects of reactor design changes and producing advanced strategies for large-scale system optimization.

TRANSITION: In addition to presentations at technical meetings and publication in the reviewed literature, results from this project are made available to a wide distribution within the SCWO technical community. Additional transition will occur with indirect support on leveraged projects with the Defense

Advanced Research Projects Agency (DARPA) and the Office of Naval Research (ONR) for shipboard waste, with the U.S. Army Applied Research, Development and Engineering Center's (ARDEC) Pine Bluff Arsenal Unit, and at the U.S. Army Aberdeen Proving Ground. Coordination with ARDEC on the ESTCP-supported Pine Bluff Arsenal SCWO plant start-up project has influenced the installation of the reactor skids.

PROJECT SUMMARY

PROJECT TITLE & ID: Fluorinated Ship-Hull Coatings for Non-Polluting Fouling Control; PP-756

RESEARCH CATEGORY: 6.2 Applied Research

LEAD AGENCY: U.S. Navy

LAB: Naval Research Laboratory - Washington, DC

PRINCIPAL INVESTIGATOR: Dr. Kenneth Wynne

FY 1998 COMPLETED PROJECT

OBJECTIVE: The overall goal of this project was to develop non-polluting, easy fouling release, hull coatings based on flexible, low surface-energy polymers. Ship hull protection from marine fouling organisms is essential for efficient fleet operation and energy conservation. Presently, the Navy standard antifouling coating contains copper as a toxicant. The copper leaching from these coatings represents an environmental hazard and is the subject of increasing regulation which will impact normal fleet operations.

BENEFIT: A non-polluting, easily cleaned coating will be synthesized which will contain no leachable toxics and will have a non-wetting, low-energy surface which resists attachment of marine fouling organisms and permits easy removal of fouling which does adhere. These coatings will benefit all operating vessels and structures and will have obvious commercial application.

ACCOMPLISHMENTS: The fouling release community has recognized that an important "first" has been achieved, namely, the demonstration that fluoropolymer elastomers demonstrate fouling release. Second and third generation fluoropolymer elastomers (fluorinated oxetanes) are being developed toward the goal of "leap-frogging" silicones and providing the "ultimate" fouling release coating. Through a systematic study of surface wettability and stability in water, cure chemistry has been discovered which greatly stabilizes coatings to chemical degradation in water. Preliminary panel testing has been carried out to quantitatively correlate fouling adhesion with surface parameters measured in the laboratory.

TRANSITION: The Naval Sea Systems Command will further test this approach. Additionally, this work, which leverages a number of funding sources and includes industrial and academic collaboration, seeks to transition to market a fouling release coating system that will strengthen the DoD infrastructure in marine materials and ship maintenance and construction.

PROJECT SUMMARY

PROJECT TITLE & ID: Demonstration of Compact, Closed-Loop-Controlled Waste Incinerator; CP-887

RESEARCH CATEGORY: 6.2 Applied Research

LEAD AGENCY: U.S. Navy

LAB: Naval Air Warfare Center - China Lake, CA

PRINCIPAL INVESTIGATOR: Dr. Klaus Schadow

FY 1998 COMPLETED PROJECT

OBJECTIVE: The objective of this project was to apply the technical basis of new compact, closed-loop-controlled waste incinerator technology developed in project CP-034 to two specific Navy incinerator programs: (1) development of a compact and efficient afterburner for a plasma arc thermal destruction system, and (2) a sludge incinerator for black-water destruction.

BENEFIT: Successful shipboard demonstration of a compact incinerator with real-time exhaust monitoring for active combustion control represents a significant step towards assured waste incineration and can be the basis for the next generation incinerators. The compact-incinerator technology will be essential for the development of environmentally sound ships beyond the year 2000. Compact incinerators are also desirable for on-shore use in the government and private sector. Compact incinerators will allow on-site waste destruction and avoid waste transportation to large incineration sites. In particular, medical waste incineration is a prime candidate in the private sector for a compact system. The closed-loop, active control of the incineration process will for the first time assure proper incineration during design and off-design operation. Successful demonstration of the assured waste incineration on-board ships will result in significant cost savings by avoiding the cost of waste off-loading and on-shore destruction, particularly in foreign countries.

ACCOMPLISHMENTS: In FY 1998, a new afterburner was initially tested at full scale (680kW) with cold ethylene and nitrogen. Extremely low emissions for CO (<35 ppm) and NO_x (<30 ppm) were achieved at only 46 ms residence time, which corresponds to a very compact system. Subsequently the afterburner was evaluated with hot, sooty pyrolysis gases, which were synchronously injected into acoustically stabilized air vortices to achieve significant reductions in emissions and increases in destruction efficiencies. No visible emissions remained and the CO levels were as low as 32 ppm. NO_x was about 35 ppm for a residence time of about 62 ms.

The performance of the afterburning process was monitored with diode-laser sensors for direct measurements of CO and instantaneous temperature fluctuation in the combustor. A correlation between the concentrations of CO and the magnitude of temperature fluctuations (corresponding to vortex coherence) was established and utilized for the control strategies. The closed-loop control system was

highly successful and adaptively optimized the afterburner performance within 100 ms at an optimized control strategy.

This project resulted in the development of the controlled after-burner for a specific incinerator (a modified GS500 pyrolysis chamber). Enhancements to the design and increasing the fuel gas path, to accommodate the greater gas volumes and decreased gas density due to the hot pyrolysis gases, were successful.

Acoustic enhancement of the Navy black-water sludge incinerator did not produce the desired results. It was concluded that re-design of the incinerator is necessary. Tests were performed with the new sludge incinerator concept with direct sludge injection into the exhaust of a pulse combustor. This study did not prove whether sludge incineration is enhanced or hindered by the presence of acoustic forcing, because of the large heat losses present in the incinerator that was used. Further testing is needed to make an adequate assessment of the impact of pulsations on sludge incineration.

TRANSITION: Continuing interaction is taking place with the Navy for: multi-functional incinerators (for sludge and oil), demonstrating acoustics retrofits, and developing an afterburner for another Department of Defense (DoD) facility under a joint development program. Three marine incinerator manufacturers interested in collaborating have been identified and a proposal for collaboration with one has been developed. The Principal Investigator is pursuing future DoD funding for a compact, integrated system for hazardous waste incineration at DoD facilities and for 6.4 research funding for shipboard advanced incineration.

PROJECT SUMMARY

PROJECT TITLE & ID: Removal and Encapsulation of Heavy Metals from Ground Water/Soil Washing Extract; CU-387

RESEARCH CATEGORY: 6.2

LEAD AGENCY: Environmental Protection Agency

LAB: National Risk Management Research Laboratory (NRMRL)

PRINCIPLE INVESTIGATOR: Subhas K. Sikdar, Ph.D., Edwin Barth, P.E.

PROBLEM: The goals of this proposed applied research (6.2) program are to develop a unique, innovative technological approach for many of the difficult problems found on DoD facilities: 1) that of removing metal contamination from dilute matrix, ground water process, waste water or soil washing extract; 2) managing metal residuals that can not be destroyed. This effort will 1) develop high-capacity low-cost adsorbents, based on cellulose or starch, natural polymer or synthetic polymers (with functional groups) for selectively adsorbing toxic metals such as lead and copper, and then 2) demonstrate permanent encapsulation of the solid adsorbent matrix by extrusion in recycled plastics such as high density polyethylene for long-term disposal. The metal contaminants (i.e. lead, copper) can be directly adsorbed from ground water or soil washing extract used to treat firing range soil. If present in a solid matrix, the metals can first be leached selectively into a concentrated aqueous medium, which then will be subjected to the low-cost adsorption technique and encapsulation. The proposed research will result in a highly efficient, yet affordable technology for remediating metal contaminated water.

Restoration of metal-contaminated water or solids is a generic problem, at many military sites. Indeed the problem is so extensive that affordable technologies are critically needed now. For ground water or soil washing extract the treatment part usually uses activated carbon or a resin, which on saturation is regenerated by acid leaching. The metals in aqueous stream are then isolated by precipitation. The precipitate sludge is further treated, then disposed of in a hazardous waste landfill. The problem may continue over the years, as the metals will gradually form leachates. It has been estimated by industry that for every one dollar of operating cost in the adsorption part of this technology, about 3 to 6 dollars are spent in regeneration. Thus developing low-cost adsorbents that do not need regeneration provides a very attractive technical approach. This is a new idea; no prior art exists.

One dominant method of metals disposal is the cement-based solidification/stabilization process. The long-term effectiveness of this technique, however, has not been determined. Alternatively vitrification has been tried, and proposed especially for radioactive wastes but does not allow for resource recovery of the encapsulated material. Encapsulating metallic wastes in thermoplastics has been demonstrated in the U.S., U.K., France, and Israel, and no leaching has been observed for a long time (years). Metals and their compounds have no detectable diffusive transport through polymer films. In landfills thermoplastics do not begin to biodegrade in less than 400 years; in low moisture environment and in absence of microbial action, therefore, these encapsulants will last much longer. The thermoplastics are also stable to high levels of irradiation, which is important for storing radioactive compounds. The longevity of

these encapsulants of course can be increased by multiple encapsulation. The Brookhaven National Laboratory has performed some preliminary work, in this area.

APPROACH: The project has several distinct parts, requiring different technical skills for their solution. First, low-cost adsorbents need to be designed and developed and produced. In the environmental restoration area, adsorbents such as carbon, zeolites, or ion exchange resins have been used. Each technology is based on the concept of regenerating the adsorbents for reuse. As has been mentioned before, even with regeneration, these adsorption processes tend to be very expensive for large dilute matrices. Moreover these adsorbents do not possess high adsorption capacity (mostly fraction of a percent), which imparts two undesirable effects on process economics, namely adsorbent cost and eventual dilution of the metals on regeneration. Highly selective adsorbents with specific ligands have made chromatography a mainstay in protein separation from very dilute solutions. In that spirit, this effort will develop low-cost adsorbents which have inexpensive but highly efficient ligands attached to them. These adsorbents will have higher capacity and high specificity for chosen metals. The resulting adsorbents will not need to be regenerated.

The technical approach consists of attaching specific amine or imine-based (or other promising) ligands on chosen adsorbents, which can be selected from cellulose, starch, saw dust, peat moss, chitin/chitosan etc., and tested for their efficacy. The engineered material most likely will be in pellets or beads form to maximize fluid flow capacity. EPA will build laboratory apparatus to demonstrate the idea of metals adsorption from contaminated water.

In another section of the project, the separation (volume reduction) data from the laboratory will be used to design experiments for encapsulating the adsorbents.

Important technical issues to overcome: (i) attaching inexpensive ligands to low-cost substrate to impart high capacity, (ii) preparing appropriate engineered (thermoplastic) materials which are easily handled, (iii) demonstrating the stability of the polymers to internal or environmental effects.

EXPECTED PAYOFF: This technological approach can be tailor-made to many civilian or military site-related problems. For example, contaminated firing range soil are found on many military sites and will be remediated utilizing soil-washing technology. This approach will establish a new paradigm in adsorption technology; i.e. disposal with adsorption without regeneration, resulting in cost savings for DoD site remediation or waste treatment.

PROJECT SUMMARY

PROJECT TITLE & ID: Selective Removal of Heavy Metals from Aqueous Wastes by Electrosorption on Functionalized Carbon Aerogels; CU-1084

RESEARCH CATEGORY: 6.2 Applied Research

LEAD AGENCY: U.S. Department of Energy

LAB: Lawrence Livermore National Lab - Livermore, CA

PRINCIPAL INVESTIGATOR: Dr. Tri Tran

FY 1997 COMPLETED PROJECT

OBJECTIVE: The objective of this project was to develop novel functionalized carbon aerogel electrodes that are integrated in an electrochemical cell for selective removal of heavy metals. Treatment of large amount of aqueous wastes containing heavy metal ions at many U.S. Department of Defense (DoD) and Department of Energy (DOE) facilities requires considerations of wide ranging technologies with flexible and, sometimes, customized capabilities. One example is the need to remove radioactive Cs^+ from a large background of Na^+ and K^+ . Another example is the removal of Resource Conservation and Recovery Act (RCRA) metals from brackish groundwaters or plating shop effluents.

The technical approach involves three integrated major tasks. The primary task is to develop functionalized carbon aerogels that would have a specific affinity for a targeted metal. Four types of carbon aerogel electrodes will be prepared and studied. The conventional resorcinol-formaldehyde-based carbon aerogel electrodes and three modified types of materials treated by thermal activation and chemical modifications (2 methods). Acidic carbon-oxygen complexes can be introduced on carbons by thermal treatment with oxidizing agents (O_2 , CO_2 , steam) or by chemical treatment in solutions with KMnO_4 , HNO_3 . Chemical treatment via silanization and amidization to introduce compounds such as porphyrin compounds (tetra(p-aminophenyl)porphyrin) will be studied. These modified electrodes are expected to have special affinity for metal cations such as Cr, Co, Cu, Ni and Zn. These novel materials will then be incorporated (second task) in an electrochemical separation cell. The cell dimension will contain active electrode surfaces of 2 inch x 4 inch. The cell is undivided and uses no membranes. The cells are polarized by programmable power supplies that have a voltage range of 0 to 1.2 V with a current range between 0 and 60 A. The third task is to investigate selective removal of 35 ppb Cr(VI) [Lawrence Livermore National Laboratory (LLNL) contaminated source level] from an aqueous solution containing other non-toxic components such as Na^+ , K^+ , and Ca^{2+} . Total dissolved solids (TDSs) in these solutions are about 500 ppm. The effects of selective removal of Cr and another heavy metal (Co, Cu, Pb, Zn and

Ni) will be investigated. The primary risk would be the complicated phenomena associated with competitive electrosorption of a heavy metal and other ions. The fabrication of and the selective separation with functionalized electrodes have not been investigated in the past.

BENEFIT: This project will provide DoD and DOE a novel and promising technology for efficient waste remediation. It has significant implications and applications in a wide range of areas besides metal separation. The project also leveraged SERDP investment in capabilities and knowledge on Capacitive Deionization and its three successful demonstration projects at one DOE and two DoD sites.

ACCOMPLISHMENTS: In FY97, LLNL researchers focused their efforts on finding solutions to the specific needs of DoD and DOE facilities to treat large amount of aqueous wastes containing heavy metal ions. This integrated experimental program has worked toward developing tailored carbon aerogel electrode materials that are modified chemically and physically to enhance the selective separation of a targeted metal from an aqueous stream. The research has begun to demonstrate and/or identify factors affecting selective removal of a model species, Cr. Other metal ions such as Co, Cu, Pb, Zn and Ni and selected mixtures will be considered. Researchers have also initiated the study of the effects of interfering phenomena such as side reactions, poisoning, and preferential removal of concomitant undesired species.

TRANSITION: This projects will transition its result directly DoD and DOE sites, providing a novel and promising technology for efficient waste remediation.

APPENDIX C

EPA Research Projects Potentially Applicable to Shipboard Incidental Liquid Wastes

APPENDIX C

The Office of Research and Development (ORD) is the scientific and technological arm of the US Environmental Protection Agency (EPA). ORD is organized around a basic strategy of risk assessment and risk management to remediate environmental and human health problems. It supports basic, peer-reviewed, scientific research in partnership with the academic scientific community to develop environmental technology necessary to ensure effective policy and regulatory decisions.

ORD research topics were reviewed, and those technologies that could be applied to shipboard incidental liquid wastes were identified and included in this appendix.

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Investigation of Catalysts to Enhance the Photo-Oxidation of Organics in Wastewaters

EPA Grant Number:

Title: Investigation of Catalysts to Enhance the Photo-Oxidation of Organics in Wastewaters

Investigator: Dr. James H. Porter

Institution:

UV Technologies, Inc.

P.O. Box 410186

East Cambridge, MA 02141-0002

Company Phone Number: 617 666-5500

Business Representative: Dr. James H. Porter

Project Period:

Project Amount: \$70,000

Research Category:

Description:

In the past five years, UV-Peroxide and/or Ozone systems have become the treatment of preference for removal of toxic organics in waste water because the contaminant species are chemically converted to benign components. These systems, however, have been limited to treating organics in groundwaters where organic concentrations rarely exceed a few tens of parts per million by weight. At higher organic concentrations, commercial systems have had very limited success.

The full potential of UV oxidation has not been achieved because of the limited understanding of the interaction of fluid mechanics, energy transfer and absorption, and reaction kinetics on the optimal design of photochemical reactors. Recent advances made by UV Technologies, Inc. scientists have allowed them to extend the concentration range for treatment and suggest further improvements which may be made.

One such suggestion is the use of a photocatalyst in a novel, in situ arrangement in a photocatalytic reactor. This project will explore the effectiveness of a catalyst employed in this arrangement.

Supplemental Keywords: small business, SBIR, wastewater treatment, engineering, and chemistry.

Last Updated: April 17, 1997

Wastewater Remediation by Catalytic Wet Oxidation

EPA Grant Number: 104TAM2358

Title: Wastewater Remediation by Catalytic Wet Oxidation

Investigator: Aydin Akgerman

Institution

Texas A & M University

EPA Project Officer:

Project Period:

Project Amount:

Research Category:

Description

Although there are many established technologies for the treatment of dissolved organics in wastewater ranging from biodegradation to granulated activated carbon adsorption to photocatalytic oxidation, none is applicable to treatment of heavily contaminated waters (moderate to high levels of organic concentration) where the organic species may even be in a separate phase. Furthermore, most of these technologies result in a waste stream (such as sludge, contaminated carbon) that requires further treatment. In this study, we propose to evaluate the efficiency of catalytic wet oxidation as an alternative technology for the removal of organic compounds from aqueous waste streams. In this technology, the organics are converted into environmentally acceptable end products, such as carbon dioxide and water, and thus no new form of waste is produced.

Catalytic wet oxidation provides an excellent alternative for the remediation of waste water streams containing organics. The first objective of this study was to evaluate catalyst activity and stability for use in wet oxidation in a batch reactor. Using phenol as the model compound, we have shown that platinum on titanium catalyst (Englehart) is the suitable catalyst for wet oxidation.

Reaction temperature and catalyst loading optimization studies have been completed and a kinetic model has been fit to experimental phenol disappearance data. Our second objective is to evaluate the catalysts for long periods on stream in a trickle bed reactor, which will be optimized through the kinetic data, obtained in the batch system. Finally, our third objective is to study model systems and actual refinery and/or chemical industry waste water streams in a laboratory scale trickle bed reactor in order to obtain sufficient data for design and cost estimates of an industrial scale catalytic wet oxidation process.

As model organic contaminants, we will use both polar and non-polar compounds such as hydrocarbons (toluene, tetralin), oxygenates (phenol, oils), chlorinated compounds (dichlorobenzene, chlorophenol) and nitro compounds (anilines, diazo compounds) in order to evaluate the effect of different functional groups on reaction by-products. In addition, we will use synthetic mixtures of these compounds as well as complex mixtures such as creosotes.

Last Updated: August 17, 1998

Development, Characterization, and Performance Evaluation of Ferrous-Ferric Oxide Adsorbents for Metal Removal from Contaminated Groundwater

Title: Development, Characterization, and Performance Evaluation of Ferrous-Ferric Oxide Adsorbents for Metal Removal from Contaminated Groundwater

Principal Investigators Peter O. Nelson

Institution:

Oregon State University (Supported by R2D2 Program)

Goal: The goal of this research is the development and characterization of a mixed oxidation state (ferrous-ferric) iron oxide composite adsorbent for simultaneous removal of adsorbable and electroactive metals from contaminated groundwater. The intended application of the sorbent material is in a permeable barrier interceptor trench. As such, desirable properties of the sorbent material are high permeability, rapid reactivity with target metals, high capacity for metals removal, and regenerability.

Rationale: Remediation of metals-contaminated groundwater focused on ex-situ or in-situ treatment processes. Both methods are often limited by their expense and extended extraction time. An alternative to these approaches is in-situ treatment by interception of the contaminant plume by a passive barrier that removes or transforms contaminants in place. This study will increase our understanding of mixed oxidation state (ferrous-ferric) iron oxide for removal of adsorbable and electroactive metals in in-situ treatment in an interceptor trench.

Approach: Several approaches will be followed in preparation of the ferrous-ferric iron oxide adsorbent. Ferrous-ferric iron oxide adsorbent will be prepared by coating magnetite on silica sand or by coating commercially available magnetite with $\text{Fe}(\text{OH})_3(\text{s})$ precipitate (ferrihydrite). The coated sand will be characterized to determine kinetics and equilibrium removal capacity of the sorbable and electroactive metals. $\text{Cr}(\text{VI})$ and $\text{Pb}(\text{II})$ are selected as the model metals to test the performance of the mixed oxidation state (ferrous-ferric) sorbent material. Batch reactor experiments will be used to determine sorption kinetics and equilibrium constants. Packed-bed column experiments will be used to more closely simulate field conditions of porous media flow.

Status: Magnetite-coated sand (MCS) was prepared by precipitation of iron(III)-hydroxide on 0.60-0.85 mm Ottawa sand (99.8% quartz (SiO_2)), rinsed with 5% ammonium acetate solution, oven-dried, and heated under nitrogen at 400 °C which yields magnetite. The product was characterized by chemical analysis, X-ray diffraction (XRD), and BET surface area. Batch and column studies are in progress to assess the performance of MCS for removal of metals. pH adsorption edge data for various initial lead concentrations show that Pb removal increased with increasing pH from less than 20% at pH = 3 to nearly 100% at pH = 6. Chromate removal by MCS at pH values 3 to 6 showed both adsorption and reduction, with adsorption equilibrium achieved within 24 hours while the reduction continued at a decreasing rate for up to several weeks, apparently limited by the rate of $\text{Fe}(\text{II})$ dissolution from MCS. $\text{Cr}(\text{VI})$ removal by MCS increased with decreasing pH. This can be explained by increasing MCS dissolution at lower pH

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values, consequently increasing Fe(II) release and Cr(VI) reduction, and also by increasing Cr(VI) adsorption at lower pH values.

Last Updated: December 29, 1997

Hybrid Steam-Plasma Torch

Awarding Agency: National Science Foundation

SBIR Contract Number: 9560997

Title: Hybrid Steam-Plasma Torch

Principal Investigator: Lawrence C. Farrar

Company Name:

Montec Associates, Inc.

1850 Four Mile Vue Road

Butte, MT 59701

Telephone Number: 406-496-5555

Business Representative:

Project Period: 6 months

Project Amount: \$75,000

Research Category: Hazardous/Solid Waste

Description:

This SBIR Phase I project explores a novel hybrid steam-plasma (HSP) torch that has broad application for advanced materials synthesis, chemical conversion, waste redemption, coating deposition, and gasification. The research objectives aim at a prototype HSP torch and focus on demonstrating its application in plasma spray operations. The demonstration focuses on reliability and ease of use in an industrial environment. The Phase I research will address issues like requirements for a durable electrode material for the steam-plasma environment. Plasma spraying is expected to have a large market potential. If Phase I is successful, Montec Associates plans to conduct detailed evaluations on the metallurgical nature of the sprayed metal and of its bonding characteristics with substrates. Use of the HSP torch is expected to improve process productivity and open new applications for plasma spray technology. As a generic processing tool, it may open a broad range of chemical processing applications. These include nano-powered synthesis, conversion of methane to acetylene, and gasification of black liquor in the pulp industry. A significant market for this technology may be found in the treatment of hazardous chemical and biological agents, including CFCs, PCBs, and other toxic or carcinogenic substances.

Supplemental Keywords: small business, SBIR, hazardous waste, chemistry, engineering, and NSF.

Last Updated: November 17, 1997

Novel Nonporous Nanofiltration Membrane for Wastewater Treatment

EPA Grant Number:

Title: Novel Nonporous Nanofiltration Membrane for Wastewater Treatment

Investigator: Dr. J. G. Wijmans

Institution:

Membrane Technology and Research, Inc.
1360 Willow Road, Suite 103
Menlo Park, CA 94025
415 328-2228

Business Representative: Ms. E. G. Weiss

Project Period:

Project Amount: \$65,000

Research Category: Municipal and Industrial Wastewater Treatment and Pollution Control

Description:

U.S. industry generates large volumes of wastewater that contains suspended particles, emulsified liquids, dissolved macromolecules, and/or dissolved organic compounds. Nanofiltration can produce dischargeable water from these streams. However, because current nanofiltration membranes are finely porous and only moderately hydrophilic, they are subject to fouling, particularly by particulates and macromolecules.

In this Phase I research program, a novel type of fouling-resistant composite membrane for nanofiltration applications will be developed. The composite membranes will consist of an ultrathin (0.2-0.5 μm), nonporous, highly water-permeable layer supported by microporous membrane. This novel membrane will be fouling resistant due to the extremely hydrophilic nature and the nonporous surface of the selective layer. In Phase I, Membrane Technology and Research, Inc., (MTR) will demonstrate the non-fouling properties in MTR's laboratories. In Phase II, the membrane will be fabricated into modules for demonstration in a pilot-scale system.

Supplemental Keywords: small business, SBIR, wastewater treatment, engineering, and chemistry

Last Updated: April 17, 1997

Novel Sorbents for Sorption and Recovery of Heavy Metals from Wastewater

EPA Grant Number:

Title: Novel Sorbents for Sorption and Recovery of Heavy Metals from Wastewater

Investigator: Dr. Shantha Sarangapani

Institution:

ICET, Inc.

916 Pleasant Street, Unit 12

Norwood, MA 02062

617 769-6064

Business Representative: Dr. Shantha Sarangapani

Project Period:

Project Amount: \$65,000

Research Category: Municipal and Industrial Wastewater Treatment and Pollution Control

Description:

An efficient method for directly removing chromate and metals such as nickel, zinc, cadmium, mercury, cobalt, chromium(III), lead in two separate stages is proposed. The highly capacity sorbents could be regenerated, recovering the chromate and other metals separately. The regeneration is expected to be efficient and is simply based on changing the pH from one extreme to another.

Bench scale characterizations of chromate specific sorbents and the ones for other metals will be carried out for their sorption capacity, adsorption isotherms, desorption conditions, cycle life and efficiency. The metals from the sorbents, except for chromate, will be recovered by electrowinning after concentration. The chromate will be concentrated, recrystallized, and recycled.

Using the best set of sorbents, an environmental engineering company will conduct bench scale testing for a continuous process to assess the merits of the proposed sorbents and will present a detailed report.

Supplemental Keywords: small business, SBIR, wastewater treatment, engineering, and chemistry

Last Updated: April 17, 1997

On-Line Production of Oxidant for UV Oxidation Processes

EPA Grant Number:

Title: On-Line Production of Oxidant for UV Oxidation Processes

Investigator: Dr. James H. Porter

Institution:

UV Technologies, Inc.

P.O. Box 410186

East Cambridge, MA 02141-0002

Company Phone Number: 617 666-5500

Business Representative: Dr. James H. Porter

Project Period: .

Project Amount: \$225,000

Research Category:

Description:

In UV-H₂O₂ advanced oxidation systems, for wastewater treatment, the cost of purchased hydrogen begins to dominate electric power costs as contaminant concentrations increase. It was successfully demonstrated in Phase I that oxidant could be produced on-line in the presence of the contaminant at a cost less than the purchased price of hydrogen peroxide. The unique method of on-line oxidant production has great potential especially when treating industrial strength aqueous waste. The Phase II effort will explore contaminant streams for which the process is applicable and the limits of its applicability.

Supplemental Keywords: small business, SBIR, engineering, and chemistry

Last Updated: April 21, 1997

Reactor Technology for Aqueous Phase Catalytic Oxidation of Organics

Awarding Agency: Department of Defense

SBIR Contract Number:

Title: Reactor Technology for Aqueous Phase Catalytic Oxidation of Organics

Principal Investigator: James R. Akse

Company Name:

Umpqua Research Company

P.O. Box 609

Myrtle Creek, OR 97457

Telephone Number: 503-863-7770

Business Representative:

Project Period:

Project Amount: \$747,062

Research Category: Water

Description:

The mineralization of refractory aqueous organic contaminants has been demonstrated during the Phase I program by using low-temperature aqueous phase heterogeneous catalytic oxidation. Jet A, trichloroethylene, and dinitrophenol have been oxidized in a plug flow reactor over a bimetallic noble metal catalyst at temperatures less than 140°C and pressures below 60 psi. Previous work has highlighted the versatility of this technology for treating widely differing classes of organic compounds that are common to contaminated ground and surface waters, including phenol, benzene, alcohols, esters, glycols, chlorinated hydrocarbons, and methylene blue. Lessons learned during the Phase I program have identified three areas of improvement, which will result in a mature, economically viable process suitable for Phase III development. Phase II efforts will include the development of an advanced reactor design capable of sustained high oxidation rates, improved methods for maintenance of the oxidant level, and an oxidation-resistant and mechanically stable catalyst with an extended operational lifetime. An optimized prototype reactor-catalyst combination will be constructed and tested on refractory wastewaters of interest to the Air Force. Sufficient wastewater treatment data will demonstrate the economic viability of this technology by using a more robust catalyst and optimized reactor design and operation.

Supplemental Keywords: small business, SBIR, wastewater treatment, chemistry, DOD

Last Updated: November 12, 1997

On-Site Recovery of Glycols from Airport Deicing Fluid Using Polymeric/Ceramic Composite Membranes

EPA Grant Number:

Title: On-Site Recovery of Glycols from Airport Deicing Fluid Using Polymeric/Ceramic Composite Membranes

Investigator: Dr. Paul K. T. Liu

Institution:

Media and Process Technology, Inc.

1155 William Pitt Way

Pittsburgh, PA 15238

Company Phone Number: 412 826-3711

Business Representative: Dr. Paul K. T. Liu

Project Period:

Project Amount: \$225,000

Research Category: Water

Description:

As a result of governmental regulation and the inadequacies of conventional treatment technology, waste aircraft deicing fluid has become both an economic and environmental liability for airports throughout the U.S. and Canada. Media and Process Technology, Inc., has developed an integrated membrane base system, centered on its novel polymeric/ceramic composite membrane technology, to overcome these problems. This technology has been demonstrated to be technically feasible and economically attractive during the Phase I program. Because of the demonstrated low capital and operating cost requirements, ease of operation, compact size, and rapid capital payback, these systems can be installed at airports throughout the country to convert the glycol disposal problem into a profitable recovery operation. The Phase II research program will focus on product and process optimization and then demonstration of the technology in the field at pilot scale.

Supplemental Keywords: small business, SBIR, wastewater treatment, engineering, and chemistry

Last Updated: April 21, 1997

Development of an Improved BIO-SOK for Use in Bilge to Reduce Nonpoint Source Pollution

EPA Contract Number: 68D98138

Title: Development of an Improved BIO-SOK for Use in Bilge to Reduce Nonpoint Source Pollution

Investigator: Dr. W. Michael Griffin

Small Business:

GMS Technologies

P.O. Box 2353

Cranberry Township, PA 16066

Telephone Number: (412) 776-3977

EPA Contact: SBIR Program Manager

Phase: I

Project Period: 6 months

Project Amount: \$69,932

Research Category: Wastewater

Abstract:

The purpose of this SBIR project is to improve BIO-SOK, an existing oil spill response technology. Subsequently, this technology can be applied to a growing nonpoint source problem stemming from oily waste and fuel discharges in the recreational boating industry. Because the technology has been proven effective for oil spill response, this SBIR project will focus on refining the technology. Ultimately, this will result in a product that is more effective, technically more consistent, and less expensive to produce than its current formulation. To achieve these product improvements, the project team will meet the following four objectives under this SBIR: (1) develop a model bilge system capable of evaluating product formula variations; (2) conduct a series of discrete studies that will evaluate formula variations; (3) improve product performance in biodegrading oil wastes, reduce manufacturing costs, and increase the overall quality of the technology; and (4) develop a final optimal product formulation and delivery system that will reduce oily discharges from recreational boats.

Supplemental Keywords: small business, SBIR, wastewater treatment, pollution prevention, engineering, chemistry, and EPA

Last Updated: June 1, 1999

The Development and Scale Up of an Enhanced Mass Transport Resin for Efficient and Cost Effective Heavy Metals Removal and Recovery

EPA Grant Number: 68D98139

Title: The Development and Scale Up of an Enhanced Mass Transport Resin for Efficient and Cost Effective Heavy Metals Removal and Recovery

Investigator: Richard A. Hamilton

Institution:

SolmeteX, Inc.

29 Cook Street

Billerica, MA 01821

Telephone Number: (978) 262-9890

Business Representative:

Phase: I

Project Period: 6 months

Project Amount: \$67,916

Research Category: Wastewater

Description:

In aqueous solutions, where metal contamination is of low concentration but still unacceptable for discharge, and flow rates are high, there is no technology that can be reasonably applied to remove the metals. The unavailability of technology or the excessive cost of existing technology has been problematic for low concentration of metals such as mercury, silver, chromium, cadmium, arsenic, and lead. The purpose of this SBIR project is to develop and scale up an enhanced mass transport resin for efficient and cost effective heavy metals removed and recovery. Under this project, the feasibility of making large polymer beads (approximately 800 microns) with bimodal pore distribution consisting of large "through pores" (1-5 microns) will be determined. These beads will allow mass transport enhancements that increase the speed of separation; the smaller, diffusive pores (100-500# angstroms) lining the through-pores will provide extremely high surface area. A "through-pore" allows flow to pass through the interior of the particle under high flow operating conditions to enhance mass transport within the particle. Flow through these pores will be convective, minimizing the effects of the boundary layer, thus significantly accelerating the kinetics of binding as compared to traditional bead-based technology. This project also will determine the scaling processes for making 40-micron enhanced mass transport beads and scaling to 800 micron beads with the same mass transport characteristics and low price for applications in wastewater and process water for the removal of metals. It may be possible to scale the process for making these beads to make large beads that take advantage of the enhanced mass transport, thereby reducing process time and cost for wastewater and metal removal applications.

Supplemental Keywords: small business, SBIR, wastewater, groundwater, remediation, engineering, chemistry, and EPA

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Last Updated: October 8, 1998

High-Performance Extraction of Heavy Metals with Tethered Metal-Binding Ligands

EPA Contract Number: 68D98151

Title: High-Performance Extraction of Heavy Metals with Tethered Metal-Binding Ligands

Investigator: Dr. Richard F. Hammen

Small Business:

ChelaTech, Inc.

2837 Fort Missoula Road

Missoula, MT 59804

Telephone Number: (406) 728-5897

EPA Contact: SBIR Program Manager

Phase: I

Project Period: 6 months

Project Amount: \$70,000

Research Category: Heavy Metals

Abstract:

The removal of metals from contaminated water is critical to many manufacturing industries. Both internal requirements and external environmental regulations place an economic premium on producing high-purity water that is free of detectable metal ion contamination (zero discharge). Conventional ion exchange technologies used today can only achieve zero discharge with exponentially increasing costs, due to the limitations of the kinetics of diffusion of metals to the surface of ion exchange resins. To avoid boundary layer diffusion limitation, ChelaTech has developed a technology of covalently attaching a variety of tether molecules to porous silica gel. The tether length can be controlled and is made to be 15-400 Angstroms long. The tether is then covalently coupled to an appropriate ligand or metal-binding reagent. By "dangling" the reagent away from the solid surface, the reagent interacts with solute molecules pumped through the porous bed with unprecedented reaction and adsorption kinetics. This project will prepare High-Performance Extraction media with high-affinity metal binding agents that are selective for extracting mercury, cadmium, hexavalent chrome, and arsenate ions from contaminated water. The media will be tested for their efficacy and economics of performance.

Supplemental Keywords: small business, SBIR, remediation, heavy metals, wastewater, engineering, chemistry, and EPA

Last Updated: June 1, 1999

Selective Removals of Toxic Anions of Metals, Metalloids, and Metal-Ligand Complexes Using Novel Synthetic Sorbents

EPA Grant Number: R81-9228

Title Selective Removals of Toxic Anions of Metals, Metalloids, and Metal-Ligand Complexes
Using Novel Synthetic Sorbents

Institution:

Lehigh University

Principal Investigator: Arup Sengupta

Project Period: 2 years

Project Amount: \$186,579

Research Category: Environmental Engineering

Description:

Commonly used polymeric or naturally occurring sorbents are often ineffective for selective sorption of (1) metal-ligand anionic complexes, (2) oxy-anions of Cr(IV) at varying pH, and (3) oxy-anions of toxic metalloids, namely, Se(IV), As(V), and As(III). In their work the researchers have identified polymeric sorbents with the three following distinctly different types of functional groups which may help overcome the shortcomings of commonly used sorbents: (1) pyridyl functional groups for removals of metal-ligand complexes, (2) special types of quaternary ammonium functional groups for chromate removals, and (3) specialty chelating polymers with immobilized copper (II) for selective sorption of As(V) and Se(IV) oxy-anions. This project embodies a detailed plan to carry out a series of laboratory experiments to (1) explore and evaluate various properties of these sorbents through appropriate understanding of underlying sorption mechanisms and (2) estimate key process parameters for comparison with commonly used sorbents. One of the key challenges of the proposed research is to show that minor modifications of the chemistry at sorption sites can result in significant sorption enhancement for several toxic solutes under seemingly unfavorable conditions.

Last Updated: December 2, 1997

High Efficiency Electrochemical Treatment of Groundwater Contaminated with Heavy Metals

EPA Contract Number:

Title: High Efficiency Electrochemical Treatment of Groundwater Contaminated with Heavy Metals

Investigator: Dr. Chengdong Zhou

Small Business:

Faraday Technology, Inc.
3155 Research Blvd., Suite 105
Dayton, OH 45420
513 252-2113

EPA Contact: SBIR Program Manager

Project Period:

Project Amount: \$64,752

Research Category: Removal of Heavy Metals from Superfund Sites

Abstract:

This SBIR Phase I project will demonstrate the feasibility of an innovative electrochemical process for high efficiency simultaneous recovery of mixed heavy metals from contaminated groundwater. Electrochemical recovery of metals from wastewater is a promising approach for metal recycle. However, the conventional electrochemical method is not efficient to treat dilute wastewater. Additionally, when the wastewater contains two or more heavy metals, the metal with the more negative reduction potential is difficult to recover. For example, when wastewater containing the mixture of copper and lead is treated, lead can be removed efficiently only after the copper concentration is much lower than the lead concentration. Faraday Technology's innovative approach will demonstrate an efficient, simultaneous electrochemical/ion-exchange process.

Supplemental Keywords: small business, SBIR, engineering, chemistry

Last Updated: May 25, 1999

Heavy Metals Removal from Contaminated Water Solutions

Title: Heavy Metals Removal from Contaminated Water Solutions

Principal Investigators: Z. Lewandowski, G.G. Geesey, and F.L. Roe

Institution:

Montana State University

Goal:

The goal of this project is to quantify the process of heavy metals removal by binding to biopolymers from dilute aqueous solutions containing more than one metal.

Rationale:

Extracellular polymers extracted from living microorganisms constitute an attractive alternative for heavy metals removal from dilute aqueous solutions. However, demonstrated technologies do not offer any rational means of predicting the process kinetics as a function of water chemical composition. Thus far the documented research effort is largely related to binding single metals from aqueous solutions. Such convenient simplification is unacceptable for most technical applications of the process. For example, it is a rare exception that a water is contaminated with a single heavy metal. In frequently encountered situations when more than one heavy metal is present in the solution, existing models do not apply, and the result of the process cannot be predicted.

Approach:

Investigators propose describing the kinetics and thermodynamics of metals binding to biopolymers from solutions of many metals. Relevant parameters for process modeling will be obtained from measurements of binding constants, binding capacities, selectivity coefficients, diffusion coefficients, and rates of metal binding reaction. Predictive value of the models will be experimentally verified.

Status:

Biopolymer gel bead binding to heavy metals in water taken from the Berkeley Pit has been studied, and field studies using beads for heavy metal uptake at acid mine drainage sites have been initiated. In order to make use of this technology economically feasible, the beads must be regenerated and reused many times. Regeneration and reuse studies have begun. In mixtures of copper and zinc, binding constants and binding capacities under competition have been determined, and hydrogen ion has been included as a cation. Since concentrations of metals in the solution were relatively high, metal alginate gel beads were formed *in situ*. The experimental data closely fit the extended Langmuir model, allowing binding group density and stability constants to be determined. A model which predicts final concentrations of divalent cations in solutions comprised of mixtures of the metal ions and protons in the presence of alginate biopolymer gel beads is being developed. The model predicts equilibrium concentrations of copper, zinc, and hydrogen ions in the presence of alginate gel

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beads. Results show that alginate is much more selective for copper than for zinc. A key finding has been that the maximum binding capacity for alginate is independent of metal type. Investigators are comparing bead regeneration efficacy using equilibrium shifting plus electrodeposition to equilibrium shifting alone and to electrodeposition alone. Investigators are preparing to submit a patent application related to biopolymer regeneration. This project is in its third year.

Clients/Users:

Results are of interest to other researchers, private industry, and regulatory personnel.

Last Updated: December 29, 1997

Development of Self-Supporting Microporous Ceramic Membranes for Use in Ultrafiltration, Reverse Osmosis, and Adsorption Processes

Title: Development of Self-Supporting Microporous Ceramic Membranes for Use in Ultrafiltration, Reverse Osmosis, and Adsorption Processes

Principal Investigators: C.G. Hill Jr. and M.A. Anderson

Institution:
University of Wisconsin-Madison

Goals:

To fabricate and characterize modules of self-supporting ceramic membranes which have a high ratio of surface area to volume and which can be produced in a cost-effective manner.

Rationale:

While ceramic membranes can be employed under conditions where organic polymer membranes are susceptible to rapid degradation (e.g., in applications where high temperatures and organic solvents are employed), commercialization of ceramic membranes has been rather restricted. This situation is, in part, a consequence of their high cost and the low ratio of surface area to volume characteristic of these materials. Normally, ceramic membranes are slip-cast on porous extruded ceramic supports fabricated mostly of alpha alumina. These generally take the form of tubes, but can also be formed as monolithic "honeycomb" structures. The resultant low yield and low ratio of surface area to volume ratio lead to economic situations which favor the use of these materials only in extremely high "value-added" applications.

Approach:

A dipping procedure is used to cast suspended colloidal particles onto supporting fabrics which can subsequently be removed by firing. This approach appears to provide an inexpensive route for the preparation of a high-surface area to volume ceramic membrane. The precursor colloidal suspensions of a variety of different metal oxides can be prepared in a wide range of particle sizes. This approach offers opportunities to prepare microfilters, ultrafilters or even reverse osmosis or gas separation membranes using the same technology.

Status:

To date we have successfully fabricated materials in the form of sheets which are both self-supporting and sufficiently robust to provide the strength necessary to develop a working module. The next step will be to assemble several of these sheets into a working module. This task remains to be completed. Completion of this task will be required before the data necessary to evaluate this technology can be obtained.

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Last Updated: March 21, 1997

1997 Progress Report: Development of the Environmental Technologies Design Options Tools (ETDOTs)

Title: 1997 Progress Report: Development of the Environmental Technologies Design Options Tools (ETDOTs)

Principal Investigator: David W. Hand, John C. Crittenden, David R. Hokanson, Alex S. Mayer, James R. Mihelcic, and Tony N. Rogers; and Michael J. Semmens

Institution:
Michigan Technological University
University of Minnesota

Goal:

The Environmental Technologies Design Options Tools (ETDOTs) are a compilation of self-contained tools for use in assessing and implementing effective treatment strategies for gaseous, aqueous, organic, and solid waste by-product streams. ETDOT will assist CPAS in evaluating the technical and economic feasibility of source reduction, versus end-of-pipe treatment and waste segregation, versus treatment at a central facility. It is envisioned that eventually ETDOT or its component parts will be integrated with process simulators, or other manufacturing design tools, to provide more effective analysis evaluation and incentive for source reduction for pollution prevention.

Rationale:

Currently, there is much interest by the industrial and regulatory communities in quantifying air, water, and solid pollutant emissions from waste treatment facilities, and in estimating the fate and treatability of specific potential pollutants produced during the manufacturing process. The goal of both communities is to effectively reduce generation of difficult and costly-to-treat pollutants, and optimize destruction of easy-to-treat pollutants in a cost effective and environmentally safe manner.

Before this goal can be achieved, reliable mathematical models, which describe industrial manufacturing and pollution treatment processes, must be developed and coupled into a user-friendly modular form. This project is aimed at developing advanced pollution treatment models, and integrating them with industrial manufacturing process simulators.

Approach:

Models are being developed for metal and organic chemical fate during conventional wastewater treatment, air stripping and carbon adsorption. The software is being developed for each unit process as a stand-alone package with the ultimate goal of linking them into the overall framework of CPAS. Software is being validated from plant data including different industrial sources.

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Status:

This project is undertaking the development of a total of nine software tools. Five of these tools have been completed or nearly completed during the past year: 1) Fate of Volatile Organic (FaVOr) compounds in wastewater treatment facilities; 2) Fate of Metals (FaMe) in wastewater treatment facilities; 3) gas- and liquid-phase Adsorption Design Software (AdDesignS); 4) Software to Estimate Physical Properties (StEPP); and 5) Aeration System Analysis Program (ASAP). Other tools under earlier stages of development in the past year include 6) Advanced Oxidation Process Software (AdOx); 7) Membrane Process Model Software (MPMS); 8) Multi-Phase Multi-Component Catalytic Reactor Software (CatReac); 9) Ion Exchange Process Model Software (IonEx).

A brief description of the scope and status of each tool is presented below.

(1) FaVOr

FaVOr was developed to aid design engineers in determining the fate of VOCs in conventional wastewater treatment facilities. In many industrial applications, conventional activated sludge waste treatment facilities are used to treat industrial waste streams containing VOCs. FaVOr enables design engineers to evaluate the impact of VOCs on a treatment system, identifying potential compliance issues and incentives for source reduction. FaVOr will also evaluate the feasibility of using these conventional waste treatment systems to remove volatile organic compounds from waste streams. FaVOr is in beta testing stage and will be completed in late Spring 1998. Pending satisfaction of tester comments, release is expected in early Summer 1998.

(2) FaMe

FaMe was developed to aid design engineers in determining the fate of metals in conventional wastewater treatment facilities. In many industrial applications, conventional activated sludge waste treatment facilities are used to treat industrial waste streams containing metals. FaMe enables design engineers to focus on minimizing waste metals that are difficult to treat.

FaMe's front-end software architecture and model code has been completed resulting in a functional prototype. Based on a prioritization of potential interest and impact and associated funding limitations, FaMe will not be developed further under the current project.

(3) AdDesignS

AdDesignS was developed to aid design engineers in performing adsorption design calculations. AdDesignS consists of equilibrium and mass transfer models which are used to provide gas and liquid phase multi-component adsorption design calculations for fixed-bed adsorbers. The AdDesignS equilibrium isotherm database currently contains 650 aqueous phase isotherms for more than 300 compounds on 15 adsorbents and 300 gas phase isotherms for 150 compounds on two adsorbents. In addition, isotherm parameter estimation algorithms are also provided.

AdDesignS has been completed and passed the alpha testing stage. The tool has been turned over to the CPAS core group for distribution to beta testers. Over 70 professionals from industry, academia and government have offered to beta test the software. It is anticipated

that final beta testing will be completed in the Winter of 1997-98. Expected release date is in early Spring 1998.

(4) StEPP

StEPP has been primarily developed under the Physical Properties Management System project. The linkage of StEPP to individual treatment modules and other development has been supported under this project.

(5) ASAP

ASAP was developed to aid design engineers in performing air stripping design calculations for the removal of Volatile Organic Compounds (VOCs) from aqueous waste streams. ASAP consists of three models applicable to aeration systems: packed tower aeration, bubble aeration, and surface aeration. ASAP has two modes; design mode for sizing new systems and rating mode for evaluating existing systems.

ASAP has been completed and passed the alpha testing stage. The tool has been turned over to the CPAS core group for distribution to beta testers. It is anticipated that beta testing will be completed in early Winter of 1997-98. At this time, the CPAS core group will perform the final modifications followed by marketing and distribution in early Spring 1998.

(6) AdOx

AdOx is being developed to aid engineers in the design of advanced oxidation processes (AOPs). These technologies may have significant use in water-reuse applications. The present work in the development of AdOx focused on the fundamental model development, model code development, and model verification for an hydrogen peroxide in the presence of UV-light. The model was verified by predicting the decomposition rate of organic contaminants in water.

The dynamic kinetic model developed under this project can predict the parent organic compound destruction and hydrogen peroxide consumption in both completely mixed batch reactors and completely mixed flow reactors. The model's capability of including the effect of background organic matter on the process efficiency in laboratory scale studies has been successfully verified. In addition, the consideration of pH decrease during the process due to the formation of mineral acids and carbon dioxide further improves model performance. A model front end will be developed during the Spring of 1998 and alpha tested.

(7) MPMS

MPMS is being developed to predict the separation performance of microporous membranes for a variety of operating conditions. This tool is being developed under the project, "Predictive Tool for Ultrafiltration Performance" by Dr. Michael Semmens of the University of Minnesota.

(8) CatReac

A model to predict the performance of a Multi-phase Low Temperature Catalytic Reactor System (e.g. trickle bed reactor system) has been developed. The model incorporates the following assumptions and mechanisms: 1) plug-flow in the gas and aqueous phases, 2) by-product contaminant formation and destruction in the catalyst phase described by first-order

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kinetics, 3) gas and water partitioning described by Henry's law, 4) mass transport across the gas-water and water-solid interfaces described by film diffusion, and 5) mass transport in the catalyst phase described by pore diffusion.

CatReac has been tested against analytical solutions (when available) and experimental results, for the decomposition of some primary and secondary alcohol type compounds. The model has shown good agreement with both analytical and experimental results. Additional model development work will include the multi-component competitive interactions among competing solutes and further model verification with experimental data. CatReac development, testing, and verification will be completed by the end of Winter 1998.

(9) IonEx

IonEx is being developed to aid design engineers in performing fixed-bed ion exchange design calculations. IonEx is an equilibrium multi-component fixed-bed model that can be used to predict the performance of several types of resin beds: strong acid cation exchange, strong base anion exchange, weak base anion exchange, and mixed bed strong anion and cation exchange. The model is presently in the development and testing stage. A model front end will be developed during the Spring of 1998 and alpha tested. Original Project Abstract

1997 Progress Report

Last Updated: July 6, 1998

Process for Heavy Metal Removal from Industrial Wastewater

Title: Process for Heavy Metal Removal from Industrial Wastewater

Small Business:

LSR Technologies, Inc.
898 Main Street
Acton, MA 01720
(508) 635-0123

Principal Investigator: Dr. Zhen Wu Lin

EPA Contact: SBIR Program Manager, Region 1

Project Amount: \$165,000

Key Words: Liquid Membrane, Facilitated Transport

Description:

Protection of groundwater and marine waters is a complex issue and a vital public concern. Once contaminated, it can be technically difficult and enormously expensive to clean up. One way to protect these waters from contamination is through the control of industrial discharges. This project involves a new liquid membrane process for removing the heavy metals from industrial wastewater streams. The specific contaminant addressed in this work is copper removal, which is a serious concern because of its toxicity to aquatic life. The proposed liquid membrane process has several advantages over other methods such as solvent extraction, conventional supported liquid membrane, and emulsion liquid membrane processes. Some of these advantages include high permeability, membrane stability, combining extraction and stripping steps in the same unit, and the potential to produce high contaminant concentrations in the stripping solution.

In the Phase I program, a lab-scale testing system was developed to demonstrate the technical feasibility of the proposed liquid membrane system using an aqueous copper solution. A total of 26 tests were completed with copper concentrations in the feed stream ranging from 100 to 600 mg/L. The liquid membrane system achieved up to 99.99% copper removal from the feed stream, lowering its copper concentration in one case from 439 mg/L to 0.059 mg/l. Membrane stability and other technical objectives were also demonstrated. With some optimization, better results can be expected. With its demonstrated ability for heavy metal removal, and with further development, the proposed liquid membrane process should find acceptance in the metal processing, metal finishing, and metal plating industries, especially the small shops for which its economical size would be attractive.

Last Updated: May 25, 1999

Trace Element Adsorption in Porous Particle Packed Beds

Title: Trace Element Adsorption in Porous Particle Packed Beds

Principal Investigators: James O. Leckie

Institution:

Stanford University (Supported by R2D2 Program)

Goal:

The objective of this project is to develop the empirical data base and mathematical model requisite to trace element treatment technology based on trace element adsorption onto packed beds of high adsorption capacity, porous alumina particles to bring waste streams into compliance with increasingly stringent NPDES standards. Research activities are to be directed toward establishing optimal design and operational characteristics for the proposed technology.

Rationale:

Chemical precipitation has been the most widely used technique of trace element removal from wastewater for several decades. Though chemical precipitation has proved to be effective over a narrow range of operating conditions, it is beset with a number of problems including the inability of achieving increasingly stringent NPDES in-stream permit standards. Adsorption promises to be a more efficient method of trace element removal, especially over a wider pH range and to concentrations lower than those achievable by precipitation. Additional advantages include the ability to remove cations and anions simultaneously and the ability to regenerate the adsorbent by adjusting contacting solution conditions (e.g., pH, presence of ligands, etc.). Despite inherent advantages over precipitation, the potential of developing packed bed adsorption into a feasible treatment technology has not yet been thoroughly investigated.

Approach:

The proposed technology will use packed beds of adsorbent particles for treating waste solutions as such a technology can be modularized and requires a small footprint and low maintenance. The project will use commercially available alumina particles that exhibit strong adsorption characteristics along with fast uptake rates for the target contaminants. Our studies have shown that for fast adsorption, the adsorbent should have significant pore volume in the macro- and mesoporous regions. Cadmium and selenite are being used as model contaminants for the study. The study will generate a high quality empirical database from extensive batch and column studies of adsorption. A mathematical model will be developed for simulating adsorption processes in continuous-flow column reactors. The model, once developed and verified, can be used to predict column adsorber performance and is intended to serve as a tool in designing and operating the proposed treatment scheme.

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Status:

Six commercially available alumina adsorbents (CP-100, DD-6, DD-660, DD-431, and S-400; all from ALCOA, PA) and Metal::X (from Solmetex, MA)) were selected on the basis of their surface area and macro- and mesopore content. The adsorbents were ground and sized into four size fractions. Scanning Electron Micrographs and X-ray diffraction patterns have been used to characterize the adsorbents. Equilibrium and time-dependent studies of cadmium sorption have been carried out with these adsorbents as a function of pH, pore-structure, adsorbent size and presence of ligands like chloride. The rate data is being analyzed with a batch reactor model. Additionally, the potential use of the model KINEQL is being investigated for modeling the effects of variable solution compositions on the rate of adsorption. Additional batch and column experiments are underway to investigate the effect of other ligands like thiosulfate and cyanide on cadmium sorption.

Last Updated: April 29, 1999

Design and Synthesis of CO₂-Soluble Affinity Ligands for Use in CO₂ Extraction of Proteins

EPA Grant Number: R824730

Title: Design and Synthesis of CO₂-Soluble Affinity Ligands for Use in CO₂ Extraction of Proteins

Investigator: Eric Beckman and Alan Russell

Institution:

University of Pittsburgh

EPA Project Officer: Gregory Ondich

Project Period: October 1, 1995 - September 30, 1998

Project Amount: \$150,000

Research Category: Technology for a Sustainable Environment

Description

This proposal involves the design of highly CO₂-soluble ligands for the extraction of molecules of biological origin. Carbon dioxide is a relatively benign solvent, and one where recovery of solutes from solution is easily accomplished via depressurization. Unfortunately, CO₂ is a low dielectric fluid, and thus will not solubilize polar/hydrophilic molecules such as are commonly generated in biotechnical processes. Further, CO₂ is a poor solvent for many commonly used extractant molecules, such as surfactants and chelating agents. Thus, this proposal focuses on the design of extractants/ligands particularly for use in CO₂, to allow extension of CO₂ to processes where its use is currently untenable. This is a jointly funded NSF/EPA project. In the EPA part of the project, we are focusing on the design of CO₂-soluble chiral mobile phase agents (CMPA's) for the separation of enantiomers of ibuprofen and naproxen. A well-designed CMPA interacts specifically with one enantiomer of a racemic mixture, and thus allows separation, often times via salt formation and thus precipitation. Our goal is to combine the selectivity of a CMPA with the pressure-sensitive phase behavior inherent to CO₂-based solutions to increase selectivity in a CMPA-moderated separation.

Supplemental Keywords: Carbon-dioxide-soluble affinity ligands; biological extraction; separation of enantiomer; racemic target molecules; chiral mobile phase ligands; carbon-dioxide-philic tails; fluoroalkyl and fluoroether

Last Updated: December 2, 1997

High Flash Solvent Recovery Using Dual Purpose Ceramic Membrane Technology

EPA Contract Number: 68D70045

Title: High Flash Solvent Recovery Using Dual Purpose Ceramic Membrane Technology

Principal Investigator: Dr. Paul K.T. Liu

Small Business:

Media and Process Technology, Inc.

1155 William Pitt Way

Pittsburgh, PA 15238

Telephone Number: 412-826-3721

EPA Contact: SBIR Program Manager

Project Period: 6 months

Project Amount: \$69,558

Research Category: Treatment, Recycling, and Disposal of Solid Wastes, Hazardous Wastes, and Sediments

Abstract:

Throughout the United States and around the world, a variety of industries are moving from conventional to high flash solvents, including dibasic and other esters, glycol ethers, and terpenes (d-limonene isomers). For instance, approximately 80% of the cleaning solvents used in the screen printing industry, representing more than \$50 million per year in solvent sales, are high flash solvents. Although solvent costs range from \$15 to \$30 per gallon, recycling is limited because of the generally small average waste volumes generated in these highly segmented industries. At present, conventional waste reclamation on this scale is incapable of delivering on spec recycled solvent. In response, Media and Process Technology, Inc. (M&P) has developed an innovative low-cost, high-performance ceramic membrane technology that can recover high-quality, high flash solvents from spent material in an environmentally friendly manner. Moreover, this technology has dual use capability and can be used to recover spent rinse waters in these industries. Process feasibility has been demonstrated in recent bench treatability tests. In this Phase I effort, M&P proposes to scale up the bench tests to the pilot level to conduct various optimization and long-term performance tests.

Supplemental Keywords: small business, SBIR, recycling, pollution prevention, engineering, and chemistry

Last Updated: May 25, 1999

APPENDIX D

Department of Energy Projects Potentially Applicable to Incidental Shipboard Liquid Wastes

APPENDIX D

The Office of Science and Technology (OST) that is within the Department of Energy's Office of Environmental Management develops new technologies to remediate contaminated sites. Technologies that are being developed include those to accelerate cleanup, reduce costs, reduce risk to cleanup workers, or enable cleanup activities for which no cost effective technologies exists. OST research projects were reviewed, and those technologies that could be applied to Navy incidental shipboard liquid wastes were identified and included in this appendix.

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Department of Energy

Research Projects

REPORT RECORD

The Effect of Dissolved Solids on the Destruction of Organics by Ultraviolet Oxidation. Hyatt, N.M. Westinghouse Hanford Co., Richland, WA (United States) 6 Apr 1995, 67p. DOE Contract AC0687RL10930. Sup.Doc.Num. E 1.99:DE95010564. NTIS Order Number DE95010564. Primary Report Number: WHC-SD-C018H-TRP-015. Source: OSTI (DOE and DOE contractors only); NTIS (Public Sales); GPO Dep. (Depository Libraries)

The 200 Area Effluent Treatment Facility (ETF) was designed and built to treat and dispose of the 242-A evaporator process condensate (PC). Because of the robustness of the facility, there is the possibility of utilizing it to treat not only the PC, but also various waste waters generated during the environmental restoration of the Hanford site. These waste waters could include purge water/groundwater and fuel basin water. The groundwater at the Hanford site is contaminated with organic chemicals such as carbon tetrachloride. It also contains a high level of nitrates. The ETF is a proposed means to treat this contaminated groundwater with the organics being destroyed in the ultraviolet oxidation (UV/OX) process. Nitrates are known to absorb ultraviolet (UV) light. Because the ETF will be adding sulfuric acid as pH adjustment and treating waste water streams with ammonia and nitrate, it is prudent that the individual effects of these constituents on the organic oxidation rates be understood. Four series of tests were derived to determine the effects of dissolved solids on the destruction of organic chemicals in the UV/OX process. These were as follows: (1) volatilization test to verify that organic volatilization was not occurring; (2) UV transmittance tests to study effects of various levels of dissolved solids on the transmittance of UV light through the test solution; (3) baseline kinetic tests to establish baseline oxidation rates without the presence of dissolved solids; and (4) kinetic tests with dissolved solids present to study effects of the dissolved solids on the organic oxidation. The conclusions show that nitrate is the ion which causes the greatest decrease in oxidation rate. Sodium, sulfate, and ammonium will minimally influence the oxidation rate. These results can be used in developing a comprehensive model in the future.

Department of Energy

Research Projects

Electrochemical Treatment of Liquid Radioactive Wastes

University of South Carolina

Columbia, South Carolina

PROBLEM STATEMENT:

High-level radioactive wastes from the production of special nuclear materials at SRS and throughout the DOE complex contain hazardous species such as nitrate, nitrite, chromate, heavy metals, and long-lived radionuclides. Development of waste treatment technologies to reduce the possible release and improve the performance of permanent waste forms for these wastes are needed. Electrochemical processes are attractive candidates because of the wide range of applicability as well as reaction selectivity. Studies carried out at the SRTC have demonstrated the feasibility of destroying nitrate and nitrite and removing technetium-99 and ruthenium-106 from alkaline waste solutions at the laboratory scale with both simulant solutions and actual waste. Some work has been carried out to determine the optimum conditions for the destruction of nitrate and nitrite from alkaline solutions. However, additional work is needed to complete electrochemical cell optimization and to develop engineering models and process flow sheets so that process optimization, design, and cost estimation of pilot plant and full-scale equipment can be made.

RESEARCH OBJECTIVES:

- Demonstrate electrochemical processes at the laboratory scale for the destruction of nitrate, nitrite, and organic compounds, and the removal of hazardous metals from simulated waste streams that are produced at the SRS and throughout the DOE complex.
- Develop engineering models and conceptual flow sheets that can be used for the optimization of and the design and cost estimation of pilot plant and full-scale equipment for an electrochemical treatment process.
- Evaluate materials of construction for equipment used in the processes.
- Evaluate other unit operations associated with the electrochemical processes such as offgas treatment and recovery of chemical values.

MAJOR DELIVERABLE

- Summary technical reports upon completion of each phase of work.
- Annual report summarizing all work completed during the year if no technical reports have been submitted during the year.
- Final report.

SUCSESSES

Papers presented at Spring 1994 meeting of the Electrochemical Society. Dr. White presented a seminar entitled "Electrochemical Treatment Scale-Up" to Efficient Separations and Processing Integrated Program (ESPIP) in Dallas, TX on 11/9/94. His talk seemed to raise the level of interest in electrochemical reduction of nitrate and nitrite. One Master's thesis has resulted from this project. Interim report on flow-through porous electrodes submitted. Milestone report on the dynamic process flow sheet submitted.

PI: Dr. Ralph E. White

Department of Energy

Research Projects

Photolytic Transformations of Hazardous Organics in Multiphase Media

Project Id: P/ORNL--ERKCC07

Last Amendment Date: January 12, 1999

Research Organization: ORNL (Oak Ridge National Laboratory)

Web Site: <http://www.ornl.gov>

Sponsoring Program: Office of Energy Research

Funding Mechanism: Managing and Operations

Location: Oak Ridge, Tennessee 37831

Point of Contact: Buchanan, A C III

Contract #: AC05-84OR21400

Phone: 423-576-2168

Email: BUCHANANAC@ornl.gov

Start Date: October 01, 1994

Est. Completion Date: September 30, 2020

FY1995 Funding: \$384,577

FY1996 Funding: \$359,064

FY1997 Funding: \$366,584

Estimated Future Funding: FY1999-365000; FY2000-379000

Type of Research: Basic

B&R Codes: KC0302010

Subject Areas: CHEMICAL SCIENCES, ENERGY RESEARCH

Project Description

This research program emphasizes fundamental investigations into the influence of surface chemical composition and structure on the photochemistry of adsorbed hazardous organics. The primary goals of this research are to enhance a basic understanding of photochemical reactions occurring at industrially and environmentally important interfaces, and to delineate the role of surface interactions in controlling the observed chemistry, kinetics, and mechanisms. Polycyclic aromatic hydrocarbons (PAH) have been a focal point of these studies, many of which are EPA priority pollutants generated in the environment through fossil fuel production and consumption. The photochemistry and photophysics of a systematically varied range of PAH structures adsorbed at solid/liquid and solid/gas interfaces have been investigated. Product analysis, physical characterization of surfaces, and in situ steady state and transient spectroscopic techniques are the principal methodologies used in these investigations. Highly polar substrates, such as SiO₂, dramatically effect the photochemistry of weakly interacting organics, as typified by unsubstituted PAHs. Contributions from electron transfer and singlet molecular oxygen mediated PAH photochemical oxidation pathways, and the impact of molecular pairing on the surface, have been elucidated as a function of PAH structure. Surface adsorbed water has been shown to exert significant influence on the rates and product distributions observed for PAH photochemistry at the SiO₂/air interface. This research will lead to a better understanding of how molecular interactions influence chemical processes in heterogeneous media, and how these factors control the environmental fate and residence times of PAHs and related anthropogenic materials.

Department of Energy

Research Projects

Development of Novel Reverse-Osmosis Membrane with High Rejections for Organic Compounds

Project Id: P/OAK--FG03-92ER81422

Last Amendment Date: March 07, 1997

Research Organization: Bend Research, Inc.

Under contract to: Oakland Operations Office

Web Site: <http://www.bendres.com>

Sponsoring Program: Office of Energy Research

Funding Mechanism: GRANT

Location: Bend, Oregon 97701

Point of Contact: Marianelli, R.S.

Contract #: FG03-92ER81422

Phone: 301-903-5804

Start Date: July 29, 1992

Est. Completion Date: May 25, 1996

FY1996 Funding: \$5,156

B&R Codes: KM0000000

Subject Areas: Industry;Non-radioactive

Project Description

Chemical process industry (CPI) separations consume as much as 4.4 quads of energy annually in the United States. Many of these separations involve removing organic compounds from aqueous process streams. Conventional technologies are energy intensive or have environmental drawbacks that make their use less than optimal. Additionally, some processes also destroy the organic compounds, precluding the possibility of recovering or recycling them. Reverse-osmosis (RO) membrane processes offer the potential to significantly improve and simplify treatment of these industrial process streams, but their use has been limited by their inability to remove many industrially important organics. The goal of this program is to develop a new class of RO membranes that can reject high percentages of organic compounds while maintaining high water fluxes. These improved organic-rejecting RO membranes could be used alone or in combination with other technologies in hybrid wastewater-treatment systems that would otherwise be impractical, given the performance of current RO membranes. In Phase I researchers demonstrated the feasibility of the approach by developing membranes with a rejection of 98% for a target organic (phenol) and a water flux of 25 L/m²h. A technical and economic analysis indicates that this performance will result in wastewater-treatment systems with capital and operating costs that are only 60% of the costs for systems based on conventional technologies. Additionally, systems based on the organic-rejecting RO membranes will use only 20% of the energy required by conventional processes. The objectives of Phase II are (1) to continue the development of these organic rejecting RO membranes, focusing on developing membranes for removal of polar organics, aromatics, and chlorinated hydrocarbons; (2) to incorporate these organic rejecting membranes into solvent-resistant hollow-fiber modules; (3) to scale up modules to a size that will allow for meaningful field tests; and (4) to field-test the technology extensively. This work will pave the way for immediate commercialization of the technology with the Phase III partner.

Department of Energy

Research Projects

Development Studies for a Novel Wet-Oxidation Process

Project Id: P/METC--AC21-92MC29107

Last Amendment
Date: February 03,
1998

Research Organization: Delphi Research, Inc.

Under contract to:
METC

Sponsoring Program: Assistant Secretary for Environmental Restoration &
Waste Management , Assistant Secretary for Fossil Energy , DOE

Funding Mechanism:
CONTRACT

Location: Albuquerque, New Mexico 87102

Point of Contact:
Kothari, V.P.

Contract #: AC21-92MC29107

Phone: 304-291-4579

Start Date: September 22, 1992

Est. Completion Date:
December 31, 1996

FY1995 Funding: \$3,363,993

FY1996 Funding: \$4,781,046

Type of Research: Applied

B&R Codes: EW4035000

Subject Areas: Land;Site Studies;TECHNOLOGY DEVELOPMENT;ENVIRONMENTAL
MANAGEMENT

Project Description

The objective is to develop a catalytic wet-oxidation process for the treatment of multicomponent wastes, with the aim of providing a versatile treatment method that can destroy hazardous organics compounds while containing and concentrating metals from contaminated soils.

Department of Energy

Research Projects

Supercritical Water Oxidation Data Acquisition

Project Id: P/ID--FC07-94ID13303

Last Amendment Date:
March 07, 1997

Research Organization: Stone and Webster Engineering Corp.

Under contract to: Idaho
Operations Office

Sponsoring Program: Office of Chief Financial Officer , Assistant Secretary
for Environmental Restoration & Waste Management

Funding Mechanism:
Cooperative Agreement

Location: Boston, Massachusetts 02210

Point of Contact: Noble,
C.

Contract #: FC07-94ID13303

Phone: 208-526-1369

Start Date: September 29, 1994

Est. Completion Date:
April 26, 1996

FY1995 Funding: \$1,214,000

FY1996 Funding: \$616,069

B&R Codes: EW4000000

Project Description

The primary objective of this project is to demonstrate the effectiveness of the SWEC/MODAR SCWO process for treating a variety of wastes. These include (1) Simulated DOE mixed waste, and 2) actual waste generated by the Department of the Navy. This demonstration will focus on optimizing the following variables (1) complete destruction of the organic constituents; (2) Effective neutralization of acid forming anions; (3) Control of the solids generated during in situ neutralization or contained in the feedstock (affects both reliability of operation and concentration of radionuclide; and (4) Evaluation of materials of construction.

Department of Energy

Research Projects

Ion-Selective Ceramic Membranes for Separation of Radioactive Wastes

Project Id: P/OAK-FG03-95ER82018

Last Amendment Date: March 07, 1997

Research Organization: Materials and Systems Research, Inc.

Under contract to: Oakland Operations Office

Sponsoring Program: Office of Energy Research

Funding Mechanism: GRANT

Location: Salt Lake City, Utah 84115

Point of Contact: Carroll, M.

Contract #: FG03-95ER82018

Phone: 510-486-6479

Start Date: September 01, 1995

Est. Completion Date: March 23, 1996

FY1995 Funding: \$74,981

FY1996 Funding: \$51,401

B&R Codes: KM0000000

Project Description

The principal objective of the project is to demonstrate the use of electrochemical cells for the separation of radioactive waste and salt splitting using highly ion-selective ceramic membranes. A plan of work is proposed to fabricate sodium ion conducting ceramic membranes in the form of thin films over porous supports, as well as discs. A protective coating will be deposited on these materials to suppress or eliminate potential corrosion in acidic media. The membranes will be examined by SEM and XRD. Electrochemical cells will be designed, constructed and used to test the ceramic membranes at 700 °C. Aqueous salt solutions containing nitrates of Na, Cs, Rb, and Sr will be electrolyzed through these ceramic membranes in order to demonstrate the ion-selectivity of the membranes. The catholyte and anolyte solutions will be chemically analyzed. It is anticipated that these membranes will exhibit excellent ion selectivity.

Department of Energy

Research Projects

A Portable Supercritical Fluid Extraction System for Direct Extraction of Heavy Metals from Wastewater

Project Id: P/CH--FG02-95ER81954

Last Amendment Date: March 07, 1997

Research Organization: Durability, Inc.

Under contract to: Chicago Operations Office

Sponsoring Program: Office of Energy Research

Funding Mechanism: GRANT

Location: Blacksburg, Virginia 24060

Point of Contact: Ferrell, W.

Contract #: FG02-95ER81954

Phone: 301-903-0043

Start Date: September 01, 1995

Est. Completion Date: July 23, 1996

FY1995 Funding: \$72,833

FY1996 Funding: \$66,716

B&R Codes: KM0000000

Project Description

This project deals with development of a portable supercritical fluid extraction system which can directly extract heavy metals from wastewater. A distinct advantage of this system is that it can remove these contaminants directly from wastewater resident at government and industrial facilities. The extraction process is accomplished by introducing fluorinated chelating agent (Hexafluoro acetylacetonate), or bistrifluoroethylene dithiocarbamate) to the contaminated sample, thereby complexing the metal and allowing the formed neutral metal chelate to be extracted in situ with supercritical CO₂ or modified supercritical CO₂. This method is very cost effective, since there is no solvent to dispose, and is very efficient due to physical and chemical properties of supercritical fluids.

Department of Energy

Research Projects

Electrochemical Destruction of Nitrates

Project Id: P/SRTC-9500132005

Last Amendment Date: June 14, 1996

Research Organization: SRTC (Savannah River Technology Center) **Web Site:** <http://www.srs.gov>

Sponsoring Program: Assistant Secretary for Environmental Restoration & Waste Management

Funding Mechanism: Managing and Operations

Location: Aiken, South Carolina 29801

Point of Contact: D. T. Hobbs

Contract #: AC09-89SR18035

Phone: 803- 725-2838

FY1995 Funding: \$888,000

B&R Codes: EW4030000

Project Description

Electrochemical treatment processes were developed for the destruction of organic compounds and nitrates/nitrites and the removal of other hazardous species from liquid waste stored throughout the DOE complex. The development program consisted of five major tasks: (1) evaluation of different electrochemical reactors for the destruction and removal of hazardous waste components, (2) development and validation of engineering process models, (3) radioactive laboratory-scale tests, (4) demonstration of the technology in an engineering-scale size reactor, and (5) analysis and evaluation of testing data. The development program team was comprised of individuals from federal, academic, and private industry. Work was carried out in DOE, academic, and private industrial laboratories. Possible benefits of this technology include: (1) improved radionuclide separation as a result of the removal of organic complexants, (2) reduction in the concentrations of hazardous and radioactive species in the waste (e.g., removal of nitrate, nitrite, mercury, chromium, cadmium, technetium-99, and ruthenium-106), (3) reduction in the size of the off-gas handling equipment for the vitrification of low-level wastes by reducing the source of NO_x emissions, (4) recovery of chemicals of value (e.g., sodium hydroxide), and (5) reduction in the volume of waste requiring disposal.

Department of Energy

Research Projects

Reductive Obilization Oxide - Bound Metals

Project Id: P/CH-FG02-90ER60946

Last Amendment Date: March 23, 1998

Research Organization: JOHNS HOPKINS
UNIVERSITY

Under contract to: Chicago Operations Office

Sponsoring Program: Office of Energy Research

Funding Mechanism: GRANT

Location: Baltimore, Maryland 21218-0000

Point of Contact: WOBBER FRANK J

Contract #: FG02-90ER60946

Phone: 301-353-5549

Start Date: March 13, 1990

Est. Completion Date: June 30, 1997

FY1996 Funding: \$132,076

FY1997 Funding: \$132,076

FY1997 Funding: \$132,075

Type of Research: Basic

B&R Codes: KP0000000

Subject Areas: Land;Chemical;BIOLOGICAL AND ENVIRONMENTAL RESEARCH;ENERGY
RESEARCH

Project Description

This project is concerned with the mobilization of MnO_2 - and $FeOOH$ -bound toxic metals in subsurface arising from an influx of natural organic matter or organics-containing wastes. Work is reported that examines how reductant, complexant, and adsorptive characteristics of constituent organic chemicals affect the oxidation state and solid-solution partitioning of cobalt, nickel, copper, and lead.

Department of Energy

Research Projects

Jointly Sponsored Research Projects

Project Id: P/FETC-MGN-DE-FC21-93MC30127

Last Amendment Date: November 09, 1997

Research Organization: FETC-MGN (Morgantown Energy Technology Center)

Web Site: <http://www.metc.doe.gov>

Sponsoring Program: Assistant Secretary for Fossil Energy

Funding Mechanism: Cooperative Agreement

Location: Laramie, Wyoming 82071

Point of Contact: Das, Kamalendu

Contract #: NONE

Phone: (304)285-4065

Email: KDAS@FETC.DOE.GOV

Est. Completion Date: March 26, 1998

Start Date: March 26, 1993

FY1996 Funding: \$1,587,219

FY1997 Funding: \$2,050,754

FY1997 Funding: \$2,050,754

Type of Research: Applied

B&R Codes: AV0100000

Subject Areas: COOPERATIVE R&D; FOSSIL ENERGY

Project Description

In order to realize the proposed goals, WRI has been focusing research, development, demonstration, and commercialization activities in three major areas: 1. Energy Programs emphasize increased production and utilization of domestic energy resources and include enhanced oil recovery, coal beneficiation and upgrading, coalbed methane recovery, and renewable energy resources. 2. Environmental Programs minimize the impact of energy production and utilization by providing technology to clean underground oily wastes, mitigate acid mine drainage, and demonstrate uses of solid wastes from clean coal technologies and fluidized bed combustion systems. 3. Technology Enhancement encompasses resource characterization studies, development of improved environmental monitors and sensors, and improved models and techniques to predict dispersion of hazardous gas release.

Department of Energy

Research Projects

Adsorption/Membrane Filtration as a Contaminant Concentration and Separation Process for Mixed Wastes and Tank Wastes

Project Id: P/ID-FG07-96ER62313

Last Amendment Date:
December 17, 1998

Research Organization: WASHINGTON UNIVERSITY OF

Under contract to: Idaho
Operations Office

Sponsoring Program: Assistant Secretary for Environmental
Restoration & Waste Management

Funding Mechanism: GRANT

Location: Seattle, Washington 98195-0000

Point of Contact:
HIRSCH,ROLAND

Contract #: FG07-96ER62313

Phone: 301-903-3213

Start Date: September 06, 1996

Est. Completion Date:
September 14, 1999

FY1997 Funding: \$220,272

B&R Codes: EW4510000

Department of Energy

Research Projects

Application of Biosorb, a Novel Technology for the Treatment of Produced Water from Oil E&P Operations

Project Id: P/NPTO-G4P60823

Last Amendment Date: November 05, 1997

Research Organization: NPTO (National Petroleum Technology Office)

Web Site: <http://www.bpo.gov>

Sponsoring Program: Assistant Secretary for Fossil Energy

Funding Mechanism: Subcontract

Location: Chantilly, Virginia 22021

Point of Contact: Lindsey, Rhonda P.

Contract #: NONE

Phone: 9183374407

Start Date: August 15, 1996

Email: rlindsey@bpo.gov

Est. Completion Date: February 14, 1997

Estimated Future Funding: 0

B&R Codes: AC1015000

Subject Areas: EXPLORATION AND PRODUCTION ENVIRONMENTAL RESEARCH; FOSSIL ENERGY

Project Description

Provide a one step cost-effective, technically efficient, remediation system for the mitigation of organics, sulphur species, metals at lower concentrations and remove radionuclides (where applicable) from the produced waters including wastewaters from oil and gas production sites; render the produced water useful or fit for disposal under the zero discharge regulatory constraints.

Department of Energy

Research Projects

Electrochemical Treatment of Liquid Wastes

Project Id: P/SRTC-9706114018

Last Amendment Date: March 18, 1998

Research Organization: SRTC (Savannah River Technology Center) **Web Site:** <http://www.srs.gov>

Sponsoring Program: Assistant Secretary for Environmental Restoration & Waste Management

Funding Mechanism: Managing and Operations

Location: Aiken, South Carolina 29808-001

Point of Contact: Hobbs, David

Contract #: AC09-96SR18500

Phone: (803) 725-2838

Email:
DAVID.HOBBS@SRS.GOV

Start Date: October 01, 1996

Est. Completion Date:
September 30, 1997

FY1997 Funding: \$387,000

FY1997 Funding: \$387,000

Type of Research: Development

B&R Codes: EW4030000

Subject Areas: TECHNOLOGY DEVELOPMENT; ENVIRONMENTAL MANAGEMENT

Project Description

This task is at the engineering development stage. Electrochemical processes have been demonstrated for the destruction of nitrates, nitrite and organic compounds in SRS and Hanford high-level waste. Activities this year will focus on providing support for EM-30, and the Tanks Focus Area to design a nitrate destruction system and complete transfer of nitrate/nitrite destruction technology to EM-30 at SRS. Resolve remaining process control activities and work with TFA and EM-30 to identify and resolve any problems associated with evolution of ammonia or hydrogen. Work done at LANL and LLNL on nitrate construction will be accessed and reviewed to be sure technology is fully understood in the context of prior work. Determine the feasibility of removing Tc from Hanford waste. The University of S. Carolina will complete design of a porous electrode system for use in reducing dilute species such as chromate and pertechnetate at SRS. Determine the feasibility of using electrochemical technology to separate RCRA metals and actinides from dilute wastes.

Department of Energy

Research Projects

Waste Separations Using Selective Sorbents

Project Id: P/ANL--001941

Research Organization: ANL (Argonne National Laboratory)

Sponsoring Program: Assistant Secretary for Environmental Restoration & Waste Management

Location: Lemont, Illinois 60439

Contract #: W-31109-ENG-38

Last Amendment Date:
November 21, 1997

Web Site: <http://www.anl.gov>

Funding Mechanism: Managing and Operations

Point of Contact: Helt, J.E.

Phone: 630-252-7335

Start Date: October 01, 1996

Est. Completion Date: October 18, 1997

FY1997 Funding: \$17,000

FY1997 Funding: \$17,000

Type of Research: Development

B&R Codes: EX3110010

Subject Areas: WASTE MANAGEMENT (NON-DEFENSE); ENVIRONMENTAL MANAGEMENT

Project Description

This project combines Argonne's expertise in radionuclide and chemical separations with an industrial participant's expertise in membrane-based separations. A membrane extraction technology has been developed to effectively separate certain organic compounds, radionuclides, and other components from waste streams. The membranes can be embedded with sorbent materials having an affinity for selected waste components. Previously the use of selective sorbent materials has been demonstrated to remove radiostrontium and technetium from environmental waste samples. In the present project, the parties are exploring the development of new sorbents, membranes, procedures, and systems to efficiently separate components in waste streams. The new technology will be applicable primarily in low-volume waste streams, like those generated in DOE research laboratories. The improved procedure should significantly reduce waste processing and disposal costs by reducing the volume of the most hazardous waste components and separating them. The work focuses on wastes typically generated at Argonne's facilities. The procedures developed should also be applicable at other DOE, government, and private laboratories.

Department of Energy

Research Projects

Photocatalytic & Chemical Oxidation

Project Id: P/NREL--DO6E

Last Amendment Date:
December 07, 1998

Research Organization: NREL (National Renewable Energy Laboratory)

Web Site: <http://www.nrel.gov>

Sponsoring Program: Assistant Secretary for Environmental Restoration & Waste Management

Funding Mechanism: Managing and Operations

Location: Golden, Colorado 80401-3393

Point of Contact: Blake, Daniel M.

Contract #: AC02-83CH10093

Phone: 303-275-3702

FY1997 Funding: \$118,310

B&R Codes: EW4510000

Subject Areas: ENVIRONMENTAL MANAGEMENT SCIENCE PROGRAM

Project Description

Supercritical carbon dioxide extraction and cleaning is being developed for a number of applications that affect environmental-cleanup and waste minimization goals. Work done on this project includes exploring the chemistry required to provide a unit operation for maintaining purity of (i.e., polishing) liquid or supercritical carbon dioxide in process systems that recirculate the fluid phase for reasons of environmental compliance and waste minimization. The results of this work will also provide new information that addresses questions that are key to the fundamental understanding of photocatalytic chemistry and the chemistry of carbon dioxide fixation. This work builds on a broad base of knowledge that exists for photocatalytic chemistry, use of supercritical carbon dioxide, and design of photoreactors for operation at elevated pressure.

Department of Energy

Research Projects

Transformation of Heavy Metal Contaminants in Sulfate-Reducing Sub-Surface Environments: The Role of Thiolated Compounds and Hydrogen Sulfide

Project Id: P/BNL--AS-458-ESTD

Last Amendment Date: December 03, 1998

Research Organization: BNL (Brookhaven National Laboratory)

Web Site: <http://www.bnl.gov>

Sponsoring Program: Office of Energy Research

Funding Mechanism: Managing and Operations

Location: Upton, New York 11973-5000

Point of Contact: Premuzic, Eugene T.

Contract #: AC02-76CH00016

Phone: 516-344-2893

Type of Research: Basic

B&R Codes: KP1301010

Subject Areas: BIOLOGICAL AND ENVIRONMENTAL RESEARCH; ENERGY RESEARCH

Project Description

Microbial transformations play an important role in controlling the speciation and mobility of several metallic and metalloid elements in the biosphere, and have applications for bioremediation. Recently, there has been an increasing interest in bacterial sulfate reduction from this viewpoint because it provides a biological basis for precipitating many heavy metals as sulfides. Because sulfate concentration is high in seawater, bacterial sulfate reduction is a dominant process in organic-rich marine sediments. Recent work revealed high levels of organic sulfhydryl compounds or thiols in sulfate-reducing sediments. They occur in a wide range of molecular weights and hydrophilicity. While low-molecular-weight thiols form soluble complexes of the metals, high-molecular-weight ones, such as humic thiols, can bind the metals to the sedimentary particulate phase. Thiols form their strongest bonds with large, easily polarizable heavy-metal ions such as Cd(II), Hg(II), and Pb(II), and, thus, should play an important role in transforming these metals in anaerobic environments. Our research proposed here will focus on the first two of these highly toxic elements, Cd(II) and Hg(II), and be aimed at a fuller understanding of their transformations in organic-rich sulfate-reducing environments. An important issue is the role of thiol complexation in relation to sulfide precipitation for sequestering metal ions in anaerobic systems. The kind of sedimentary thiols involved in metal complexation and the type of metal-thiol complexes formed will be studied. We will investigate whether anaerobic bacteria biosynthesize thiolated proteins (such as metallothioneins) or similar proteins in response to metals in the environment. A suite of complementary techniques, including x-ray absorption spectroscopy, Nuclear Magnetic Resonance (NMR) spectroscopy, and liquid chromatography-mass spectrometry, will be used to characterize sulfur and metal speciation in the anaerobic systems. We expect that this research will yield new insights about transformations of heavy metal species in sulfate-reducing systems. Such a knowledge is critical for developing effective bioremediation approaches for removing heavy-metal contaminants in the environment using the power of anaerobic microbes.

Department of Energy

Research Projects

Ozone Treatment of Soluble Organics in Produced Water

Project Id: P/ORNL--FEAC307

Last Amendment Date: January 12, 1999

Research Organization: ORNL (Oak Ridge National Laboratory)

Web Site: <http://www.ornl.gov>

Sponsoring Program: Assistant Secretary for Fossil Energy

Funding Mechanism: Managing and Operations

Location: Oak Ridge, Tennessee 37831

Point of Contact: Judkins, Roddie Reag

Contract #: AC05-84OR21400

Phone: 423-574-4572

Email: JUDKINSRR@ornl.gov

Start Date: May 01, 1998

Estimated Future Funding: FY1999-400000;FY2000-289000

B&R Codes: AC1015000

Subject Areas: EXPLORATION AND PRODUCTION ENVIRONMENTAL RESEARCH;FOSSIL ENERGY

Project Description

This project will extend the previous PERF research to improve the applicability of ozonation for treating produced water. It will be one task of a new PERF initiative to address the industry-wide problem of handling soluble organics. The goal of this project will be to maximize oxidation of water-soluble organics during a single-pass operation. Secondary goals include reduction of effluent toxicity, color, odor, TOC and COD. The project will investigate: (1) ozone and hydrogen peroxide production by electrochemical methods, (2) increasing the mass transfer rate in the reactor by forming micro bubbles during ozone injection into the produced water, and (3) using ultraviolet irradiation to enhance the reaction if needed.

Department of Energy

Research Projects

REPORT RECORD

Air-Nitric Acid Destructive Oxidation of Organic Wastes. Smith, J.R., Westinghouse Savannah River Co., Aiken, SC (United States) [1993], 8p, DOE Contract AC0989SR18035. Sup.Doc.Num. E 1.99:DE93041121, NTIS Order Number DE93041121, Primary Report Number: WSRC-MS-93-169. Source: OSTI (DOE and DOE contractors only); NTIS (Public Sales), GPO Dep. (Depository Libraries).

Many organic materials have been completely oxidized to CO_2 , CO , and inorganic acids in a 0.1M HNO_3 /14.8M H_3PO_4 solution with air sparging. Addition of 0.001M Pd_{42} reduces the CO to near 1% of the released carbon gases. To accomplish complete oxidation the solution temperature must be maintained above 130–150°C. Organic materials quantitatively destroyed include neoprene, cellulose, EDTA, TBP, tartaric acid, and nitromethane. The oxidation is usually complete in a few hours for soluble organic materials. The oxidation rate for non-aliphatic organic solids is moderately fast and surface area dependent. The rate for aliphatic organic compounds (polyethylene, PVC, and n-dodecane) is relatively very slow. This is due to the large energy required to abstract a hydrogen atom from these compounds, 99 kcal/mole. The combination of $\text{NO}_2\cdot$ and $\text{H}\cdot$ to produce HNO_2 releases only 88 kcal/mole. Under conditions of high $\text{NO}_2\cdot$ concentration it should be possible to oxidize these aliphatic compounds.

Department of Energy

Research Projects

REPORT RECORD

Alternative Oxidation Technologies for Organic Mixed Waste . Borduin, L.C. [Los Alamos National Lab., NM (United States)]; Fewell, T. [Lockheed Martin Idaho Technologies Inc., Idaho Falls, ID (United States)]. [1998]. 8p . DOE Contract AC0794ID13223. Sup.Doc.Num. E 1.99:DE98056067. NTIS Order Number DE98056067 . Source: OSTI (DOE and DOE contractors only); NTIS (Public Sales); GPO Dep. (Depository Libraries)

The Mixed Waste Focus Area (MWFA) is currently supporting the development and demonstration of several alternative oxidation technology (AOT) processes for treatment of combustible mixed low-level wastes. AOTs have been defined as technologies that destroy organic material without using open-flame reactions. AOTs include both thermal and nonthermal processes that oxidize organic wastes but operate under significantly different physical and chemical conditions than incinerators. Nonthermal processes currently being studied include Delphi DETOX and acid digestion at the Savannah River Site (SRS), and direct chemical oxidation at Lawrence Livermore National Laboratory (LLNL). All three technologies are at advanced stages of development or are entering the demonstration phase. Nonflame thermal processes include catalytic chemical oxidation, which is being developed and deployed at Lawrence Berkeley National Laboratory (LBNL), and steam reforming, a commercial process being supported by the Department of Energy (DOE). Although testing is complete on some AOT technologies, most require additional support to complete some or all of the identified development objectives. Brief descriptions, status, and planned paths forward for each of the technologies are presented.

Department of Energy

Research Projects

REPORT RECORD

Alkaline Detergent Recycling Via Ultrafiltration . Steffani, C.; Meltzer, M. . Lawrence Livermore National Lab., CA (United States) . Jun 1995 . 3p . DOE Contract W7405ENG48 . Sup.Doc.Num. E 1.99:DE95017282 . NTIS Order Number DE95017282 . Primary Report Number: UCRL-ID--121138 . Source: OSTI (DOE and DOE contractors only); NTIS (Public Sales); GPO Dep. (Depository Libraries)

The metal finishing industry uses alkaline cleaners and detergents to remove oils and dirt from manufactured parts, often before they are painted or plated. The use of these cleaners has grown because environmental regulations are phasing out ozone depleting substances and placing restrictions on the use and disposal of many hazardous solvents. Lawrence Livermore National Laboratory is examining ultrafiltration as a cleaning approach that reclaims the cleaning solutions and minimizes wastes. The ultrafiltration membrane is made from sheets of polymerized organic film. The sheets are rolled onto a supporting frame and installed in a tube. Spent cleaning solution is pumped into a filter chamber and filtered through the membrane that captures oils and dirt and allows water and detergent to pass. The membrane is monitored and when pressure builds from oil and dirt, an automatic system cleans the surface to maintain solution flow and filtration quality. The results show that the ultrafiltration does not disturb the detergent concentration or alkalinity but removed almost all the oils and dirt leaving the solution in condition to be reused.

Department of Energy

Research Projects

REPORT RECORD

Engineering Design and Test Plan for Demonstrating DETOX Treatment of Mixed Wastes.

Goldblatt, S.; Dhooge, P. . Delphi Research, Inc., Albuquerque, NM (United States) . [1995] . 13p . DOE Contract AC2192MC29107 . Sup.Doc.Num. E 1.99:DE95007496. NTIS Order Number DE95007496 . Primary Report Number: DOE/MC/29107-95/C0412 . Source: OSTI (DOE and DOE contractors only); NTIS (Public Sales); GPO Dep. (Depository Libraries)

DETOX is a cocatalyzed wet oxidation process in which the catalysts are a relatively great concentration of iron ions [typically as iron(III) chloride] in the presence of small amounts of platinum and ruthenium ions. Organic compounds are oxidized completely to carbon dioxide, water, and (if chlorinated) hydrogen chloride. The process has shown promise as a non-thermal alternative to incineration for treatment and/or volume reduction of hazardous, radioactive, and mixed wastes. Design and fabrication of a demonstration unit capable of destroying 25 Kg/hr of organic material is now in progress. This paper describes the Title 2 design of the demonstration unit, and the planned demonstration effort at Savannah River Site (SRS) and Weldon Spring Site Remedial Action Project (WSSRAP).

Department of Energy

Research Projects

Electrochemical Treatment of Liquid Radioactive Wastes

University of South Carolina

Columbia, South Carolina

PROBLEM STATEMENT:

High-level radioactive wastes from the production of special nuclear materials at SRS and throughout the DOE complex contain hazardous species such as nitrate, nitrite, chromate, heavy metals, and long-lived radionuclides. Development of waste treatment technologies to reduce the possible release and improve the performance of permanent wasteforms for these wastes are needed. Electrochemical processes are attractive candidates because of the wide range of applicability as well as reaction selectivity. Studies carried out at the SRTC have demonstrated the feasibility of destroying nitrate and nitrite and removing technetium-99 and ruthenium-106 from alkaline waste solutions at the laboratory scale with both simulant solutions and actual waste. Some work has been carried out to determine the optimum conditions for the destruction of nitrate and nitrite from alkaline solutions. However, additional work is needed to complete electrochemical cell optimization and to develop engineering models and process flowsheets so that process optimization, design and cost estimation of pilot plant and full-scale equipment can be made.

RESEARCH OBJECTIVES:

- Demonstrate electrochemical processes at the laboratory scale for the destruction of nitrate, nitrite, and organic compounds, and the removal of hazardous metals from simulated waste streams that are produced at the SRS and throughout the DOE complex.
- Develop engineering models and conceptual flowsheets which can be used for the optimization of and the design and cost estimation of pilot plant and full-scale equipment for an electrochemical treatment process.
- Evaluate materials of construction for equipment used in the processes.
- Evaluate other unit operations associated with the electrochemical processes such as offgas treatment and recovery of chemical values.

MAJOR DELIVERABLE

1. Summary technical reports upon completion of each phase of work.
2. Annual report summarizing all work completed during the year if no technical reports have been submitted during the year.
3. Final report.

SUCSESSES

Papers presented at Spring 1994 meeting of the Electrochemical Society. Dr. White presented a seminar entitled "Electrochemical Treatment Scale-Up" to Efficient Separations and Processing Integrated Program (ESPIP) in Dallas, TX on 11/9/94. His talk seemed to raise the level of interest in electrochemical reduction of nitrate and nitrite. One Master's thesis has resulted from this project. Interim report on flow-through porous electrodes submitted. Milestone report on the dynamic process flowsheet submitted.

PI: Dr. Ralph E. White

Department of Energy

Research Projects

REPORT RECORD

Electrodialysis-Ion Exchange for the Separation of Dissolved Salts . Baroch, C.J.; Grant, P.J. . Wastren, Inc., Idaho Falls, ID (United States) . 1995 . 11p . DOE Contract AR2195MC32112 . Sup.Doc.Num. E 1.99:DE96003688. NTIS Order Number DE96003688 . Primary Report Number: DOE/MC/32112--96/CO632 . Source: OSTI (DOE and DOE contractors only); NTIS (Public Sales); GPO Dep. (Depository Libraries)

The Department of Energy generates and stores a significant quantity of low level, high level, and mixed wastes. As some of the DOE facilities are decontaminated and decommissioned, additional and possibly different forms of wastes will be generated. A significant portion of these wastes are aqueous streams containing acids, bases, and salts, or are wet solids containing inorganic salts. Some of these wastes are quite dilute solutions, whereas others contain large quantities of nitrates either in the form of dissolved salts or acids. Many of the wastes are also contaminated with heavy metals, radioactive products, or organics. Some of these wastes are in storage because a satisfactory treatment and disposal processes have not been developed. This report describes the process of electrodialysis-ion exchange (EDIX) for treating aqueous wastes streams consisting of nitrates, sodium, organics, heavy metals, and radioactive specie.

Department of Energy

Research Projects

REPORT RECORD

Evaporative Oxidation Treatability Test Report . Rust Geotech, Inc., Grand Junction, CO (United States) . Apr 1995 . 190p . DOE Contract AC0486ID12584 . Sup.Doc.Num. E 1.99:DE96003278. NTIS Order Number DE96003278 . Primary Report Number: DOE/ID/12584-214 . Source: OSTI (DOE and DOE contractors only); NTIS (Public Sales); GPO Dep. (Depository Libraries)

In 1992, Congress passed the Federal Facilities Compliance Act that requires the U.S. Department of Energy (DOE) to treat and dispose of its mixed waste in accordance with the Resource Conservation and Recovery Act (RCRA) land disposal restrictions (LDRs). In response to the need for mixed-waste treatment capacity where available off-site commercial treatment facilities do not exist or cannot be used, the DOE Albuquerque Operations Office (DOE-AL) organized a Treatment Selection Team to match mixed wastes with treatment options and develop a strategy for treatment of its mixed wastes. DOE-AL manages operations at nine sites with mixed-waste inventories. The Treatment Selection Team determined a need to develop mobile treatment capacity to treat wastes at the sites where the wastes are generated. Treatment processes used for mixed waste not only must address the hazardous component (i.e., meet LDRs) but also must contain the radioactive component in a form that allows final disposal while protecting workers, the public, and the environment. On the basis of recommendations of the Treatment Selection Team, DOE-AL assigned projects to the sites to bring mixed-waste treatment capacity on-line. The three technologies assigned to the DOE Grand Junction Projects Office (GJPO) are evaporative oxidation, thermal desorption, and treated wastewater evaporation. Rust Geotech, the DOE-GJPO prime contractor, was assigned to design and fabricate mobile treatment units (MTUs) for these three technologies and to deliver the MTUs to selected DOE-AL sites. To conduct treatability tests at the GJPO, Rust leased a pilot-scale evaporative oxidation unit from the Clemson Technical Center (CTC), Anderson, South Carolina. The purpose of this report is to document the findings and results of tests performed using this equipment.

Department of Energy

Research Projects

REPORT RECORD

Photo-Oxidation of Organic Compounds in Liquid Low-Level Mixed Wastes at the INEL . Gering, K.L.; Schwendiman, G.L. . Idaho National Engineering Lab., Idaho Falls, ID (United States) . [1996] . 10p . DOE Contract NODATA . Sup.Doc.Num. E 1.99:DE96014102. NTIS Order Number DE96014102 Source: OSTI (DOE and DOE contractors only); NTIS (Public Sales); GPO Dep. (Depository Libraries)

A bench-scale oxidation apparatus is implemented to study the effectiveness of using an artificial ultraviolet source, a 175-watt medium pressure mercury vapor lamp, to enhance the destruction of organic contaminants in water with chemical oxidants. The waste streams used in this study are samples or surrogates of mixed wastes at the Idaho National Engineering Laboratory. The contaminants that are investigated include methylene chloride, 1,1,1-trichloroethane, 1, 1-dichloroethane, acetone, 2-propanol, and ethylenediamine tetraacetic acid. We focus on H_2O_2 -based oxidizers for our treatment scheme, which include the UV/ H_2O_2 system, the dark Fenton system (H_2O_2/Fe^{2+}), and the photo-assisted Fenton system (UV/ H_2O_2/Fe^{3+}) is used in particular. Variables include concentration of the chemical oxidizer, concentration of the organic contaminant, and the elapsed reaction time. Results indicate that the photo-assisted Fenton system provides the best overall performance of the oxidizing systems listed above, where decreases in concentrations of methylene chloride, 1,1,1-trichloroethane, 1,1-dichloroethane, 2-propanol, and ethylenediamine tetraacetic acid were seen. However, UV-oxidation treatment provided no measurable benefit for a mixed waste containing acetone in the presence of 2-propanol.

Department of Energy

Research Projects

REPORT RECORD

Development of a Membrane-Based Process for the Treatment of Oily Waste Waters; Final Report, March 4, 1992--March 5, 1994 . McCray, S.B. . Bend Research, Inc., OR (United States) . 25 May 1994 . 34p . DOE Contract AC2292MT92005 . Sup.Doc.Num. E 1.99:DE94018795. NTIS Order Number DE94018795 . Primary Report Number: DOE/MT/92005--9 . Source: OSTI (DOE and DOE contractors only); NTIS (Public Sales); GPO Dep. (Depository Libraries)

This is a final report from Bend Research, Inc., (BRI) to the U.S. Department of Energy (DOE) for work performed under Contract No. DE-AC22- 92MT92005, titled "Development of a Membrane-Based Process for the Treatment of Oily Waste Waters." This report covers the period from March 4, 1992, to March 5, 1994. The overall goal of this program was to develop an economical oily-water treatment system based on reverse osmosis (RO). The RO system would be used to (1) reduce oil production costs by reducing the volume of waste water that must be disposed of, (2) form the basis of a generic waste-water treatment system that can easily be integrated into oil-field operations, especially at production facilities that are small or in remote locations; and (3) produce water clean enough to meet existing and anticipated environmental regulations. The specific focus of this program was the development of a hollow-fiber membrane module capable of treating oily waste waters.

Department of Energy

Research Projects

REPORT RECORD

Research and Development to Overcome Fouling of Membranes. Final Report . Narang, S.C.; Sharma, S.K.; Hum, G.; Ventura, S.C.; Roberts, D.L.; Gottschlich, D.; Ahner, N. . [1998] . 57p . DOE Contract FC3689ID12906 . Sup.Doc.Num. E 1.99:DE99000085. NTIS Order Number DE99000085 . Source: OSTI (DOE and DOE contractors only); NTIS (Public Sales); GPO Dep. (Depository Libraries)

To overcome fouling of membranes, SRI International is developing a unique piezoelectric backing for ultrafiltration membranes. This backing is capable of producing local turbulence next to the membrane to minimize concentration polarization and the rate of buildup of solutes and particulate matter on the membrane surface. We have studied piezoelectrically assisted ultrafiltration in more detail, with the objective to apply this process to industrial ultrafiltrations. We conducted several ultrafiltration experiments on flat sheet membranes with model dextran solutions and with electrocoat paint to study flux enhancement as a function of parameters such as feed flow rate, feed pressure, as well as the piezodriver-membrane system.

Department of Energy

Research Projects

REPORT RECORD

Water-Soluble Metal-Binding Polymers with Ultrafiltration: A Technology for the Removal, Concentration, and Recovery of Metal Ions from Aqueous Streams . Smith, B.F.; Robison, T.W.; Jarvinen, G.D. . [1997] . 33p . DOE Contract W7405ENG36 . Sup.Doc.Num. E 1.99:DE98003723. NTIS Order Number DE98003723 . Source: OSTI (DOE and DOE contractors only); NTIS (Public Sales); GPO Dep. (Depository Libraries)

The use of water-soluble metal-binding polymers coupled with ultrafiltration (UF) is a technology under development to selectively concentrate and recover valuable or regulated metal-ions from dilute process or waste waters. The polymers have a sufficiently large molecular size that they can be separated and concentrated using commercially available UF technology. The polymers can then be reused by changing the solution conditions to release the metal-ions, which are recovered in a concentrated form for recycle or disposal. Pilot-scale demonstrations have been completed for a variety of waste streams containing low concentrations of metal ions including electroplating wastes (zinc and nickel) and nuclear waste streams (plutonium and americium). Many other potential commercial applications exist including remediation of contaminated solids. An overview of both the pilot-scale demonstrated applications and small scale testing of this technology are presented.

Department of Energy

Research Projects

REPORT RECORD

Electrochemical Oxidation as an Alternative to Incineration for Mixed Wastes . Chiba, Z.; Schumacher, B.; Lewis, P.; Murguia, L. . Lawrence Livermore National Lab., CA (United States) . Feb 1995 . 10p . DOE Contract W7405ENG48 . Sup.Doc.Num. E 1.99:DE95008369. NTIS Order Number DE95008369 . Primary Report Number: UCRL-JC--119133 . Source: OSTI (DOE and DOE contractors only); NTIS (Public Sales); GPO Dep. (Depository Libraries)

Mediated Electrochemical Oxidation (MEO) is an aqueous process which oxidizes organics electrochemically at low temperatures and ambient pressures. The process can be used to treat mixed wastes containing hazardous organics by destroying the organic components of the wastes. The radioactive components of the wastes are dissolved in the electrolyte where they can be recovered if desired, or immobilized for disposal. The process of destroying organics is accomplished via a mediator, which is in the form of metallic ions in solution. At Lawrence Livermore National Laboratory (LLNL) we have worked with several mediators, including silver, cobalt and cerium. We have tested mediators in nitric as well as sulfuric acids. We have recently completed extensive experimental studies on cobalt-sulfuric acid and silver-nitric acid systems for destroying the major organic components of Rocky Flats Plant combustible mixed wastes. Organics tested were: Trimsol (a cutting oil), cellulose (including paper and cloth), rubber (latex), plastics (Tyvek, polyethylene and polyvinyl chloride) and biomass (bacteria). The process was capable of destroying almost all of the organics tested, attaining high destruction efficiencies at reasonable coulombic efficiencies. The only exception was polyvinyl chloride, which was destroyed very slowly resulting in poor coulombic efficiencies. Besides the process development work mentioned above, we are working on the design of a pilot-plant scale integrated system to be installed in the Mixed Waste Management Facility (MWMF) at LLNL. The system will also be completely integrated with upstream and downstream processes (for example, feed preparation, off-gas and water treatment, and final forms encapsulation). The conceptual design for the NEO-MWMF system has been completed and preliminary design work has been initiated. Demonstration of the process with low-level mixed wastes is expected to commence in 1998

Department of Energy

Research Projects

REPORT RECORD

Development of a Membrane-Based Process for the Treatment of Oily Waste Waters. Annual Report, March 4, 1993--March 5, 1995 . McCray, S.B. . Bend Research, Inc., OR (United States) . 30 Aug 1995 . 34p . DOE Contract AC2292MT92005 . Sup.Doc.Num. E 1.99:DE96004425. NTIS Order Number DE96004425 . Primary Report Number: DOE/MT/92005--T5 . Source: OSTI (DOE and DOE contractors only); NTIS (Public Sales); GPO Dep. (Depository Libraries)

The goal of this program was to develop an economical oily-water treatment system based on reverse-osmosis (RO) membrane technology. The RO system would be used to: (1) reduce oil-production costs by reducing the volume of waste water for which disposal is required; (2) form the basis of a generic waste-water treatment system that can easily be integrated into oil-field operations, especially at production facilities that are small or in remote locations; and (3) produce water clean enough to meet current and anticipated environmental regulations. The specific focus of this program was to develop a hollow-fiber membrane module capable of treating oily waste waters. Typically, the organics in oily waste water swell or dissolve the materials used in conventional polymeric membranes and modules. Our goal was to develop hollow-fiber membranes and modules that were more solvent-resistant than conventional membrane modules. We successfully achieved this goal. During the course of this program, we developed thin-film-composite (TFC) membranes, which consisted of a solvent-resistant selective coating placed on a solvent-resistant hollow-fiber support. These TFC membranes were used in low-cost, hollow-fiber modules, which were made using solvent-resistant components. The modules were tube-side-feed modules, in which the oily waste water travels down the inside (lumen) of the hollow fiber. The selective coating allows water to pass freely through the wall of the fiber, but restricts the transport of oil and grease and some of the dissolved organics and salts in the feed. Using these modules, more than 90% of the oily waste water can be recovered as clean permeate (suitable for discharge), while the remaining 10% is removed as oily-water concentrate (which can be recycled for recovery of the oil or disposed of in an environmentally acceptable manner).

Department of Energy

Research Projects

REPORT RECORD

Performance of In Situ Chemical Oxidation Field Demonstrations at DOE Sites. Cline, S.R.; West, O.R.; Siegrist, R.L.; Holden, W.L. Oak Ridge National Lab., TN (United States). 1997. 10p. Sponsored by USDOE Office of Environmental Restoration and Waste Management, Washington, DC (United States). DOE Contract AC05-96OR22464. From In situ remediation of the geoenvironment conference; Minneapolis, MN (United States); 5-7 Oct 1997. Order Number DE97004725. Source: OSTI; NTIS; INIS; GPO Dep.

Researchers at the Oak Ridge National Laboratory (ORNL) have been investigating the use of in situ chemical oxidation to remediate organic contaminants (VOCs, SVOCs, and PCBs) in soils and groundwater at the laboratory and field scales. Field scale design parameters (e.g., oxidant loading rates and oxidant delivery techniques) are often dictated by site conditions (e.g., soil properties and initial contaminant concentrations). Chemical destruction of organic compounds can be accomplished using a variety of oxidants. Recent research has involved field scale in situ chemical oxidation demonstrations using H_2O_2 and KMnO_4 in conjunction with soil mixing as the oxidant delivery mechanism. A description of some of these fields' activities and future field-scale work is presented here.

Department of Energy

Research Projects

REPORT RECORD

Hydrothermal Oxidation of Navy Shipboard Excess Hazardous Materials. LaJeunesse, C.A.; Haroldsen, B.L.; Rice, S.F.; Brown, B.G. . Sandia National Labs., Albuquerque, NM (United States) . Mar 1997 . 49p . DOE Contract AC0494AL85000 . Sup.Doc.Num. E 1.99:DE97052275. NTIS Order Number DE97052275 . Source: OSTI (DOE and DOE contractors only); NTIS (Public Sales); GPO Dep. (Depository Libraries)

This study demonstrated effective destruction, using a novel supercritical water oxidation reactor, of oil, jet fuel, and hydraulic fluid, common excess hazardous materials found on-board Navy vessels. This reactor uses an advanced injector design to mix the hazardous compounds with water, oxidizer, and a supplementary fuel and it uses a transpiring wall to protect the surface of the reactor from corrosion and salt deposition. Our program was divided into four parts. First, basic chemical kinetic data were generated in a simple, tubular-configured reactor for short reaction times (<1 second) and long reaction times (5 seconds) as a function of temperature. Second, using the data, an engineering model was developed for the more complicated industrial reactor mentioned above. Third, the three hazardous materials were destroyed in a quarter-scale version of the industrial reactor. Finally, the test data were compared with the model. The model and the experimental results for the quarter-scale reactor are described and compared in this report. A companion report discusses the first part of the program to generate basic chemical kinetic data. The injector and reactor worked as expected. The oxidation reaction with the supplementary fuel was initiated between 400 °C and 450 °C. The released energy raised the reactor temperature to greater than 600 °C. At that temperature, the hazardous materials were efficiently destroyed in less than five seconds. The model shows good agreement with the test data and has proven to be a useful tool in designing the system and understanding the test results.

Department of Energy

Research Projects

REPORT RECORD

Packed-Bed Reactor/Silent-Discharge Plasma Design Data Report . Rust Geotech, Inc., Grand Junction, CO (United States) . May 1996 . 147p . DOE Contract AC0494AL96907 . Sup.Doc.Num. E 1.99:DE96013674. NTIS Order Number DE96013674 . Primary Report Number: GJPO-MWTP--18-Rev.1 . Source: OSTI (DOE and DOE contractors only); NTIS (Public Sales); GPO Dep. (Depository Libraries)

In 1992, Congress passed the Federal Facility Compliance Act requiring the U.S. Department of Energy (DOE) to treat and dispose of its mixed waste in accordance with Resource Conservation and Recovery Act (RCRA) land disposal restrictions (LDRs). The DOE Albuquerque Operations Office (AL) currently does not have adequate systems to treat the mixed wastes generated and stored at the nine DOE-AL sites. In response to the need for mixed-waste treatment capacity, DOE-AL organized a Treatment Selection Team under the Mixed-Waste Treatment Program (MWTP) to match mixed wastes with treatment options and develop a strategy for treatment of its mixed waste. The strategy developed by the Treatment Selection Team, as described in the AL Mixed-Waste Treatment Plan (DOE 1994), is to use available off-site commercial treatment facilities for all wastes that can be successfully and cost-effectively treated by such facilities. Where no appropriate commercial treatment facilities exist, mobile treatment units (MTUs) would be developed to treat wastes at the sites where the wastes are generated. Treatment processes used for mixed waste must not only address the hazardous component (i.e., meet LDRs) but also must contain the radioactive component in a form that allows final disposal while protecting workers, the public, and the environment. The packed-bed reactor/silent discharge plasma was chosen as a potential candidate for the treatment of the mixed wastes. The process is described.

Department of Energy

Research Projects

REPORT RECORD

Polymer Filtration: A New Technology for Selective Metals Recovery . Smith, B.F.; Robison, T.W.; Courmoyer, M.E.; Wilson, K.V.; Sauer, N.N.; Mullen, K.I.; Lu, M.T.; Jarvinen, J.J. . Los Alamos National Lab., NM (United States) . [1995] . 10p . DOE Contract W7405ENG36 . Sup.Doc.Num. E 1.99:DE95009438. NTIS Order Number DE95009438 . Primary Report Number: LA-UR--94-1432 . Source: OSTI (DOE and DOE contractors only); NTIS (Public Sales); GPO Dep. (Depository Libraries)

Polymer Filtration (PF) was evaluated for the recovery of electroplating metal ions (zinc and nickel) from rinse waters. Polymer Filtration combines the use of water-soluble metal-binding polymers and ultra-filtration to concentrate metal ions from dilute rinse water solutions. The metal ions are retained by the polymers; the smaller, unbound species freely pass through the ultrafiltration membrane. By using this process the ultrafiltered permeate more than meets EPA discharge limits. The metal ions are recovered from the concentrated polymer solution by pH adjustment using diafiltration and can be recycled to the original electroplating baths with no deleterious effects on the test panels. Metal-ion recovery is accomplished without producing sludge

Department of Energy

Research Projects

Isolation of Metals from Liquid Wastes: Reactive Scavenging in Turbulent Thermal Reactors

Year of Award: 1997.

Lead Principal Investigator:

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University of Arizona
Tucson, Arizona 85721
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Description Provided by Investigator:

Metal-bearing liquids constitute a major part of the DOE waste inventory. This waste is extremely varied with respect to metals (radionuclides, heavy metals, transuranics) and other species (e.g., organics). For much of this waste, concentration of metals to reduce the volume requiring special isolation is critical. One potentially suitable technology is high-temperature reactive capture of volatile metals by readily available collectable particulate sorbents (kaolinite, bauxite, and limestone) injected downstream of a flame zone. High temperature reaction between metal vapor and sorbent forms environmentally benign products that are water unleachable.

We propose to begin developing the fundamental science base for understanding and evaluating a class of processes applicable to a broad range of aqueous and nonaqueous feedwastes. We propose a three-pronged experimental and computational approach building on our previous work in each area. We will:

- investigate kinetics in a laminar-flow reactor in which the simple flow does not confound extraction of kinetic data. *Ex situ* size-segregated particle analysis will provide data on speciation and kinetics. Drop evaporation and trajectories will be studied using *in situ* laser-induced molecular fluorescence.
- build fundamental models of drop dynamics and evaporation, reaction, particle-size evolution, gas-to-particle conversion, etc., that allow data from the laminar flow reactor at Arizona to be used to predict behavior in a larger, turbulent-flow reactor.
- use data (particle-size distribution, *ex situ* size-segregated particle analysis, etc.) From EPA's 82 kW reactor to improve and validate models that will enable rational evaluation of specific processes.

The work will contribute to rational evaluation of high-temperature thermal processes for DOE metal-bearing liquid waste through the ability to predict particle-size distribution, speciation, and size-segregated speciation. Specifically, we will address critical scientific issues relating to high-temperature reactive capture of metals from liquid wastes.

Department of Energy

Research Projects

Selective Removal/Recovery of RCRA Metal

Project Id: P/LANL—MK45

Last Amendment Date: December 11, 1997

Research Organization: LANL (Los Alamos National Laboratory)

Web Site: <http://www.lanl.gov>

Sponsoring Program: Asst. Secretary for Environmental Restoration & Waste Management

Funding Mechanism: Managing and Operations

Location: Los Alamos, New Mexico 87545-0000

Point of Contact: Erdal Bruce Robert

Contract #: W-7405-ENG-36

Phone: 505-667-5338

Start Date: November 15, 1996

Email: erdal@lanl.gov

FY1997 Funding: \$296,041

Est. Completion Date: August 07, 1997

Type of Research: Applied

B&R Codes: EW4030000

Project Description

LA-UR 97-4121: Selective Removal/Recovery of RCRA Metals from Waste and Process Effluents - This project will develop and optimize Polymer Filtration for specific DOE process streams containing RCRA metals and coordinate this technology with the needs of the commercial sector to assure that technology transfer occurs. Polymer Filtration Technology (PF) uses water-soluble metal-binding polymers to sequester metal ions in dilute solution. The water-soluble polymers have a sufficiently large molecular size that they can be separated and concentrated using commercial ultrafiltration membranes. Water, small organic molecules, and unbound metals pass freely through the ultrafiltration membrane while concentrating the metal-binding polymer. The polymers can then be reused by changing the solution conditions to release the metal ions. The metal-ions are recovered in concentrated form for recycle or disposal using a diafiltration process.

Department of Energy

Research Projects

Solubilization of Trace Organics in Block Copolymer Micelles for Environmental Separations Using Membrane Extraction Principles

Project Id: P/CH—FG02-92ER14262

Last Amendment Date: October 11, 1995

Research Organization: Massachusetts Institute of Technology

Web Site: <http://www.mit.edu>

Sponsoring Program: Office of Energy Research

Funding Mechanism: GRANT

Location: Cambridge, Massachusetts 02139

Point of Contact: Dewey, H. J.

Contract #: FG02-92ER14262

Phone: 301-903-5802

Start Date: May 01, 1992

Est. Completion Date: April 30, 1995

Under Contract to: Chicago Operations Office

Project Description

Block copolymer micelles are being investigated as versatile solvents for the removal and/or recovery of organic contaminants from aqueous solutions. The work consists of (i) development of a comprehensive data base on the solubility enhancements for a range of volatile organics of environmental interest, (ii) characterization of these micelles using light scattering, UV/Vis and fluorescence spectroscopy, densitometry, surface tensiometry, and titration, perfusion and differential scanning calorimetry, (iii) Monte Carlo numerical simulation of the effects of solutes on the structure of the micelles, and (iv) a demonstration of the effectiveness of this approach using hollow fiber membrane contactors. The engineering aspects of the proposed separations scheme is a major focus, with both experimental studies and an engineering economic evaluation. Regeneration of the block copolymer micellar solutions using temperature swings to disrupt the micelles, followed by steam stripping, is currently being explored, and the results are to be included in an economic evaluation of the overall process. Acrylic polyampholytes are a new class of polymers that will be investigated as they have the potential to be regenerated by pH swings rather than by thermal means.

Department of Energy

Research Projects

Ozone Treatment of Soluble Organics in Produced Water

Project Id: P/ORNL—FEA307

Last Amendment Date: January 12, 1999

Research Organization: ORNL (Oak Ridge National Laboratory)

Web Site: <http://www.ornl.gov>

Sponsoring Program: Asst. Secretary for Fossil Energy

Funding Mechanism: Managing and Operations

Location: Oak Ridge, Tennessee 37831

Point of Contact: Judkins, Roddie Reag

Contract #: AC05-84OR21400

Phone: 423-574-4572

Start Date: May 01, 1998

Email: JUDKINSRR@ornl.gov

FY1997 Funding: FY1999-\$400,000; FY2000-\$289,000

B&R Codes: AC1015000

Project Description

This project will extend the previous PERF research to improve the applicability of ozonation for treating produced water. It will be one task of a new PERF initiative to address the industry-wide problem of handling soluble organics. The goal of this project will be to maximize oxidation of water-soluble organics during a single-pass operation. Secondary goals include reduction of effluent toxicity, color, odor, TOC and COD. The project will investigate: (1) ozone and hydrogen peroxide production by electrochemical methods, (2) increasing the mass transfer rate in the reactor by forming micro bubbles during ozone injection into the produced water, and (3) using ultraviolet irradiation to enhance the reaction if needed.

Department of Energy

Research Projects

Advanced Energy Projects: Novel Biomimetic Titanium Oxide Photocatalysts for Selective Heavy Metals Removed

Project Id: P/ANL—001914

Last Amendment Date: December 03, 1998

Research Organization: ANL (Argonne National Laboratory)

Web Site: <http://www.anl.gov>

Sponsoring Program: Office of Energy Research

Funding Mechanism: Managing and Operations

Location: Lemont, Illinois 60439

Point of Contact: Thurnauer, M. C.

Contract #: W-31109-ENG-38

Phone: 630-252-3570

Start Date: October 01, 1996

Email: thurnauer@anlchm.chm.anl.gov

FY1997 Funding: \$307,000

Type of Research: Basic

B&R Codes: KJ0300000

Project Description

The use of photogenerated electrons for deposition of metal layers on a TiO_2 substrate has new potential applications, in the synthesis of nanoparticle metallic catalysts and nano-circuits, or in the removal of heavy metal contaminants from wastewater and drinking water supplies by the reduction of metal ions into their less toxic, nonsoluble metallic form. We are continuing to improve photocatalysts capable of sequestering and removing highly toxic heavy metal ions and organics from aqueous solutions by reducing heavy metal ions to their metallic form. The structures of surface modifiers on the TiO_2 surface and their electrochemical properties were correlated with the charge separation distances and reduction abilities obtained after illumination of surface modified colloids. The surface structure was investigated by Fourier transform infrared (FTIR) and extended X-ray absorption fine structure (XAFS) spectroscopies, charge separation distances were determined by electron paramagnetic resonance (EPR) spectroscopy, and the change in oxidation state was followed by X-ray absorption spectroscopy (XAS). During this period we have demonstrated the deposition of 4-nm TiO_2 particles on glass supports that can be modified with surface derivatives in the same manner as in the colloid solution. We showed that the supported photocatalysts are effective in adsorbing metal ions. During illumination of either the photocatalyst/liquid junction or the dry supported photocatalyst, metal ions adsorbed on the photocatalyst surface are reduced to their metallic state. Photocatalytic reduction was found to be doubled in the presence of methanol, which is a current-doubling agent. Reduction of copper, silver, and gold was demonstrated.

Department of Energy

Research Projects

Photocatalytic & Chemical Oxidation

Project Id: P/NREL—DO6E

Last Amendment Date: December 07, 1998

Research Organization: NREL (National Renewable Energy Laboratory)

Web Site: <http://www.nrel.gov>

Sponsoring Program: Assistant Secretary for Environmental Restoration & Waste Management

Funding Mechanism: Managing and Operations

Location: Golden, Colorado 80401-3393

Point of Contact: Blake, Daniel M.

Contract #: AC02-83CH10093

Phone: 630-275-3702

FY1997 Funding: \$118,310

B&R Codes: EW4510000

Project Description

Supercritical carbon dioxide extraction and cleaning is being developed for a number of applications that affect environmental-cleanup and waste minimization goals. Work done on this project includes exploring the chemistry required to provide a unit operation for maintaining purity of (i.e., polishing) liquid or supercritical carbon dioxide in process systems that recirculate the fluid phase for reasons of environmental compliance and waste minimization. The results of this work will also provide new information that addresses questions that are key to the fundamental understanding of photocatalytic chemistry and the chemistry of carbon dioxide fixation. This work builds on a broad base of knowledge that exists for photocatalytic chemistry, use of supercritical carbon dioxide, and design of photoreactors for operation at elevated pressure.

Department of Energy

Research Projects

Development of Advanced In-Situ Techniques for Chemistry Monitoring and Corrosion Mitigation in SCWO Environments

Digby D. Macdonald, Pennsylvania State University

Karen M. Garcia, Idaho National Engineering and Environmental Laboratory
George Engelhardt, Pennsylvania State University

Research Objective

This report evaluates the two years results of our research on the development of advanced electrochemical techniques for use in supercritical water oxidation (SCWO) environments.

Research Progress and Implications

The SCWO technology was found to be a promising approach to treat a variety of hazardous wastes. However, the corrosion processes in the SCWO reactors are still a problem for further development of this technology. We have developed a flow-through electrochemical cell (FTEC) which allows us to monitor the corrosion process in real time at temperatures up to 500 °C and pressures up to 400 bar. The FTEC consists of a flow-through Ag|AgCl external pressure-balanced reference electrode, a flow-through platinum hydrogen electrode, an yttria-stabilized zirconia pH sensor, and an electrochemical noise sensor. The new FTEC has been designed to serve as a measurement vessel for our high temperature and high pressure circulation once-through flow loop and titanium alloy was chosen as the construction material. The FTEC, shown schematically in Figure 1, is used for our experiments. Two HPLC pumps are employed in the system, one for pumping the reaction solution through the loop and the other for pumping the reference solution through the reference electrode. The system pressure is sustained as a constant via a back pressure regulator. The temperature was measured using a thermocouple installed at the center of the FTEC.

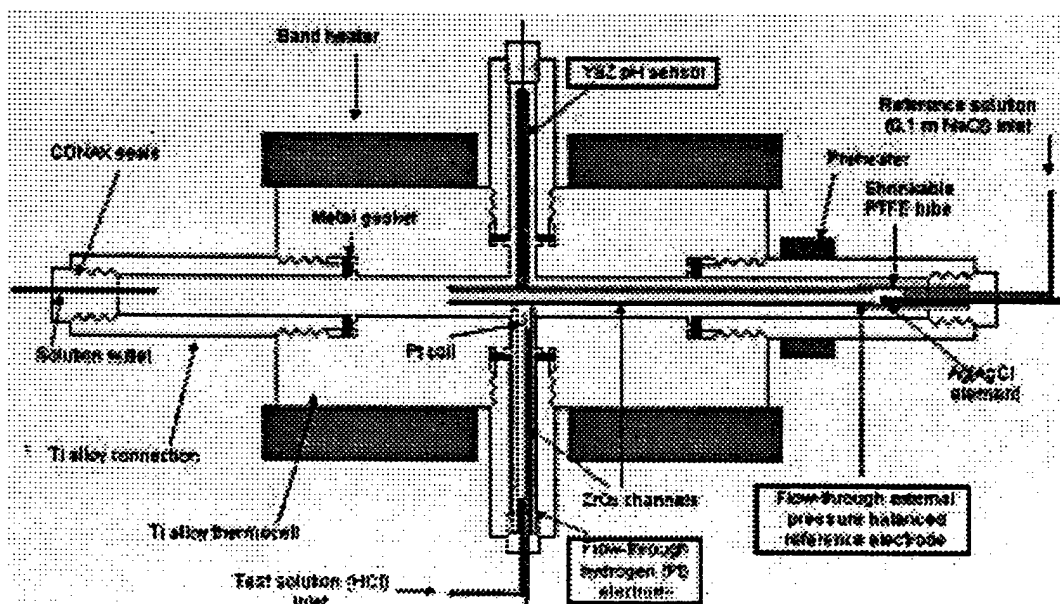


Figure 1. Diagram of the flow-through electrochemical cell (FTEC).

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Because many physico-chemical processes, including corrosion, are sensitive to the pH, the measurement and control of pH is very important for the high temperature SCWO environment. We have measured [1] the potentials of the FTEC for several $\text{HCl}_{(\text{aq})} + \text{NaCl}_{(\text{aq})}$ solutions of different concentrations of $\text{HCl}_{(\text{aq})}$ and derived the corresponding pH differences (ΔpH) over a wide range of temperatures at pressure around 350 bar. Comparison of the experimentally derived and theoretically calculated ΔpH values presented in Figure 2 clearly demonstrates the ability to measure pH with a high accuracy (better than ± 0.05 pH units). This result also shows the viability of the developed FTEC as a versatile potentiometric system for use at supercritical temperatures. During the next year of the project we will address the problem of electrochemical noise measurements and monitoring corrosion processes that occur on metallic materials exposed to super critical water.

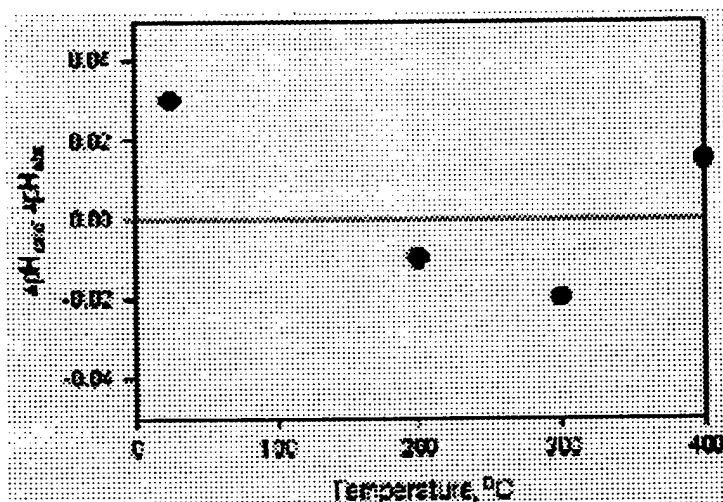


Figure 2. Comparison between theoretically calculated and experimentally measured differences in pH (ΔpH): $\Delta\text{pH} = \text{pH}(0.01\text{mHCl} + 0.1\text{mNaCl}) - \text{pH}(0.001\text{mHCl} + 0.1\text{mNaCl})$.

- [1] S.N. Lvov, X.Y. Zhou, and D.D. Macdonald, Potentiometric pH Measurements in Supercritical Aqueous Solutions, In Proc. of the 193rd Meeting of the Electrochemical Society, San Diego, 1998, Abstr. No. 1016.

Planned Activities

During the next year of the project, we will address the problem of electrochemical noise measurements and monitoring corrosion processes that occur on metallic materials exposed to super critical water.

Department of Energy

Research Projects

Cavitation Hydrothermal Oxidation: A New Remediation Process

Dr. Kenneth S. Suslick, University of Illinois at Urbana-Champaign

Research Objective

Our primary goal is to develop a quantitative understanding of cavitation phenomena in aqueous media and the development of applications of cavitation to remediation processes. Our efforts have focused on three separate areas: sonoluminescence as a probe of conditions created during cavitation collapse in aqueous media, the use of cavitation for remediation of contaminated water, and an addition of the use of ultrasound in the synthesis of novel heterogeneous catalysts for hydrodehalogenation of halocarbons under mild conditions.

Research Progress and Implications

This report summarizes work after one year of a three-year project.

In order to gain further understanding of the conditions present during cavitation, we have continued our studies of sonoluminescence^[1]. We have made recent breakthroughs in the use of emission spectroscopy for temperature and pressure measurement of cavitation events, which we expect to publish shortly. We have been able to measure *for the first time* the temperature of cavitation *in water* during multi-bubble cavitation in the presence of aromatic hydrocarbons^[2]. The emission from excited states of Cl_2 in water gives temperatures that are consistent with adiabatic compressional heating, with maximum temperatures of 4300° K. Our prior measurements of cavitation temperatures in low vapor pressure nonaqueous media gave somewhat higher temperatures of 5000 K^[1]. This work lays permanently to rest exotic mechanisms for cavitation chemistry, at least for cavitation fields.

In a new avenue of research, we have recently explored the generation of cavitation by hydrodynamic techniques and demonstrated for the first time that chemical reactions occur during turbulent flow of water and of water containing chlorocarbons^[3]. This work received substantial publicity. While the chemical effects of *acoustic* cavitation (i.e., sonochemistry and sonoluminescence) have been extensively investigated during recent years, little is known about the chemical consequences of *hydrodynamic* cavitation created during turbulent flow of liquids. Hydrodynamic cavitation is observed when large pressure differentials are generated within a turbulent liquid flow and is accompanied by a number of physical effects, erosion being most notable from a technological viewpoint. It has the potential advantage of facile scale-up: there already exist commercial high pressure flow mixing units capable of generating hydrodynamic cavitation with flows of 50 gpm (Microfluidics, Inc., Newton, MA). However, prior reports of hydrodynamically induced chemistry or luminescence and direct comparisons to sonochemistry or sonoluminescence have been extremely limited. The oxidation of iodide to triiodide in aqueous solutions containing halocarbons (e.g., CHCl_3 or CCl_4) under hydrodynamic cavitation conditions was examined in order to determine the origin of this hydrodynamic chemical reaction. This reaction also serves as a model for remediation of halocarbon contaminated water using hydrodynamic cavitation, a previously unexplored approach to remediation. The effects of several experimental variables on the I_3^- production rate were investigated. Increasing the reaction temperature inhibits the I_3^- production due to increased vapor pressure, which leads to reduced efficacy during cavitation collapse; the rate decreases exponentially with vapor pressure. The production of I_3^- is sensitive to the nature of the dissolved gas and decreases exponentially with increasing gas thermal conductivity. Thus, the chemistry observed and its response to external parameters is remarkably similar to ultrasonically induced cavitation, albeit the sonochemical rates are significantly higher at least with our current experimental configurations.

Department of Energy

Research Projects

Planned Activities

Our overall goal in this research is to develop our understanding of the reactions of organic compounds in the presence of high intensity ultrasound. To approach this goal, our planned activities will continue in three areas: 1) investigation of the local conditions formed during cavitation in water; 2) mechanistic examination of the effects of cavitation on aromatic hydrocarbons and halocarbons, and 3) determination of degradation yields as a function of experimental configurations for cavitation production with aromatics and halocarbons as toxic impurities in water. In all cases, we will continue our special emphasis on the mechanistic origins of sonochemistry, in relationship to its applications to environmental challenges. Information gained should lead to effective protocols and equipment for large-scale treatment of contaminated water and soil.

We have also developed a new research area relevant to environmental remediation chemistry that derives from our recent discovery of the catalytic *hydrodehalogenation* of halocarbons. In work not funded by the DOE, we have been actively involved in the development of sonochemical preparations of active heterogeneous catalysts^[4-6]. The localized hot spot created during acoustic cavitation is sufficient to strip ligands completely from metal complexes. This process also produces enormous cooling rates ($>10^9$ K/s) and so allows the formation of colloidal, amorphous metal aggregates. We have very recently used ultrasound to produce nanostructured MoC₂ with very high surface areas and excellent catalytic activity^[7]. Our most recent discovery is very relevant to our DOE project, however: this sonochemically prepared MoC₂ is an extremely effective and stable *hydrodehalogenation* catalyst. In gas flows with H₂, we can remove both Cl and F from essentially all halocarbons, replacing the halogen with hydrogen quantitatively and quickly without degradation of the MoC₂ catalyst (in spite of the release of HCl or HF which rapidly destroy most other catalysts), under mild conditions ($<300^\circ$ C). We have examined quantitatively the catalytic properties of supported catalysts produced sonochemically from using gas/solid microreactor kinetics monitored by GC/MS. We expect to publish this work in the near future.

Other Access to Information

1. Suslick, K.S.; Crum, L.A. "Sonochemistry and Sonoluminescence," in *Encyclopedia of Acoustics*; Crocker, M.J., ed.; Wiley-Interscience: New York, 1997; Vol. 1, Ch. 26, pp. 271-282.
2. Suslick, K.S.; Didenko, Y.T.; McNamara III, W.B. "Sonoluminescence Temperature of Aqueous Cavitation," submitted for publication.
3. Suslick, K.S.; Mdleleni, M.M.; Ries, J.T. "Chemistry Induced by Hydrodynamic Cavitation" *J. Am. Chem. Soc.*, 1997, **119**, 9303-9304.
4. Suslick, K.S. "Sonocatalysis," in *Handbook of Heterogeneous Catalysis*; Ertl, G.; Knozinger, H.; Weitkamp, J.; eds.; Wiley-VCH: Weinheim, 1997; Vol. 3, Ch. 8.6, pp. 1350-1357.
5. Suslick, K. S.; Hyeon, T.; Fang, M.; Cichowlas, A. A. "Sonochemical Preparation of Nanostructured Catalysts," *Advanced Catalysts and Nanostructured Materials*; Moser, W.R., ed. Academic Press: N.Y., 1996, pp. 197-211.
6. Suslick, K.S.; Fang, M.; Hyeon, T. "Sonochemical Synthesis of Iron Colloids" *J. Am. Chem. Soc.*, 1996, **118**, 11960-11961.
7. Hyeon, T.; Fang, M.; Suslick, K.S. "Nanostructured Molybdenum Carbide: Sonochemical Synthesis and Catalytic Properties," *J. Am. Chem. Soc.*, 1996, **118**, 5492-5493.

Department of Energy

Research Projects

Managing Tight-binding Receptors for New Separations Technologies

Dr. Daryle H. Busch, University of Kansas

Dr. Richard S. Givens, University of Kansas

Research Objective

Whereas such traditional separation methodologies as ion exchange and solvent extraction require rapid interaction between ligands and metal ions, the most strongly binding ligands invariably bind slowly; e.g., cryptates bind and dissociate more slowly than macrocycles, which are slower than open-chain chelating ligands. This project seeks to maximize the binding and dissociation rates for tight-binding receptors in order to make them more useful to separations science. An alternative slow-binding technology is also under exploration.

Research Progress and Implications

Acceleration of Binding: Sixteen months into this 3-year project, seminal examples of a new class of ligands have been designed and synthesized, and the basic premise of the project has been confirmed. This work involves the design and synthesis of very special ligands that seek to capture the best properties of open-chain chelates and macrocycles. The ligands must begin as open-chain structures so they can bind fast, but they must have reactive groups that close the structures into macrocycles upon chelation to metal ions. There exists no literature precedent for such ligands, putatively because of the great tendency of the two ends of the molecule to react with each other. Synthetic challenges were indeed encountered en route to our first generation ligand 1, a molecule in which the ligand extremities are carbonyl and amine groups that can condense to form a C=N linkage. The ligand has now been properly characterized and is available for detailed studies. Solution studies on the binding of ligand 2, which is generated in solution, have confirmed the basic hypothesis that the rate of macrocyclic complex formation can be quite rapid when metal ion templated ring closure is involved. Solution studies have also shown that the Schiff base condensations like those involved in forming macrocyclic complexes with 1 and 2 can be reversed. Second generation ligands 3 and 4 are sought; the first to provide a macrocycle with no fused pyridine ring and the second to utilize a different ring closure reaction, ester exchange. 4 has been synthesized in high yield and characterized.

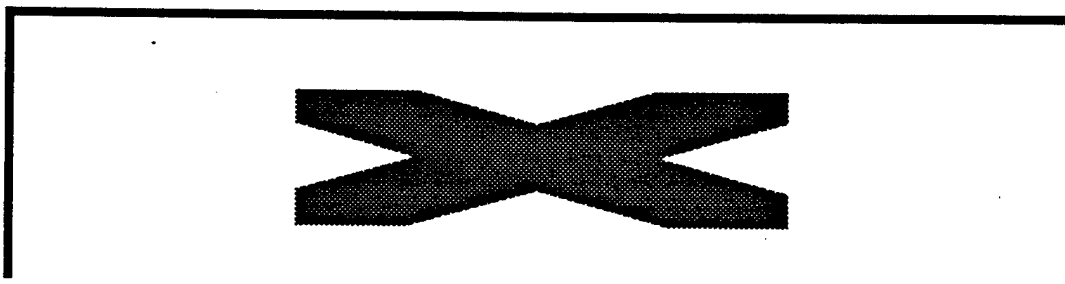


Figure 1

Planned Activities: Detailed equilibrium and kinetic studies of 1 will be conducted. Conditions for ring closure will be found for 4 and its derivatives. Synthesis of 3 will be completed. 3 and 4 will be subject to detailed study when appropriate. Third generation ligands will be designed and synthesized. Kinetic data will be compared with literature data on open-chain chelates and macrocycles.

Department of Energy

Research Projects

A Biomimic as a Possible Slow Separations Technology: Certain single cell organisms secrete powerful sequestrants (siderophores) for iron and then absorb the iron complexes back through their membranes. Imprinted macroporous polymers may provide the equivalent of the cellular membrane for selective adsorption of complexes of tight-binding ligands. Separation by such a process need not be rapid and could exploit the full selectivity and strength of binding of the strongest ligands. N,N',N'',N'''-tetrasubstituted 1,4,8,11-tetraazacyclotetradecanes (substituted cyclams) were investigated to test this concept. The substituents varied from those capable of covalent bonds (amines for Schiff base formation), good hydrogen bonders (amides) to moderate dipoles (nitriles). The mode of association also included incorporating anions (vinyl sulfonate) into the polymer. Complexes were incorporated into the matrix showing some promise, but work was discontinued to focus on other aspects of the project.

Photorelease of Metal Ions from Tightly Bound Adducts: Macrocycles capable of rapid release of tightly bound ions by photolytic fragmentation of the macrocyclic ring have been designed and are being synthesized. Two strategies for the synthesis of photolabile macrocycles have been pursued. In the first strategy, a substituted triazadioxo-15-crown-5 has been synthesized by coupling 3-benzyloxy triethylene glycol ditosylate with a protected triazaundecane diol. This nine-step synthesis to an intermediate macrocycle provides a general route to monosubstituted macrocycles. Conversion of the side chain into a photoactive ligand is in progress. Because of the lengthy procedure and low yields encountered using our earlier strategy, a second, more efficient synthesis for the substituted macrocycle was designed and carried out. In this second strategy, the ring closure is accomplished by a Grubbs olefin metathesis using phenylmethylene bis(tricyclohexylphosphine)ruthenium dichloride. The 4-oxy-7,10,13-triazahexadeca-1,15-diene was closed to 2-hydroxymethyl-1-oxo-4,8,12-triazatetradecane in excellent yield (94%). Reduction of the double bond and hydrogenolysis of the protecting benzyl group has provided a much more efficient entry into an analogous hydroxymethyl substituted macrocycle which can be further elaborated into the photoactive macrocycle. Exploratory photochemistry of bis-7,16-(di-p-methoxybenzoyl)-1,4,10,13-tetraoxo-7,16-diazacyclooctadecane has also been examined. No fragmentation of the crown ether was observed during irradiation either at 254 or 300 nm as anticipated for amides.



Figure 2

Planned Activities

Included above.

Department of Energy

Research Projects

Fundamental Studies of the Removal of Contaminants from Ground and Waste Waters via Reduction by Zero-Valent Metals

J. A. Yarmoff, University of California at Riverside

C. Amrhein, University of California at Riverside

Research Objective

Contaminated groundwater and surface waters are a problem throughout the United States and the world. In many instances, the types of contamination can be directly attributed to man's actions. For instance, the burial of wastes, casual disposal of solvents in unlined pits, and the development of irrigated agriculture have all contributed to groundwater and surface water contamination. The kinds of contaminants include chlorinated solvents and toxic trace elements that are soluble and mobile in soils and aquifers. Oxyanions of selenium, chromium, uranium, arsenic, and chlorine (as perchlorate) are frequently found as contaminants on many DOE sites. In addition, the careless disposal of cleaning solvents, such as carbon tetrachloride and trichloroethylene, has further contaminated many groundwaters at these sites. Oxyanions of selenium, nitrogen, arsenic, vanadium, uranium, chromium, and molybdenum are contaminants in agricultural areas of the Western U.S.

The management of these waters requires treatment to remove the contaminants before reuse or surface water disposal. In one instance in the Central Valley of California, the discharge of selenate-contaminated shallow groundwater to a wildlife refuge caused catastrophic bird deaths and deformities of embryos.

A potential remediation method for many of these oxyanions and chlorinated-solvents is to react the contaminated water with zero-valent iron. In this reaction, the iron serves as both an electron source and as a catalyst. Elemental iron is already being used on an experimental basis. Both in-situ reactive barriers and above-ground reactors are being developed for this purpose. However, the design and operation of these treatment systems requires a detailed process-level understanding of the interactions between the contaminants and the iron surfaces. Only limited success has been achieved in the field, partly because the basic surface chemical reactions are not well understood. We are performing fundamental investigations of the interactions of the relevant chlorinated solvents, and trace element-containing compounds with single- and poly-crystalline Fe surfaces. The aim of this work is to develop the fundamental physical and chemical understanding that is necessary for the development of cleanup techniques and procedures.

Research Progress and Implications

As of May 1998, we have performed both bulk chemical measurements of the reduction reactions and surface science studies of model chemical systems. During these first two years of funding, we have made significant progress in both areas. Initially, we focused primarily on the reduction of selenate by elemental iron. We also performed some work with chromate, perchlorate, uranyl, and carbon tetrachloride. In the following sections some of our progress is described.

We studied the factors affecting the selenate reduction reaction to determine the optimum conditions for the remediation of wastewater. We characterized the effects of pH, O_2 concentrations, ionic strength, and solution composition, degree of agitation, and iron surface pretreatment in solutions contaminated with 0.20 mg L⁻¹ selenate (+VI oxidation state). The reaction was found to be first-order with respect to selenate concentration. Increases in either the pH or ionic strength decreased the rate of selenate reduction, with pH being the more important variable. The reaction was also sensitive to changes in the

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Research Projects

preparation of the iron and type of iron. Washing with 0.01N HCl and rinsing with O₂-free water resulted in the most reproducible surface for use in these measurements. Agitation of the iron/water suspension increased the rate of reaction. Palladium coated iron metal tripled the rate of selenate reduction. There was little or no reduction of perchlorate by either iron or Pd-coated iron. Carbon tetrachloride reduction was significantly faster in oxygenated water compared to O₂-free and was not inhibited by competitive adsorption of toluene or humic acid.

In order to probe the solid species formed by the reduction of selenate with iron filings, near edge x-ray adsorption fine structure (NEXAFS) analysis of reacted iron was carried out at the Stanford Synchrotron Radiation Laboratory (SSRL). Se was found on all of the surfaces in mixtures of the (0) and (+IV) oxidation states. Samples prepared under O₂ produced a greater amount of the (0) species, while samples prepared under N₂ produced a greater portion of (+IV). Samples prepared at low pH had greater amounts of (0) than samples prepared at higher pH values.

X-ray diffraction (XRD) was used to determine the species of iron rust formed as a result of the reactions with zero-valent iron. The dominant product is lepidocrocite (g-FeOOH) with minor amounts of maghemite (g-Fe₂O₃). These are insoluble mineral forms of oxidized iron (+III oxidation state) that are suspended in the reaction solutions.

Bulk solution studies carried out with uranium and chromium have revealed that both can passivate the surface of iron. Depending on solution concentration, the reaction of uranium and chromium with iron can occur with no rust formation. This is important because of the implications of possible shutdown of the sorption and/or reduction reactions. Additionally, this passivation slows down the sorption and reduction of other trace elements. Chromium (as chromate) slowed down both the loss from solution and reduction of selenium (as selenate) by a factor of about 15. NEXAFS analysis indicated that uranium coprecipitated with selenium on the iron surface. However, the selenium was in the +VI oxidation state. This hasn't been observed in any other reactions with selenium and iron. Also, uranium seems to buffer the pH of the reaction solution, whereas other target oxyanions are associated with an increase in pH (> 9.0).

Previous studies have often overlooked the formation and reaction of green rust, which is a mixed +II/+III oxidation-state iron hydroxide mineral. It has a pyroaurite mineral structure with the anions substituting in the place of hydroxyl ions. Chloride, nitrate, sulfate, carbonate, and selenate have been reported to be in the structure of green rust. We've confirmed the presence of green rust formation in our reactions visually and chemically.

Studies of iron foils were carried out in order to utilize surface-sensitive techniques that can better characterize the surfaces. We used scanning tunneling microscopy (STM) to look at polycrystalline iron foils during the reduction of selenate, chromate, and uranyl. This was done in-situ, using an STM that is designed for operating under solution. We found that, for all three reactions, the surface morphology changed from the roughened surface characteristic of iron oxides to a smooth surface. Note that a blank run using only water showed no changes. X-ray photoelectron spectroscopy (XPS) was used to measure Fe foils following the reduction of selenate, chromate, and uranyl in aqueous solution. For all three species, films composed of partially reduced oxides were found. The reduction of U was found to be very sensitive to dissolved oxygen, while the reductions of Se and Cr are not. No changes to the native iron oxides were observed with XPS, due the inherent surface sensitivity of the technique.

In order to probe the reaction mechanism on an atomic scale, we have begun investigations of the reduction reactions of model gas-phase molecules with atomically clean iron in ultra-high vacuum (UHV). We began with the reaction of SeF₆ with iron and iron oxide surfaces, as Se in SeF₆ is in the (+VI) oxidation state just as in selenate. Polycrystalline iron foils were cleaned in vacuum by sputtering with Ar⁺ ions. The foils were then reacted with SeF₆ gas in a special UHV reaction chamber, and XPS

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was used to measure the iron foils following reaction. The spectra showed a large excess of fluorine, which indicates that the major reaction pathway involves the reduction of Se and its subsequent ejection from the surface. A small amount of adsorbed selenium does remain on the surface, which was found to be in a completely reduced form. An iron oxide was grown in-situ, and it was found to be largely unreactive to SeF_6 .

In summary, we have begun our program with a number of detailed investigations of the reduction of selenate, chromate, and uranyl by reaction with Fe surfaces. Excellent collaboration between the Physics Department and the Department of Environmental Sciences has stimulated a wealth of new ideas for this and other environmentally relevant projects.

Planned Activities

More bulk studies will be performed to determine the optimal operating conditions for reaction. This information will help determine which solutions will be later used for the surface science experiments. More NEXAFS will be done with other species, as the initial data collected following Se reduction was very useful. More STM and XPS will be performed using iron foils, but we will be first cleaning the foils with Ar + bombardment and then transferring the samples to the solution under an inert atmosphere. This will allow us to probe the actual reaction with zero-valent iron, rather than just measuring the native oxide overlayer. More detailed UHV work will also be performed in order to clarify the reaction mechanism. For example, we will repeat the SeF_6 experiments using Fe single crystals, which will eliminate grain boundary effects. We will also employ other volatile oxyanion reactants that can be reduced by iron, such as selenic acid and various chlorohydrocarbons.

Department of Energy

Research Projects

De Novo Design of Ligands for Metal Separation

Dr. Garland R. Marshall, Washington University

Research Objective

Develop computer-aided molecular design technology for ligands useful in metal separations. This includes force field parameterization of different metals in various oxidation states and de novo design of ligands optimized for specific metals including constraints to certain chemical classes of ligands.

Research Progress and Implications

This report summarizes year two of a 3-year project and focuses on force field parameterization.

Work continues on the modification of algorithms to construct metal-binding ligands from molecular fragments. The lack of an appropriate theoretically derived functional form for d-orbitals in molecular mechanics has hampered efforts to utilize these programs and our efforts have focused on correcting this deficiency in collaboration with Prof. Anders Carlsson of the Department of Physics as follows:

Our approach for parameterization of transition metal atoms is to fit an empirical potential for molecular mechanics to the potential energy surface calculated by ab initio methods. Conventional ab initio methods using Hartree-Fock theory are known to give good results for most organic molecules. Coordination compounds require the use of high-level basis functions such as triple zeta valence (TZV) to get accurate results which are highly time consuming thus restricting the ligand sizes. In order to overcome these difficulties, the density functional model²⁻⁴, which is known to give results in parallel to the popular MP2 model was used.

The d-electron energy function plays an important role in transition metal complexes. Recently, an energy function for d-electrons has been derived at Washington University based on quantum mechanical analysis.⁵ The d-shell energetics is described via the 'ligand field stabilization energy', which is given by

$$E_{LFSE} = - \sum_{ij} e(r_i) e(r_j) U(q_{ij}) \quad (1)$$

ij

$e(r_i)$, $e(r_j)$ are the coupling strengths of the individual ligands and the q_{ij} is the ligand-metal-ligand angle. $U(q_{ij})$ is an angular function defined as,

$$U(q_{ij}) = [P(\cos q_{ij})^2 - (1/5)],$$

$$\text{where } P = (3 \cos^2 q - 1) / 2.$$

The functional forms of the coupling strengths can be derived from the half-width, W , of the d-complex. The term W is related to the energies of the occupied and the empty d-orbitals by the following term;

$$\bar{5}W^2 = \sum_n (\epsilon_n - \bar{\epsilon})^2$$

n _

ϵ_n is the energy of the occupied d orbitals and $\bar{\epsilon}$ is the average energy of the occupied and unoccupied d orbitals.

In order to derive the functional form of W and coupling strengths, ab initio and density functional calculations were performed on various metal complexes. We have initially studied square planar and tetrahedral metal ammonia (Mn^{+2} , Fe^{+2} , Co^{+2} , Ni^{+2} , Cu^{+2} , Zn^{+2}) and copper-imidazole complexes. Geometry optimizations were performed at UHF for open shell systems and RHF for closed shell

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systems, using triple zeta valence (TZV) basis set in ab initio and BP/DN* in density functional model. Optimized geometries for the Cu^{+2} -imidazole complex shows good agreement with known crystal structures.

The variation of half width with respect to metal ligand distance was then computed by varying the metal-ligand distances. Detailed studies have been carried out for Cu-ammonia and Cu-imidazole complexes. The exponential functional form of the coupling strength was then derived from least squares fit and the value of $W(*)$ was optimized so that the sum of the squares of the error is minimum around the equilibrium distance. The following function is obtained from the least squares fit;

$$W(r) = W(*) + be^{-ar}$$

$W(r)$ is the half width at a particular metal-ligand distance r .

The best least squares fit gave a value of 0.035 Hartrees for $W(*)$, the coefficient b is 0.19378 Hartrees and the exponent is $1.79108 \text{ \AA}^{-1}$ for the Cu-ammonia and Cu-imidazole complexes. Further studies for various other combinations of metals and ligands are underway. Some of our preliminary studies have shown that the parameter W varies not only with the metal-ligand distance, but also with the varying ligands.

The importance of the angular term in the equation (1) can be understood by comparing the energetics of the square planar vs the tetrahedral geometries. The computed energy differences for the square vs tetrahedral complexes show the magnitude of angular term changes and hence the preference for a particular geometry which varies depending on the central metal atom.

Planned Activities

It is our intent to validate the force field parameters for various metals of interest by modeling a variety of known complexes which were not used in parameter development. These parameters will then be included in the TINKER modeling package which is available over the internet. They will also be incorporated into our de novo design software and ligands designed to be selective for various metals of interest. This will be accomplished in the remaining year of the project.

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Department of Energy

Research Projects

The Development of Cavity Ringdown Spectroscopy as a Sensitive Continuous Emission Monitor for Metals

George P. Miller, Mississippi State University

Christopher B. Winstead, Mississippi State University

Research Objective

A critical need exists for the development of methods to monitor toxic metal concentrations in remediation system offgases in real-time at parts-per-billion levels or lower. Although several technology development projects are being pursued to meet the requirements of a multi-element metals continuous emission monitor (CEM), no current technique has met all the requirements of sensitivity and data quality. The use of cavity ringdown spectroscopy (CRS) as an ultra-sensitive analytical technique is a natural extension of previous atomic absorption spectroscopy methods. However, while CRS has rapidly gained popularity among the molecular spectroscopy community, the work reported here concerns the first efforts to apply this technique to analytical atomic spectroscopy. The objective of this project is to combine CRS with the well-established tools for sample atomization, the inductively coupled plasma (ICP) and graphite furnace (GF), to provide a viable technique for on-line, trace level continuous emission monitoring of species such as toxic metals and radionuclides with detection limits comparable to ICP-mass spectroscopy (ICP-MS).

Research Progress and Implications

This report summarizes our progress in the first year of a 3-year project to develop cavity ringdown spectroscopy as a sensitive, continuous emission monitor for metals. Progress has been slightly delayed by problems associated with freeing up the matching funds necessary to purchase a new narrow-linewidth dye laser and the typical problems encountered when departments move into a new building. However, these problems have been largely solved. Our new laser system has recently arrived and additional matching funds have been obtained for the purchase of a graphite furnace. This instrument is on order and will arrive in the near future. The postdoctoral and graduate positions have been filled.

Before discussing our achievements to date, a brief outline of the technique will be useful. In a typical cavity ringdown experiment, a laser pulse is injected into a stable optical cavity formed from two highly reflective dielectric mirrors and is trapped between the mirror surfaces. The light stored in the cavity decays exponentially with a time constant determined by the mirror reflectivity and the sample concentration within the cavity. The decay time is measured using a photomultiplier tube and fitted to a single exponential function which, in turn, yields the sample concentration. For the highest reflectivity mirrors available, a pulse circulating in the cavity can result in kilometers of effective pathlength. To perform elemental analysis using CRS, an atomization source (e.g. ICP & GF) is required (see ref. 1 & refs. therein).

Initial experiments have focused on ICP-CRS using a 1.6 kW, 27.12 MHz argon ICP (standard Fassel torch) equipped with an ultrasonic nebulizer. A frequency doubled Nd:YAG laser pumped tunable dye laser with pulse duration of approximately 10 ns and repetition rate of 10 Hz. The resulting laser output is of the order of 0.3 cm^{-1} linewidth. This is approximately twice the linewidth of the absorption feature, implying that the apparent absorption linewidth is a combination of both the actual absorption and the laser linewidth. As with standard absorption spectroscopy⁴, CRS absorbance measurements require the use of a linewidth narrower than the absorption line. Thus these initial results suffer from a reduced sensitivity since a significant fraction of the pulse energy remains in the cavity even after light in

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resonance with the atomic transition has been absorbed. This problem is eliminated with the use of the new laser system.

Various radii of curvature mirrors, coated for different wavelength ranges, have been tested for cavity construction and stability. The interface between the ICP and optical cavity systems has also been investigated especially with regard to the baseline time constant stability. The cavity has been designed and tested to minimize the fluctuations caused by the introduction of the ICP into the cavity. The stability of the technique has been studied using two very different cavity configurations. Short cavities (56 cm long) were constructed from 0.5 and 5 meter radius of curvature mirrors. Both near confocal (0.5 m) and near planar (5 m) cavity geometries were tested during ICP operation and yielded a standard deviation in baseline (no analyte) ringdown times of approximately 1%. Results obtained both with and without the ICP plasma indicate that while the ICP does not appear to have severe effects on the measured time constant stability, it does slightly reduce the magnitude of the time constant. This implies additional losses in the ICP other than absorption by analyte atoms. Research is currently underway to explain this observation. The effect of spatial filtering and mode matching optical configurations on the input laser pulse have also been evaluated.

Our trace species investigations have focused, to this point, on the detection of Pb using ICP-CRS (although we have also observed Mg and OH, Fig. 7 in Ref. 1 depicts the relative absorbance measured as the laser is tuned across the 283.3 nm Pb absorption line). The initial goal in the operation of an ICP-CRS system is the production of primarily ground state analyte atoms (i.e., similar to ICP-AFS). Full optimization, however, requires consideration of the influence of ICP torch design and operation, observation height within the ICP, gases and gas flow for the ICP torch, wavelength selection, and calibration procedures. Additional important considerations are interference effects, light scatter, sample transport, matrix effects, and spectral interferences.

With the introduction of analyte into the ICP, the ringdown time clearly drops as the solution concentration increases. However, a deviation from linearity is observed at high concentrations. While such effects are common in traditional atomic absorption spectroscopy, an additional component leading to non-linearity in our data is the linewidth of the laser. Research⁴ has found an ~8 times improvement in ringdown response with a reduction to a narrow linewidth. At lower concentrations, an excellent linear response is obtained. Our preliminary results with the old laser system indicate a ppb detection limit for Pb. While this value is still one to two orders of magnitude from theoretical values for ICP-CRS, the new laser has yet to be incorporated and significant work on system optimization remains to be completed. These early results place ICP-CRS among the most sensitive of optical analysis methods for ICPs. Continued improvements are expected, with a complete multi-parameter optimization strategy to be implemented in the future. These improvements should make ICP-CRS a viable alternative to ICP-MS in many analytical environments.

Planned Activities

The remainder of Year 1 will focus a systematic study of ICP-CRS optimization and the determination of detection limits. Parallel to this, design of the GF-CRS interface will begin. In Year 2, evaluation of the argon ICP-CRS will be completed. Preliminary experiments will begin on the viability of using air-ICP-CRS as a, for example, Hg CEM monitor. System optimization of the GF-CRS option will begin. These experiments will continue through Year 3 resulting in a complete evaluation of CRS as an analytical atomic spectroscopic tool.

Information Access

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Department of Energy

Research Projects

New Anion-Exchange Resins for Improved Separations of Nuclear Materials

Dr. Mary E. Barr, Los Alamos National Laboratory

Dr. Richard A. Bartsch, Texas Tech University

Research Objective

The overall objective of our research is to develop a predictive capability which allows the facile design and implementation of multi-functionalized anion-exchange materials which selectively sorb metal complexes of interest from targeted process, waste, and environmental streams. The basic scientific issues addressed are actinide complex speciation along with modeling of the metal complex/functional-site interactions in order to determine optimal binding-site characteristics. Our new ion-exchange resins interface the rapidly developing field of ion-specific chelating ligands with robust, commercial ion-exchange technology. Various Focus Areas and Crosscutting Programs have described needs that would be favorably impacted by the new materials: Efficient Separations and Processing; Plutonium; Plumes; Mixed Waste; High-Level Tank Waste. Sites within the DOE complex which would benefit from the improved anion-exchange technology include Hanford, INEL, Los Alamos, Oak Ridge, and Savannah River.

Research Progress and Implications

As of April 1998, this report summarizes work after 1.6 years of a 3-year project. Our technical approach combines empirical testing with theoretical modeling (applied in an iterative mode) in order to determine optimal binding-site characteristics. We determine actinide-complex speciation in specific media, then develop models for the metal complex/functional-site interactions. Synthesis and evaluation of multi-functionalized extractants and ion-exchange materials that implement key features of the optimized binding site provide feedback to the modeling and design activities. Resin materials which actively facilitate the uptake of actinide complexes from solution should display both improved selectivity and kinetic properties. Our implementation of the bifunctionality concept involves N-derivatization of pyridinium units from a base poly(4-vinylpyridine) resin with a second cationic site such that the two anion-exchange sites are linked by 'spacer' arms of varying length and flexibility.

Actinide-complex speciation: The primary actinides of interest in nitrate solutions are plutonium (IV) and americium (III). We have refined plutonium mono- and di-nitrato formation complexes. As expected, in higher ionic strength media, the formation of the tetranitrato complex shifts to lower acid concentrations than in pure nitric acid. Addition of a water-soluble anion-exchange polymer to solutions of plutonium in nitric acid also shifts the solution equilibrium to favor the dianionic hexanitrato complex, but with K_d values orders of magnitude lower than for the solid resins. Even americium(III), which does not form anionic nitrato complexes in pure nitric acid media, binds to the anion-exchange resins in solutions with excess nitrate. X-ray fluorescence experiments on Eu(III) (an Am surrogate) show that addition of excess nitrate results in the removal of one to two waters of hydration, but we have not been able to determine the exact anionic species. We have, however, begun pilot-scale evaluation of one new resin for the removal of Pu(IV) and Am(III) from process waste solutions.

Synthesis and evaluation of multi-functionalized extractants and ion-exchange materials: We have synthesized and tested a 'systematic series' of bifunctional resins that examines the effects of varying the following conditions:

- 1) The chemical structure of the second cationic site: pyridium > trimethylphosphonium > trimethylammonium.

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- 2) The length and chemical structure of the spacer between the two cationic sites: generally a 4-5 atom spacer is optimal for plutonium uptake. A shorter spacer appears better for americium.
- 3) The percent crosslinking of the substrate: decreasing the crosslinking from 25% to 18% yields a ca. 50-100% increase in K_d with little impact upon resin stability.
- 4) The percent derivatization: performance increases with greater derivatization up to 100%. Most bifunctional resins, however, cannot be derivatized above 75%.

Two manuscripts (published, in press) and several presentations cover much of this work to date. We have synthesized and evaluated the first tri-functional (polystyrene-based) resin for plutonium/americium uptake. Preliminary tests of this particular material were disappointing in that, despite the higher cationic charge density, it did not display the Am(III) affinity that we had hoped for. We have completed synthesis, but not evaluation, of bifunctional extractants. We were able to achieve desired the organic miscibility for the dicationic material by adding two dodecyl groups to the pyridine functionality in the meta positions.

Modeling and design activities: We have developed partial charge and MM2 parameters for Pu, U, Th and Np(IV) nitrate systems. Using these parameters, we can very accurately model the nitrate-actinide interactions. Determination of the charge distribution of the hexanitrate dianions was problematic because of the exceptionally high orbital degeneracy of the complex. We developed a 'theoretical model' compound, the Pu(NO₃) triradical, for which partial charges could be determined using ab initio calculations. Via calculation of the electrostatic interactions between the Pu-hexanitrate dianion and the dicationic "resin site", we have correlated the 'stickiness factor' with experimental K_d s for three series of resins. Correlation is good using both formal charge and partial charge models. Two manuscripts (submitted, in preparation) cover this work to date. The models show that the butylene spacer for the trimethylammonium derivative of polyvinylpyridine changes from an 'anti' configuration in its free state to a 'syn' configuration in the docked state. This observation has led to the hypothesis that a cis-butene spacer may exhibit improved sorption kinetics. We have synthesized, but not yet evaluated, a resin based on this functionality.

Planned Activities

Most of the baseline work was conducted on resins unsuitable for column applications, so we need to correlate those results with the new 21% cross-linked materials. We have begun extending this work to other actinide complexes (chloro, carbonato) and to non-actinide complex anions. Extension of the modeling activities to obtain predictive capabilities will require determination of the major energy terms which factor into the final K_d value. We hope to obtain this information via calorimetry and determination of K_d values for extractants and soluble polymeric forms. We would also like to extend our models to include the polymeric matrices and solvent effects. We anticipate completing the preliminary work in all these areas by the end of FY98/early FY99 and using the final year (FY99) to refine the work and develop applications.

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Research Projects

Novel Ceramic-Polymer Composite Membranes for the Separation of Hazardous Liquid Waste

Yoram Cohen, University of California at Los Angeles

Research Objective

There is a growing need in the fields of pollution prevention, remediation, chemical processing, and water treatment for new processes capable of selectively separating and concentrating a target species, often present in dilute solution. Although membrane systems have been touted as the most probable means to achieve difficult liquid-phase separations, at a reduced energy consumption level relative to conventional technologies (e.g., distillation, extraction), selective membranes with adequate structural integrity and longevity are lacking. In order to meet the above challenge the current project is focused on the development of a novel and robust class of ceramic-supported polymer (CSP) membranes for pollution prevention and remediation applications that require the separation of liquid organic-aqueous and organic-organic mixtures. The CSP membranes combine the unique structural properties of ceramic membrane supports with the chemical selectivity of terminally anchored polymer phases. An important outcome of the project is a new technology for the "tailor design" of novel and robust membranes for in-processes separation for recovery and recycle, effluent treatment, and selective replacement of energy intensive separation processes (e.g., distillation) in a variety of industrial applications.

Research Progress and Implications

This report summarizes the work progress over the last 1.75 years of a 3 year project. The objectives of the project have been to develop a new class of ceramic-supported polymeric membranes that could be tailored-designed for a wide-range of applications in remediation and pollution prevention. To date, a new class of chemically modified ceramic membranes was developed for the treatment of oil-in-water emulsions and for the pervaporation removal of volatile organics from aqueous systems. These new ceramic-supported polymer (CSP) membranes are fabricated by modifying the pore surface of a ceramic membrane support by a graft polymerization process (Chaimberg and Cohen, 1994). The graft polymerization process consists of activating the membrane surface with alkoxy vinyl silanes onto which vinyl monomers are added via free-radical graft polymerization resulting in a thin surface layer of terminally anchored polymer chains. Reaction conditions are selected based on knowledge of the graft polymerization kinetics for the specific polymer/substrate system. The resultant ceramic-supported polymer (CSP) membrane is a composite structure in which mechanical strength is provided by the ceramic support and the selectivity is determined by the covalently bonded polymer brush layer. Thus, one of the unique attributes of the CSP membrane is that it can be used in environments where the polymer layer is swollen (or even completely miscible) in the mixture to be separated (Castro et al., 1993). It is important to note that the above modification process is carried out under mild conditions (e.g., temperature of about 70°C) and is well suited for large scale commercial application.

In a series of studies, the applicability of a polyvinylpyrrolidone CSP membrane was demonstrated for the treatment of oil-in-water emulsion under a variety of flow conditions (Castro et al., 1996). Improved membrane performance was achieved due to minimization of surface adsorption of the oil components. For the special case of long surface chains, significant additional performance improvement (permeate stream was attained at high Reynolds numbers. At the high Reynolds number condition, shear-induced deformation of the terminally anchored polymer chains and as a consequence the screening of the pore entry, resulted in improved permeate quality. Current studies are focused on the optimization of the polymer surface layer and quantification of chemical and hydrodynamic polymer-emulsion interactions.

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Research Projects

Pervaporation is another promising application of CSP membranes. An approach was developed to enable the selection of the specific polymer phase for a given separation task. In a series of studies it was shown, as predicted theoretically, that a Poly(vinyl acetate) CSP (PVAc/CSP) membrane can be used to separate and recover trichloroethylene (TCE) and chloroform from aqueous solutions. Enrichment factors ranging from 60-110 were obtained for the removal of TCE and chloroform from solutions near saturation down to the few parts per million range. These experiments with a tubular CSP membrane (10 cm long and 1 cm internal diameter) demonstrated that, for a single-pass operation of feed solutions of concentrations above about 200 ppm, a pure organic solvent phase was recovered with an additional organic saturated aqueous phase which can be recycled to the feed. The resistance to transport across the CSP membrane was shown to be controlled solely by the concentration boundary layer in the tube-side hydrodynamic; the boundary layer resistance decreased markedly as the tube-side Reynolds number increased to the turbulent regime. The enrichment factor (total solute concentration in permeate/solute concentration in feed) was shown to increase with the polymer graft density. It was shown, for the first time, that pervaporation is possible (with CSP membranes) even with membrane pores much larger than the solute.

The CSP membrane technology has tremendous potential for advancing the use of membranes not only for water treatment applications but also for the separation of organic/organic liquid mixtures. The CSP membranes are ready for testing and scale-up for field applications. In order to adapt the CSP membranes for a large scale applications one could utilize available arrays of tubular membranes or a multichannel membrane assembly. The graft-polymerization procedure will have to be tested for the larger scale modification and adapted as necessary. The testing of large-scale application would require the development of a pilot-scale demonstration project which is necessary for further development work. Such an endeavor, however, is beyond the scope of the present project and could be best achieved through a follow-up demonstration project. For the third year of the present project, further experimental and theoretical development work is planned to optimize the CSP membrane fabrication process.

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Planned Activities

Although a reasonable data set now exist that demonstrates the potential of CSP membranes, the optimization of membrane performance will require additional information on the precise surface morphology and its correlation with graft polymerization conditions and the surface properties of the support. In addition, better understanding of solute-brush layer interactions are needed in order to optimize membrane performance for both filtration and pervaporation applications. Several activities are planned for the third year of the project which include surface characterization by a variety of techniques (e.g., atomic force microscopy, internal reflection IR using model surfaces, contact angle measurements). We also hope to conduct a series of surface characterization studies to determine segment density distribution in collaboration with scientists from NIST. Finally, our pervaporation studies will be extended to demonstrate organic-organic separations and to establish a quantitative relationship between membrane selectivity and polymer layer morphology.

Other Access to Information

Additional information can be found at <http://www.polysep.ucla.edu/>

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Research Projects

Photocatalytic and Chemical Oxidation of Organic Compounds in Supercritical Carbon Dioxide

Dr. Daniel M. Blake, National Renewable Energy Laboratory

Research Objective

- 1) To determine if photocatalytic or other clean oxidation chemistry can be applied to the removal of organic or inorganic contaminants that are introduced into supercritical carbon dioxide during its use as an extraction and cleaning medium in DOE environmental and waste minimization applications. The targets are those contaminants left in solution after the bulk of the solutes have been separated from the fluid phase by changing pressure and/or temperature (but not evaporating the CO₂). This is applicable to development of efficient separations of contaminants from the fluid stream and will strengthen pollution prevention strategies that eliminate hazardous solvents and cleaning agents.
- 2) To explore the use of supercritical carbon dioxide as a solvent for the photocatalytic oxidation of organic compounds and to compare it to other types of oxidation chemistry. This will add to the fundamental understanding of photocatalytic oxidation chemistry of particulate semiconductors and provide new knowledge about conditions that may have relevance to the chemical fixation of carbon dioxide under photocatalytic conditions.

Research Progress and Implications

This report summarizes the results of work done during the first 1.3 years of a three year project. During the first nine months effort focussed on the design, construction and testing of a closed recirculating system that can be used to study photochemistry in supercritical carbon dioxide at pressures up to 5000 psi and temperatures up to about 50° C. This was followed by a period of work in which the photocatalytic oxidation of benzene and acetone in supercritical, liquid, and gaseous carbon dioxide containing dissolved oxygen was demonstrated. The photocatalyst was titanium dioxide supported on glass spheres. This was the first time it was possible to observe photocatalytic oxidation in a supercritical fluid and to compare reaction in the three fluid phases of a solvent. This also demonstrated that it is possible to purify supercritical and liquid carbon dioxide using photochemical oxidation with no chemical additions other than oxygen.

The oxidation of benzene produced no intermediates detectable using on line spectroscopic analysis or by gas chromatographic analysis of samples taken from the flow system. The catalyst surface did darken as the reaction proceeded indicating that oxidation products were accumulating on the surface. This is analogous to the behavior of aromatic compounds in air phase photocatalytic oxidation. The reaction of acetone under similar conditions resulted in the formation of low levels of by-products. Two were identified as products of the reaction of acetone with itself (4-methyl-3-penten-2-one and 4-hydroxy-4-methyl-2-pentanone) using gas chromatography with a mass spectrometer detector. Two other by-products also appear to be from the self-reaction of acetone. By-products of this type had not been observed in prior studies of the gas-phase photocatalytic oxidation of acetone. The by-products that have been observed can also be oxidized under the treatment conditions.

The above results establish that photocatalytic oxidation of organic compounds in supercritical carbon dioxide can be achieved. Until recently it was not possible for us to obtain high quality, quantitative kinetic data. The original flow cell used to obtain UV-Visible spectra on the recirculating fluid did not provide quantitative concentration data because the sapphire windows did not have adequate transmission characteristics below about 240 nm. A pair of windows with better transmission properties arrived as this report was being prepared.

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While waiting for the replacement windows for the flow cell, the concentration of reactants was monitored by withdrawing samples of the fluid stream for gas chromatographic analysis. This allowed progress to be made in determining some of the factors that affected the rates of reaction in a qualitative sense but the results had large error bars due to the difficulty in obtaining reproducible samples from the pressurized system using gas tight syringes. This problem was recently solved by incorporating a gas chromatograph with automatic sampling valves into the flow system.

The two on line analytical methods will now result in reliable analytical data that can be used to follow the reaction kinetics and detect and identify reaction intermediates and by-products, if any are formed.

Planned Activities

During the next four months of work quantitative kinetic data will be obtained for the photocatalytic oxidation of benzene, acetone, and ethanol in supercritical, liquid, and gas phase carbon dioxide. The nature of species adsorbed on the catalyst surface will be explored using extraction and analysis by ion chromatography or high-pressure liquid chromatography. This work will be done in collaboration with chemists at the University of Colorado at Denver. Later work will compare the results of the photocatalytic oxidation with thermal oxidation in supercritical carbon dioxide and test compounds that model those found in cleaning operations that use liquid or supercritical carbon dioxide.

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Research Projects

Removal of Heavy Metals and Organic Contaminants from Aqueous Streams by Novel Filtration Methods

Dr. Nelly M. Rodriguez, Northeastern University

Research Objective

Graphite nanofibers are a new type of material consisting of nanosized graphite platelets where only edges are exposed. Taking advantage of this unique configuration our objective is:

- To produce graphite nanofibers with structural properties suitable for the removal of contaminants from water.
- To test the suitability of the material in the removal of organic from aqueous solutions.
- To determine the ability of the nanofibers to function as an electrochemical separation medium the selective removal of metal contaminants from solutions.

Research Progress and Implications

This report summarizes work after 1.5 of a 3-year project. During this period, efforts have been concentrated on the production, characterization, and optimization of graphite nanofibers (GNF). This novel material has been developed in our laboratory from the metal catalyzed decomposition of certain hydrocarbons⁽¹⁾. The structures possess a cross-sectional area that varies between 5 to 100 nm and have lengths ranging from 5 to 100 nm⁽²⁾. High-resolution transmission electron microscopy studies have revealed that the nanofibers consist of extremely well-ordered graphite platelets, which are oriented in various directions with respect to the fiber axis⁽³⁾. The arrangement of the graphene layers can be tailored to a desired geometry by choice of the correct catalyst system and reaction conditions, and it is therefore possible to generate structures where the layers are stacked in a "ribbon", "herring-bone", or "stacked" orientation. The research has been directed on two fronts: (a) the use of the material for the removal of organic contaminants, and (b) taking advantage of the high electrical conductivity as well as high surface area of the material to use it as electrode for the electrochemical removal of metal pollutants from aqueous streams.

- (a) Use of GNF in the Removal of Organic Contaminants from Water. In the first part of this project the suitability of graphite nanofibers for the adsorption of selected organic molecules from aqueous solutions was tested by allowing a solution of a given organic to interact with selected samples of GNF. In a typical experiment, 0.2 g of the carbonaceous solid was placed in a solution containing 0.5 mL of an ethyl or butyl alcohol in 60 mL of deionized water. The material was continuously stirred and maintained at room temperature for up to 160 hours. Care was taken to prevent loss of the alcohol due to evaporation by keeping the container covered. The uptake of alcohol by the carbon was monitored as a function of time by taking samples of the solution at various periods of time that were analyzed by Gas Chromatography. Identical experiments were conducted using an active carbon sample possessing a surface area ~ 7.5 times that measured for GNF. Carbon nanofibers possessing a high degree of crystalline order have been found to exhibit excellent adsorption characteristics for the removal of small amounts of alcohol from aqueous solution. A comparison with active carbon shows that even though the nanofibers have a surface area that is 7 times lower their performance for this separation process is far superior to that displayed by the former material. A further feature to emerge from this work is the finding that pre-treatment conditions have a critical impact on the subsequent adsorption behavior; while prolonged immersion in hydrochloric was found to be extremely beneficial, a similar treatment in nitric acid virtually nullified the advantages of using nanofibers for the process.

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- (b) Use Of GNF for the Extraction of Metallic Contaminants from Aqueous Streams The potential of GNF for the removal of metals from aqueous solutions was tested in a specially built plug flow cell, which consists of two chambers filled with the carbon material. Details of the design of the cell are well documented in the literature^(4,5). In this arrangement, nanofibers in one of the chambers function as the cathode, whereas the material placed in the second compartment acts as the anode. A saturated calomel electrode was used as reference. Water is purified by flowing a solution through the cell where the metal ions are removed from solution via an electrochemical reduction process that occurs on the nanofibers present in the cathode. Once the nanofibers are saturated with the metal, the contaminant can be collected in conjunction with the carbonaceous material or, if desired, discharged into a more concentrated solution by switching the voltage. This process allows for both the purification of water as well as the recovery of the metal in a higher concentration for further application. These experiments were performed by applying a potential to the cell, which is controlled by a CMS300 PC3 potentiostat. Concentration of ions were determined by an induced coupled argon plasma (Leeman Plasma-Spec).

Preliminary work indicates that when a 170 ppm copper sulfate in 0.0166 M sulfuric acid solution (ion source) is passed over a 2.0 gram GNF bed, 2 cm in length, then up to 97% of the copper content is eliminated from the solution at a -8.5 V.

References

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Planned Activities

- We plan to use GNF for the removal of a variety of organic contaminants from aqueous solution and at the same time, develop methods for the recovery of these chemicals.
- In a complementary series of experiments efforts will be focused on the examination of various nanofiber surface treatments in an attempt to enhance their adsorption capacity.
- An investigation of the adsorption efficiency of GNF as a function of increasing the surface area of the material from 50 to 600 will be carried out.
- The effect on adsorption characteristics of organics resulting from an expansion of the GNF lattice via insertion of selected groups within the layers will be conducted.
- Finally, we shall explore the impact of increasing the degree of crystallinity of the GNF on the use of the material as an electrode in electrochemical devices.