

**THERMATRIX, INC.**  
**(formerly PURUS, INC.)**  
**(Photolytic Oxidation Process)**

**TECHNOLOGY DESCRIPTION:**

The photolytic oxidation process indirectly destroys volatile organic compounds (VOC) in soil and groundwater. The process uses a xenon pulsed-plasma flash-lamp that emits short wavelength ultraviolet (UV) light at very high intensities. The process strips the contaminants into the vapor phase, and the UV treatment converts the VOCs into less hazardous compounds.

Photolysis occurs when contaminants absorb sufficient UV light energy, transforming electrons to higher energy states and breaking molecular bonds (see figure below). Hydroxyl radicals, however, are not formed. The process requires the UV light source to emit wavelengths in the regions absorbed by the contaminant. An innovative feature of this technology is its ability to shift the UV spectral output to optimize the photolysis.

The process uses vacuum extraction or air stripping to volatilize VOCs from soils or groundwater, respectively. VOCs then enter the photolysis reactor, where a xenon flashlamp generates UV light. The plasma is produced by pulse discharge of electrical energy across two electrodes in the lamp. Ninety-nine percent destruction occurs within seconds, allowing continuous operation. Because organics are destroyed in the vapor phase, the process uses less energy than a system treating dissolved organics.

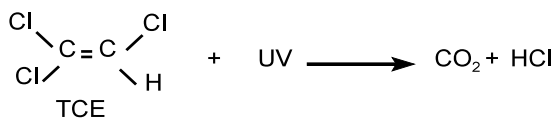
**WASTE APPLICABILITY:**

The photolytic oxidation process is designed to destroy VOCs, including dichloroethene (DCE), tetrachloroethene (PCE), trichloroethene (TCE), and vinyl chloride volatilized from soil or groundwater. Destruction of other VOCs, such as benzene, carbon tetrachloride, and 1,1,1-trichloro-ethane, is under investigation.

**STATUS:**

The photolytic oxidation process was accepted into the SITE Emerging Technology Program in March 1991. Field testing of a full-scale prototype began in October 1991. The test was conducted at the Lawrence Livermore National Laboratory Superfund site in California. The site contains soil zones highly contaminated with TCE.

During the field test, a vacuum extraction system delivered contaminated air to the unit at air flows up to 500 cubic feet per minute (cfm). Initial TCE concentrations in the air were approximately 250 parts per million by volume. The contaminant removal goal for the treatment was 99 percent. Vapor-phase carbon filters were placed downstream of the unit to satisfy California Air Quality emission control requirements during the field test. Test results are discussed below. The Final Report (EPA/540/R-93/516), the Summary Report (EPA/540/SR-93/516), and the Technology Bulletin (EPA/540/F-93/501) have been published.



UV Photolysis of TCE

The low-wavelength UV emissions allowed direct photolysis of many VOCs, particularly chlorinated compounds and freons, that would not have been possible with commercial mercury vapor lamps. TCE, PCE, and DCE were quickly destroyed. To be rapidly photolyzed, some VOCs require photosensitization or an even lower-wavelength light source.

TCE results are shown in the table below. TCE removal yielded undesirable intermediates. Greater than 85 percent of the TCE chain photo-oxidation product is dichloroacetyl chloride (DCAC). Further oxidation of DCAC is about 100 times slower than TCE photolysis and forms dichlorocarbonyl (DCC) at about 20 percent yield. At this treatment level, the DCC concentration may be excessive, requiring additional treatment. Further studies should focus on (1) the effectiveness of dry or wet scrubbers for removing acidic photo-oxidation products, (2) development of thermal or other methods for posttreatment of products such as DCAC, and (3) the use of shorter-wavelength UV lamps or catalysts to treat a broader range of VOCs.

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**TRINITY ENVIRONMENTAL TECHNOLOGIES, INC.**  
**(PCB- and Organochlorine-Contaminated Soil Detoxification)**

**TECHNOLOGY DESCRIPTION:**

This technology uses an aprotic solvent, other reagents, and heat to dehalogenate polychlorinated biphenyls (PCB) in solids to inert biphenyl and chloride salts (see figure below). First, solid material is sized to allow better contact between the reagents and PCBs. In a continuous flow reactor, the soils are heated to drive off excess water. Reagents are then added to destroy the PCBs.

The reagent, consisting of a solvent and an inorganic alkali material, completely strips chlorine from the PCB molecule. Excess alkali can be easily neutralized and is reusable in the process. Treated soil can be returned to the excavation once analytical results show that PCBs have been destroyed.

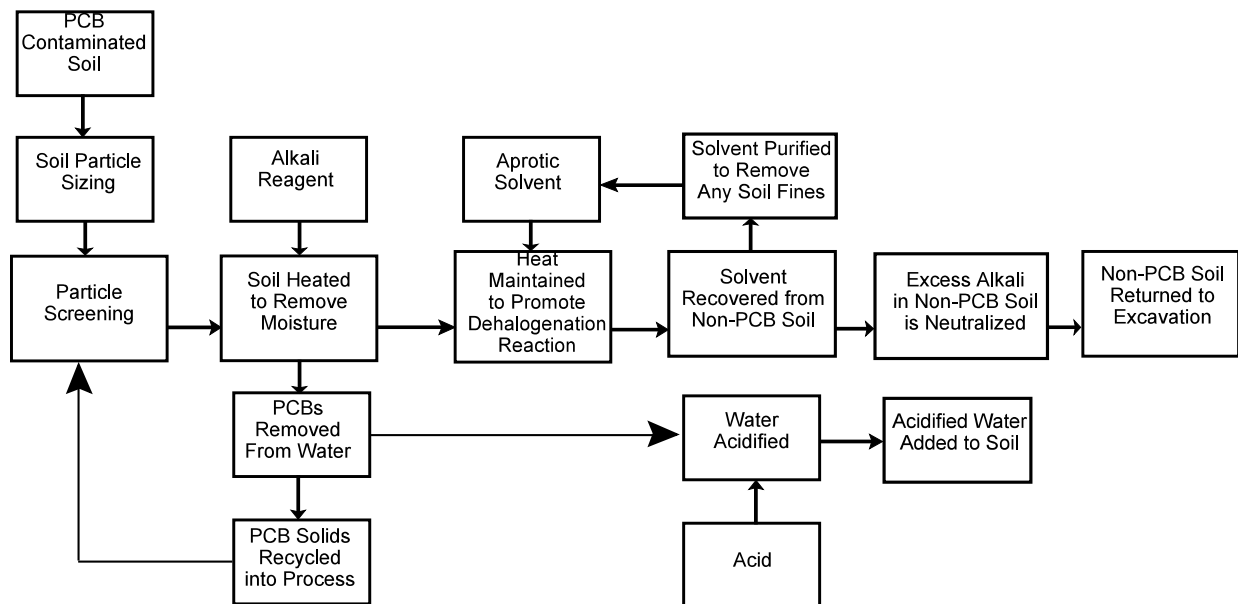
Gas chromatography/mass spectroscopy analyses of processed PCB materials show that the process produces no toxic or hazardous products.

A chlorine balance confirms that PCBs are completely dehalogenated. To further confirm chemical dehalogenation, inorganic and total organic chloride analyses are also used. The average total chloride recovery for treated soils is greater than 90 percent.

The commercial process is expected to be less costly than incineration but more expensive than land disposal. Since no stack emissions are produced, permitting the process for a remediation would be easier than incineration.

**WASTE APPLICABILITY:**

The process can treat many different solid and sludge-type materials contaminated with PCB Aroclor mixtures, specific PCB congeners, pentachlorophenol, and individual chlorinated dioxin isomers. However, other chlorinated hydrocarbons such as pesticides, herbicides, and polychlorinated dibenzofurans could also be treated by this technology.



PCB Soil Detoxification Process

## **STATUS:**

This technology was accepted into the SITE Emerging Technology Program in July 1990. The current system was developed by researchers in early 1991, after the original aqueous, caustic-based system proved ineffective at destroying PCBs.

The SITE project was completed in 1992. Trinity is investigating further improvements to the technology. Due to cost limitations, no commercialization of the investigated process is expected. A final report will not be published.

In bench-scale studies, synthetically contaminated materials have been processed to eliminate uncertainties in initial PCB concentration. This chemical process has reduced PCB concentrations from 2,000 parts per million (ppm) to less than 2 ppm in about 30 minutes using moderate power input. Further laboratory experiments are underway to determine the reaction mechanism and to enhance PCB destruction. Through additional experimentation, Trinity Environmental Technologies, Inc., expects to reduce processing time through better temperature control, more efficient mixing, and possibly more aggressive reagents.

A modular pilot-scale processor has been planned that uses several heating zones to preheat and dry the contaminated soil, followed by PCB destruction. The pilot process would be capable of processing 1 ton per hour initially. Additional modules could be added to increase process capacity, as needed. Contaminated soils from actual sites will be used to test the pilot-scale processor instead of the synthetically contaminated soils used in bench-scale testing.

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**UNITED KINGDOM ATOMIC ENERGY AUTHORITY**  
**(formerly AEA Technology Environment)**  
**(Soil Separation and Washing Process)**

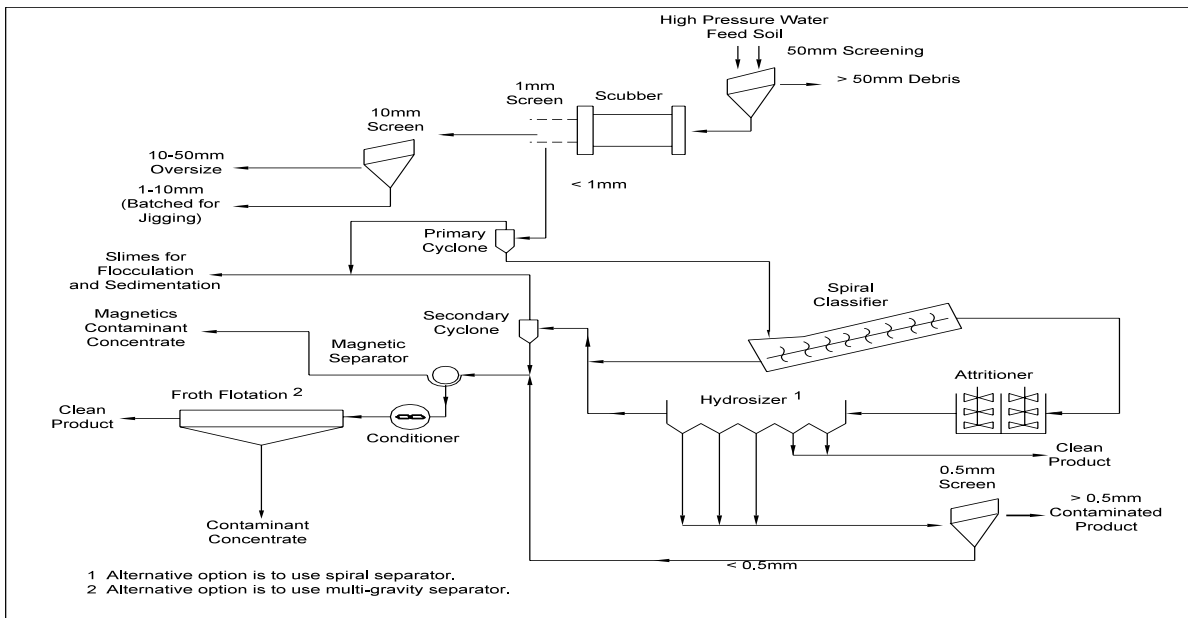
**TECHNOLOGY DESCRIPTION:**

AEA Technology Environment (AEA) has developed an ex situ soil separation and washing process that uses mineral processing technology and hardware. The process can be used (1) as a volume reduction process to release clean soil fractions and concentrate contaminants, or (2) as a pretreatment stage in a treatment train.

Because each contaminated soil is different, AEA has developed a custom physical treatment process for soil using a three-stage process: laboratory-scale characterization, separation testing and assessment, and treatment and data analysis.

AEA is experienced in conducting pilot plant testing programs on contaminated soil and mineral ores. In addition, AEA uses computer software designed to reconcile material flow data. The results of data processing lead to recommendations for full-scale

continuous flow sheets with predicted flows of solids, associated contaminant species, and water. Contaminant levels and distributions to the various products can also be estimated. Such data are required to estimate the cost and potential success of the full-scale remediation process plant. Flow sheet configuration is flexible and can be customized to address the nature and contamination of each soil or waste. A typical schematic flow sheet of the process is shown in the diagram on the previous page. The flow sheet involves screening the raw feed at 50 millimeters (mm) under powerful water jets to deagglomerate the mass. Debris greater than 50 mm in size is often decontaminated. Remaining solids and the water are passed through a drum scrubber that deagglomerates the mass further because agitation is more intense. It breaks down clay lumps and adhering material into suspension, except for surface coatings of clay and oil on fine particles. The drum scrubber discharge is screened at 1 mm, and the oversize discharge is screened at 10 mm. The 10 to 50 mm size range is often clean debris; if it is not clean then it can



Generalized Flowsheet for the Physical Treatment of Contaminated Soil

be crushed and refeed to the system. Material from 1 to 10 mm is often contaminated and requires further treatment.

For all material less than 1 mm, the clay and water are removed by hydrocycloning. The fine product, less than 10 micrometers (m), is flocculated and thickened to recover the process water for recycling. Thickened clay product, usually containing concentrated contaminants, passes to further treatment or disposal. Sands from the hydrocycloning step are further dewatered in a classifier before the third and most intense deagglomeration operation.

An attrition scrubber removes the remaining surface contamination and degrades fine clayballs. Having completed deagglomeration, the soil is fractionated by particle size or separated by specific gravity. A second stream of particles less than 10 mm is removed by hydrocycloning and joins the primary product stream. Finer sands and silt are screened at 500 mm to yield a contaminated sand for disposal or retreatment. A 10 to 500 mm fraction can be separated magnetically, by flotation, by multigravity separation, or by a combination of these methods. These stages produce a contaminant concentrate, leaving the remaining material relatively contaminant free.

The soil separation and washing process is designed to remove metals, petroleum hydrocarbons, and polynuclear aromatic hydrocarbons from soil. The process may be applied to soils from gas and coke works, petrochemical plants, coal mines, iron and steel works, foundries, and nonferrous smelting, refining, and finishing sites. The process can also treat sediments, dredgings, sludges, mine tailings, and some industrial wastes.

## **STATUS:**

The technology was accepted into the SITE Emerging Technology Program in July 1991 and completed in 1994. A Final Report was delivered to the U.S. EPA in 1994, and work done with this technology was presented the same year at the 87<sup>th</sup> Annual Meeting and Exhibition of the Air and Waste Management Association, the 20<sup>th</sup> Annual RREL Hazardous Waste Research Symposium, and the 5<sup>th</sup> Forum on Innovative Hazardous Waste Treatment Technologies: Domestic and International. Pilot trials were conducted on 30 tons of soil at a throughput rate of 0.5 ton per hour. Several test runs were performed to evaluate different flow sheet configurations. Reports on this technology can be obtained from the U.S. EPA.

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**UNIVERSITY OF DAYTON RESEARCH INSTITUTE  
(Photothermal Detoxification Unit)**

**TECHNOLOGY DESCRIPTION:**

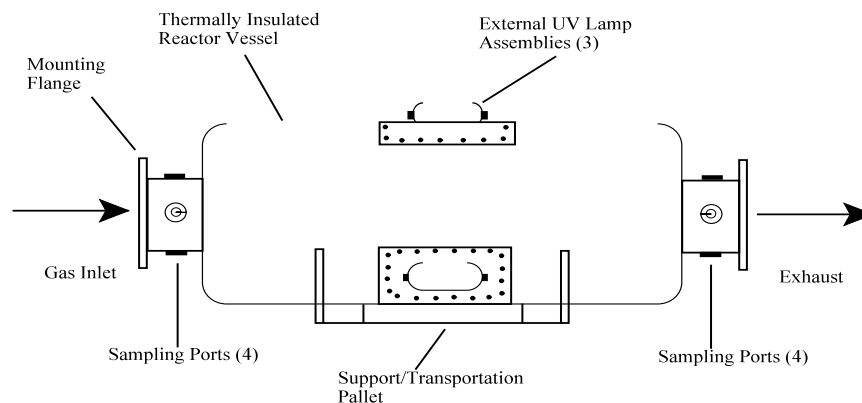
Photolytic reactions (reactions induced by exposure to ultraviolet [UV] light) can destroy certain hazardous organic wastes at relatively low temperatures. However, most photochemical processes offer relatively limited throughput rates and cannot completely mineralize the targeted wastes. For aqueous waste streams, these problems have been partially addressed by using indirect photochemical reactions involving a highly reactive photolytic initiator such as hydrogen peroxide or heterogeneous catalysts. Recently, the University of Dayton Research Institute (UDRI) developed a photolytic detoxification process to treat the gas waste streams. This process is clean and efficient and offers the speed and general applicability of a combustion process.

The photothermal detoxification unit (PDU) uses photothermal reactions conducted at temperatures higher than those used in conventional photochemical processes (200 to 500°C versus 20°C), but lower than combustion temperatures (typically greater than 1,000°C). At these elevated temperatures, photothermal reactions are energetic enough to destroy many wastes quickly and efficiently without producing complex and potentially hazardous by-products.

The PDU is a relatively simple device, consisting of an insulated reactor vessel illuminated with high-intensity UV lamps. As shown in the figure below, the lamps are mounted externally for easy maintenance and inspection. Site remediation technologies that generate high-temperature gas streams, such as thermal desorption or in situ steam stripping, can incorporate the PDU with only slight equipment modifications. The PDU can be equipped with a pre-heater for use with soil vapor extraction (SVE). Furthermore, the PDU can be equipped with conventional air pollution control devices for removal of acids and suspended particulates from the treated process stream. The PDU shown in the figure below is also equipped with built-in sampling ports for monitoring and quality assurance and quality control.

**WASTE APPLICABILITY:**

According to UDRI, the PDU has proven extremely effective at destroying the vapors of polychlorinated biphenyls, polychlorinated dibenzodioxins, polychlorinated dibenzofurans, aromatic and aliphatic ketones, and aromatic and aliphatic chlorinated solvents, as well as brominated and nitrous wastes found in soil, sludges, and aqueous streams. The PDU can be incorporated with most existing and proposed



Photothermal Detoxification Unit (PDU)

remediation processes for clean, efficient, on-site destruction of the off-gases. More specifically, high-temperature processes can directly incorporate the PDU; SVE can use the PDU fitted with a preheater; and groundwater remediation processes can use the PDU in conjunction with air stripping.

## STATUS:

The technology was accepted into the Emerging Technology Program in August 1992, and development work began in December 1992. The evaluation was completed in 1994. The Emerging Technology Report (EPA/540/R-95/526), the Emerging Technology Bulletin (EPA/540/F-95/505) and the Emerging Technology Summary (EPA/540/SR-95/526) are available from EPA. An article was also published in the *Journal of Air and Waste Management*, Volume 15, No. 2, 1995.

Emerging Technology Program data indicate that the technology performs as expected for chlorinated aromatic wastes, such as dichlorobenzene and tetrachloro-dibenzodioxin, and better than expected for relatively light chlorinated solvents, such as trichloroethene (TCE) and tetrachloroethene. Further tests with selected mixtures, including benzene, toluene, ethyl-benzene, xylene, TCE, dichlorobenzene, and water vapor, show that the process is effective at treating wastes typically found at many remediation sites. Adequate scaling and performance data are now available to proceed with the design and development of prototype full-scale units for field testing and evaluation.

Through prior programs with the U.S. Department of Energy, technology effectiveness has been thoroughly investigated using relatively long wavelength UV light (concentrated sunlight with wavelengths greater than 300 nanometers). Limited data have also been generated at shorter wavelengths (higher energy) using available industrial UV illumination systems.

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**UNIVERSITY OF HOUSTON**  
**(Concentrated Chloride Extraction and Recovery of Lead)**

**TECHNOLOGY DESCRIPTION:**

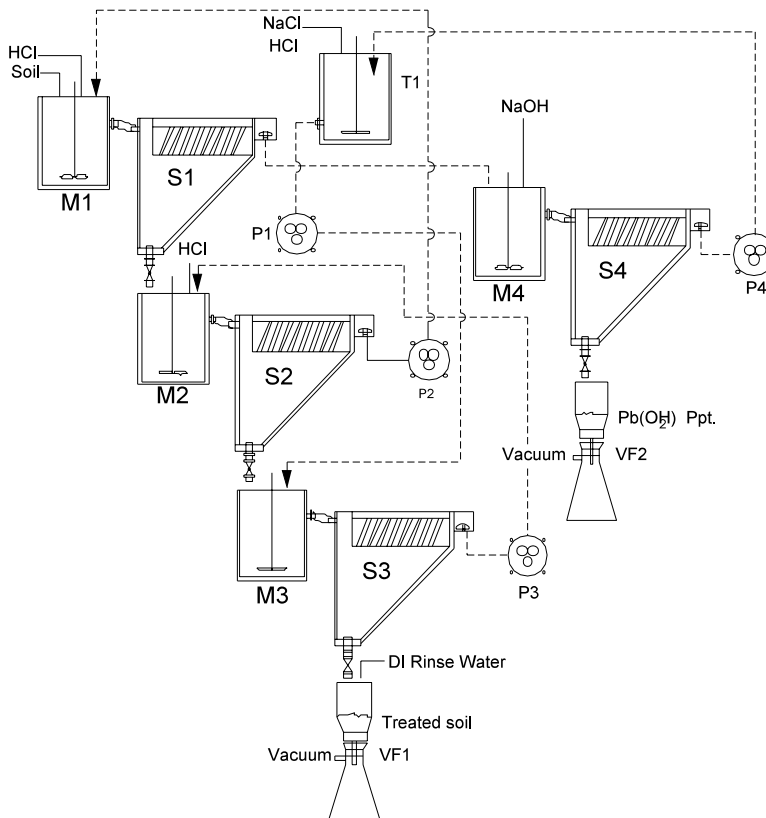
This technology recovers lead from soils using an aqueous solvent extraction process that takes advantage of the high solubility of chlorocomplexes of lead. The extract solution contains greater than 4 molar sodium chloride and operates at a pH of 4. The figure below depicts a bench-scale model of the three-stage continuous countercurrent pilot plant used to study the process.

To operate the pilot plant, soil is sieved to remove particles greater than 1.12 millimeters in diameter. The soil is then placed in the first chloride extraction tank (M1) for extraction with concentrated chloride solution. The resulting soil and solvent slurry passes

into a thickener (S1). The soil and solvent slurry has an average residence time of 1 hour in each extraction tank in the system.

The bottoms of the thickener flow by gravity to the second chloride extraction tank (M2). The solution exiting the second chloride extraction tank flows to the second thickener (S2). The bottoms of the second thickener feed the third stage.

The third stage is the last soil stage and the first solvent stage; fresh solvent enters the system at stage three. The bottoms of the third thickener (S3) flow by gravity into the soil rinse system (VF1) to remove excess salt. Soil rinsed in VF1 is clean product soil. The overflows from S3 pass to M2, the overflows from S2 pass to the M1, and the overflows from S1



Concentrated Chloride Extraction and Recovery  
of Lead (Bench-Scale Process)

pass to the lead precipitation system (M4/S4). In M4/S4, lead hydroxide  $[\text{Pb}(\text{OH})_2]$  is recovered by simply raising the pH of the spent extraction solution to 10. After  $\text{Pb}(\text{OH})_2$  removal, the spent chloride solution flows to the solvent makeup unit (T1) where it is acidified to pH 4 in preparation for reuse.

This technology produces (1) treated soil, suitable for replacement on site, and (2)  $\text{Pb}(\text{OH})_2$  that may be suitable for reprocessing to recover pure lead. The ease of solvent regeneration minimizes waste disposal. Solvent recycling is very successful, and pilot-plant tests have required little or no salt or water makeup.

The pilot plant has treated soil from two lead battery waste sites (LBWS). One LBWS soil contained a high percentage of fines (about 50 percent clay and silt), and the other contained a low percentage of fines (less than 20 percent clay and silt). The pilot plant's method of transferring soil by gravity eases much of the soil handling problems typical of high clay soils. After treatment, both soils easily passed the Toxicity Characteristic Leaching Procedure test. The total lead concentration in the high fines and low fines soil was reduced from 7 percent to about 0.15 percent and from 1.5 percent to 0.07 percent, respectively.

### **WASTE APPLICABILITY:**

This technology removes high concentrations of lead from soil, particularly at LBWS, while producing a treated soil that can be used as backfill and a recyclable, concentrated lead salt.

### **STATUS:**

This technology was accepted into the SITE Emerging Technology Program in September 1994. Batch extraction testing was completed in 1995. Treatability tests using the pilot plant to process high and low fines soils were completed in August 1996. The high fines soil came from a LBWS located in Houston, Texas, and the low fines soil came from the Sapp Battery National Priority List site in Florida. Future plans include expanding the applications of the technology by studying its effect on other wastes in soils. The technology evaluation was scheduled to be completed by August 1998.

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## UNIVERSITY OF SOUTH CAROLINA (In Situ Mitigation of Acid Water)

### TECHNOLOGY DESCRIPTION:

The in situ acid water mitigation process addresses the acid drainage problem associated with exposed sulfide-bearing minerals from sources including mine waste rock and abandoned metallic mines. Acid drainage forms under natural conditions when iron disulfides are exposed to the atmosphere and water, spontaneously oxidizing them to produce a complex of highly soluble iron sulfates and salts. These salts hydrolyze to produce an acid-, iron-, and sulfate-enriched drainage that adversely affects the environment.

The in situ mitigation strategy modifies the hydrology and geochemical conditions of the site through land surface reconstruction and selective placement of limestone.

Limestone is used as the alkaline source material because it has long-term availability, is generally inexpensive, and is safe to handle. For the chemical balances to be effective, the site must receive enough rainfall to produce seeps or drainages that continually contact the limestone. Rainfall, therefore, helps to remediate the site, rather than increasing the acid drainage.

During mine construction, lysimeters and limestone chimneys are installed to collect surface runoff and funnel it into the waste rock dump. Acidic material is capped with impermeable material to divert water from the acid cores. This design causes the net acid load to be lower than the alkaline load, resulting in benign, nonacid drainage.



Overview of Site Lysimeters

## **WASTE APPLICABILITY:**

The technology mitigates acid drainage from abandoned waste dumps and mines. It can be applied to any site in a humid area where limestone is available.

## **STATUS:**

This technology was accepted into the SITE Emerging Technology Program in March 1990. Studies under the Emerging Technology Program are complete. A peer-reviewed journal article has been prepared and submitted.

For the SITE evaluation, six large-scale lysimeters (12 feet wide, 8 feet high, and 16 feet deep) were constructed and lined with 20-mil polyvinyl chloride plastic (see photograph on previous page). The lysimeters drained through an outlet pipe into 55-gallon collection barrels. Piezometers in the lysimeter floor monitored the hydrology and chemistry of the completed lysimeter. During June 1991, 50 tons of acid-producing mine waste rock was packed into each lysimeter.

The effluent from each lysimeter was monitored for 1 year to establish a quality baseline. In the second phase of the study, selected lysimeters were topically treated, maintaining two lysimeters as controls to compare the efficacy of the acid abatement strategy. In addition, a rain gauge was installed at the site for mass balance measurements. An ancillary study correlating laboratory and field results is complete.

In the last phase of the 3-year study, little if any leachate was collected due to drought conditions in the southeast U.S. With the return of normal rainfall, sufficient leachate was collected to compare the treated lysimeters against the controls to evaluate the treatment's effectiveness. The treated lysimeters, in general, showed a 20 to 25 percent reduction in acid formation. The acidities measured about 10,000 milligrams per liter (mg/L) for the untreated lysimeters, while acidities from the treated lysimeters measured about 7,000 mg/L. This study was conducted on a very high acid-producing waste rock, representing a near worst-case situation. The process should be more successful on milder acid sources.

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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:**

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.

Recent tests have shown that the technology can be used to remove heavy metals selectively from waste solutions that contain orders of magnitude of higher concentrations of Al, and that it can be used to remove Sr from highly alkaline wastewater (pH>14, for example, alkaline nuclear wastes).

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**UNIVERSITY OF WISCONSIN-MADISON**  
**(Photoelectrocatalytic Degradation and Removal)**

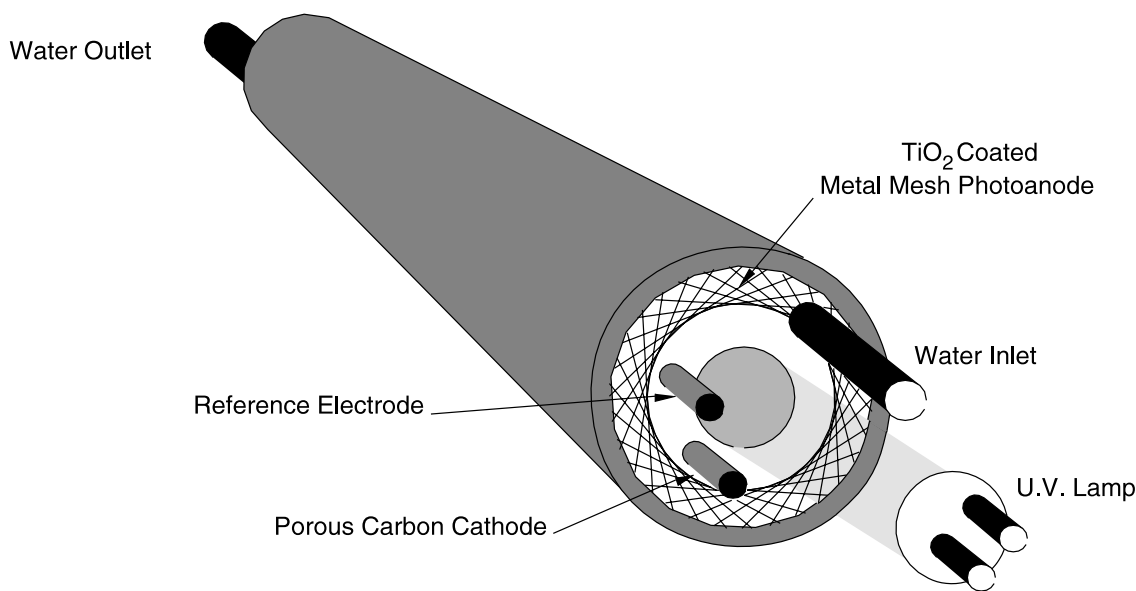
**TECHNOLOGY DESCRIPTION:**

The University of Wisconsin-Madison (UW-Madison) is developing a photocatalytic technology that uses titanium dioxide (TiO<sub>2</sub>) 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<sub>2</sub> 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<sub>2</sub> 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 is capable of collecting 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<sub>2</sub> systems used to treat 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<sub>2</sub> treatment of contaminated groundwater.

This technology represents an improvement 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. It also eliminates the need for an additional unit to separate and recover the catalyst from the purified water after the reaction is complete.



Photoreactor Design using Ceramic Film

## 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 (less than 0.1 standard cubic feet per minute).

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**UV TECHNOLOGIES, INC.**  
**(formerly Energy and Environmental Engineering, Inc.)**  
**(UV CATOX™ Process)**

**TECHNOLOGY DESCRIPTION:**

The UV CATOX™ process photochemically oxidizes organic compounds in wastewater using hydrogen peroxide, a chemical oxidant, ultraviolet (UV) radiation, and a photocatalyst. The photochemical reaction has the potential to reduce high concentrations (200,000 or more parts per million [ppm]) of organics in water to nondetectable levels. The energy from UV radiation is predominantly absorbed by the organic compound and the oxidant, making both species reactive. The process can be used as a final treatment step to reduce organic contamination in industrial wastewater and groundwater to acceptable discharge limits.

The existing bench-scale system treats solutions containing up to several thousand ppm of total organic carbon at a rate of 3 gallons per minute. The bench-scale system consists of a photochemical reactor, where oxidation occurs, and associated tanks, pumps, and controls. The UV lamps are high-intensity lamps that penetrate the wastewater more effectively. The portable, skid-mounted system's design depends on the chemical composition of the wastewater or groundwater being treated.

Typically, the contaminated wastewater is pumped through a filter unit to remove suspended particles. Next, the filtrate is mixed with stoichiometric quantities of hydrogen peroxide. Finally, this mixture is fed to the photochemical reactor and irradiated. Reaction products are carbon dioxide, water, and the appropriate halogen acid. Reaction kinetics depend on (1) contaminant concentration, (2) peroxide concentration, (3) irradiation dose, and (4) radiation spectral frequency.

**WASTE APPLICABILITY:**

The UV CATOX™ process treats industrial wastewater and groundwater containing organics at concentrations up to several thousand ppm. Destruction efficiencies greater than two orders of magnitude have been obtained for chlorobenzene, chlorophenol, and phenol, with low to moderate dose rates and initial concentrations of 200 ppm. Destruction efficiencies of three orders of magnitude have been demonstrated on simulated industrial waste streams representative of textile dyeing operations, with higher dose rates and an initial concentration of 200 ppm.

**STATUS:**

Studies of the UV CATOX™ process under the SITE Emerging Technology Program are complete, and the technology has been invited to participate in the SITE Demonstration Program. The Emerging Technology Report (EPA/540/SR-92/080), Emerging Technology Bulletin (EPA/540/F-92/004), and Emerging Technology Summary (EPA/540/SR-92/080) are available from EPA.

Work involving the on-line production of oxidants and the effectiveness of the photocatalytic substrate is underway under funding from EPA Small Business Industry Research Phase II and Phase I awards.

Representative results from recent trials using the UV CATOX™ process are summarized in the table below. Results are shown as the electric energy dose per gram-mole of initial contaminant to cause one decade of contaminant destruction.

Contaminant <sup>1)</sup>	Dose (kW-hr/ gmole/decade) <sup>2)</sup>
Chlorobenzene	7
Trichloroethene	5
Trichloroethane [500]	1
Tetrachloroethene	6
1,1,1-Trichloroethane	33
1,1,1-Trichloroethene [1,000]	7
Benzene, toluene, ethylbenzene, & xylene	5
Reactive Black Dye 5	26
Direct Yellow Dye 106	103
Direct Red Dye 83	31
Reactive Blue Dye 19	50
1-Chloronaphthalene [15]	27
Ethylene, diamine, & triacetic acid	17
Methanol	3
Textile waste (sulfur & indigo dyes) [740]	11
Textile waste (fiber reactive dyes) [270]	7
Chemical waste (formaldehyde & thiourea) [8,200]	1

<sup>1)</sup>All are 100 parts per million,  
except as noted

<sup>2)</sup> kilowatt-hour per gram-mole per decade

The technology has been improved since the EPA reports were published. These improvements include (1) using the UV lamp as the energy source; (2) improving the photochemical reactor design; (3) improving the lamp design, including lamp intensity and spectral characteristics; and (4) fixing the catalyst.

A cost-competitive UV CATOX™ system can be designed and built to treat industrial wastewater with contaminant levels of 10 to 10,000 ppm.

### FOR FURTHER INFORMATION:

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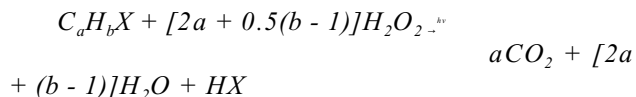
**UV TECHNOLOGIES, INC.**  
**(formerly Energy and Environmental Engineering, Inc.)**  
**(UV CATOX™ Process)**

**TECHNOLOGY DESCRIPTION:**

The UV CATOX™ process photochemically oxidizes organic compounds in wastewater using hydrogen peroxide, a chemical oxidant, ultraviolet (UV) radiation, and a photocatalyst. The photochemical reaction has the potential to reduce high concentrations (200,000 or more parts per million [ppm]) of organics in water to nondetectable levels. The energy from UV radiation is predominantly absorbed by the organic compound and the oxidant, making both species reactive. The process can be used as a final treatment step to reduce organic contamination in industrial wastewater and groundwater to acceptable discharge limits.

The existing bench-scale system treats solutions containing up to several thousand ppm of total organic carbon at a rate of 3 gallons per minute. The bench-scale system consists of a photochemical reactor, where oxidation occurs, and associated tanks, pumps, and controls. The UV lamps are high-intensity lamps that penetrate the wastewater more effectively. The portable, skid-mounted system's design depends on the chemical composition of the wastewater or groundwater being treated.

Typically, the contaminated wastewater is pumped through a filter unit to remove suspended particles. Next, the filtrate is mixed with stoichiometric quantities of hydrogen peroxide. Finally, this mixture is fed to the photochemical reactor and irradiated. The overall reaction is as follows:



where C<sub>a</sub>H<sub>b</sub>X represents a halogenated contaminant in the aqueous phase. Reaction products are carbon dioxide, water, and the appropriate halogen acid. Reaction kinetics depend on (1) contaminant concentration, (2) peroxide concentration, (3) irradiation dose, and (4) radiation spectral frequency.

**WASTE APPLICABILITY:**

The UV CATOX™ process treats industrial wastewater and groundwater containing organics at concentrations up to several thousand ppm. Destruction efficiencies greater than two orders of magnitude have been obtained for chlorobenzene, chlorophenol, and phenol, with low to moderate dose rates and initial concentrations of 200 ppm. Destruction efficiencies of three orders of magnitude have been demonstrated on simulated industrial waste streams representative of textile dyeing operations, with higher dose rates and an initial concentration of 200 ppm.

**STATUS:**

Studies of the UV CATOX™ process under the SITE Emerging Technology Program are complete, and the technology has been invited to participate in the SITE Demonstration Program. The Emerging Technology Report (EPA/540/SR-92/080), Emerging Technology Bulletin (EPA/540/F-92/004), and Emerging Technology Summary (EPA/540/SR-92/080) are available from EPA.

Work involving the on-line production of oxidants and the effectiveness of the photocatalytic substrate is underway under funding from EPA Small Business Industry Research Phase II and Phase I awards.

Representative results from recent trials using the UV CATOX™ process are summarized in the table below. Results are shown as the electric energy dose per gram-mole of initial contaminant to cause one decade of contaminant destruction.

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Reactive Black Dye 5	26
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Reactive Blue Dye 19	50
1-Chloronaphthalene [15]	27
Ethylene, diamine, & triacetic acid	17
Methanol	3
Textile waste (sulfur & indigo dyes) [740]	11
Textile waste (fiber reactive dyes) [270]	7
Chemical waste (formaldehyde & thiourea) [8,200]	1

\* All are 100 parts per million, except as noted

\*\* kilowatt-hour per gram-mole per decade

A cost-competitive UV CATOX™ system can be designed and built to treat industrial wastewater with contaminant levels of 10 to 10,000 ppm.

### FOR FURTHER INFORMATION:

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The technology has been improved since the EPA reports were published. These improvements include (1) using the UV lamp as the energy source; (2) improving the photochemical reactor design; (3) improving the lamp design, including lamp intensity and spectral characteristics; and (4) fixing the catalyst.

**VORTEC CORPORATION  
(Oxidation and Vitrification Process)**

**TECHNOLOGY DESCRIPTION:**

Vortec Corporation (Vortec) has developed an oxidation and vitrification process for remediating soils, sediments, sludges, and industrial wastes contaminated with organics, inorganics, and heavy metals. The process can oxidize and vitrify materials introduced as dry granulated materials or slurries.

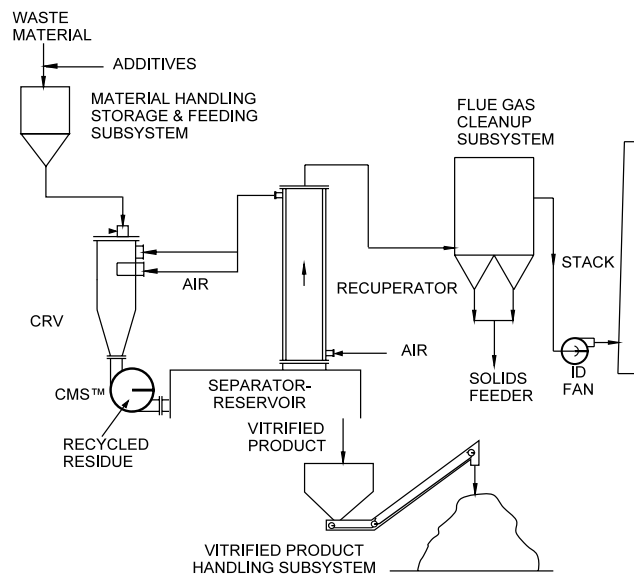
The figure below illustrates the Vortec oxidation and vitrification process. Its basic elements include (1) a cyclone melting system (CMS<sup>®</sup>); (2) a material handling, storage, and feeding subsystem; (3) a vitrified product separation and reservoir assembly; (4) a waste heat recovery air preheater (recuperator); (5) an air pollution control subsystem; and (6) a vitrified product handling subsystem.

The Vortec CMS<sup>®</sup> is the primary waste processing system and consists of two major assemblies: a counterrotating vortex (CRV) in-flight suspension preheater and a cyclone melter. First, slurried or dry-contaminated soil is introduced into the CRV. The CRV (1) uses the auxiliary fuel introduced directly into the CRB; (2) preheats the suspended waste

materials along with any glass-forming additives mixed with soil; and (3) oxidizes any organic constituents in the soil/waste. The average temperature of materials leaving the CRV reactor chamber is between 2,200 and 2,800°F, depending on the melting characteristics of the processed soils.

The preheated solid materials exit the CRV and enter the cyclone melter, where they are dispersed to the chamber walls to form a molten glass product. The vitrified, molten glass product and the exhaust gases exit the cyclone melter through a tangential exit channel and enter a glass- and gas-separation chamber.

The exhaust gases then enter an air preheater for waste heat recovery and are subsequently delivered to the air pollution control subsystem for particulate and acid gas removal. The molten glass product exits the glass- and gas-separation chamber through the tap and is delivered to a water quench assembly for subsequent disposal.



**Vortec Vitrification Process**

Unique features of the Vortec oxidation and vitrification process include the following:

- Processes solid waste contaminated with both organic and heavy metal contaminants
- Uses various fuels, including gas, oil, coal, and waste
- Handles waste quantities ranging from 5 tons per day to more than 400 tons per day
- Recycles particulate residue collected in the air pollution control subsystem into the CMS<sup>®</sup>. These recycled materials are incorporated into the glass product, resulting in zero solid waste discharge.
- Produces a vitrified product that is nontoxic according to EPA toxicity characteristic leaching procedure (TCLP) standards. The product also immobilizes heavy metals and has long-term stability.

### **WASTE APPLICABILITY:**

The Vortec oxidation and vitrification process treats soils, sediments, sludges, and heavy metal contamination. The high temperatures in the CRV successfully oxidize organic materials included with the waste. The inorganic constituents in the waste material determine the amount and type of glass-forming additives required to produce a vitrified product. This process can be modified to produce a glass cullet that consistently meets TCLP requirements.

### **STATUS:**

The Vortec oxidation and vitrification process was accepted into the SITE Emerging Technology Program in May 1991. Research under the Emerging Technology Program was completed in winter 1994, and Vortec was invited to participate in the SITE Demonstration Program.

A 50-ton-per-day system has been purchased by Ormet Aluminum Corporation of Wheeling, West Virginia for recycling aluminum spent pot liners, a cyanide- and fluoride-containing waste (K088). The recycling system became operational in 1996.

The Vortec CMS<sup>®</sup> is classified by the U.S. EPA as Best Demonstrated Available Technology (BDAT) for the processing of K088 waste. Additional projects with the aluminum industry and other industrial waste generators are in progress.

A 25-ton-per-day, transportable system for treating contaminated soil at a Department of Energy site in Paducah, Kentucky was delivered in 1999.

Vortec is offering commercial systems and licenses for the CMS<sup>®</sup> system.

### **FOR FURTHER INFORMATION:**

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**WESTERN PRODUCT RECOVERY GROUP, INC.**  
**(Coordinate, Chemical Bonding, and Adsorption Process)**

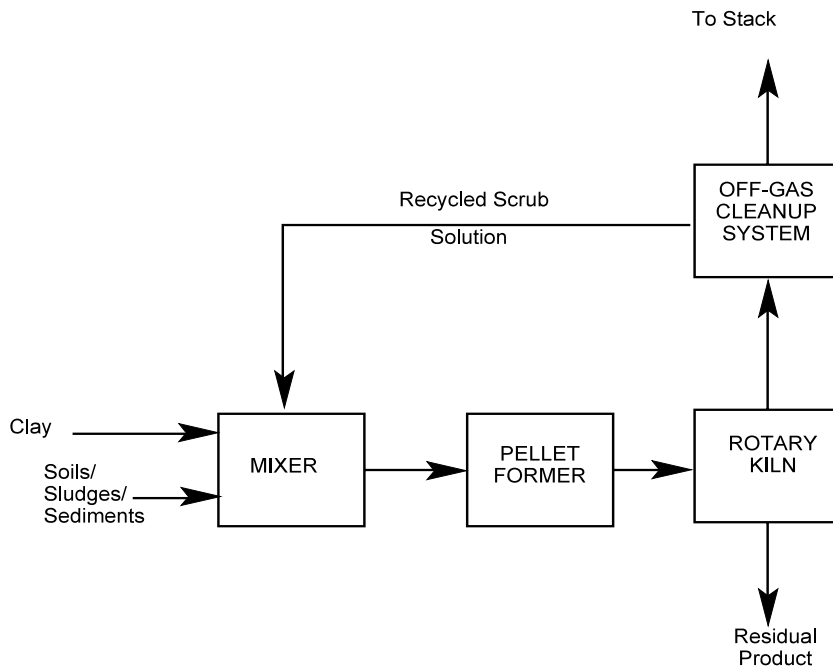
**TECHNOLOGY DESCRIPTION:**

The coordinate, chemical bonding, and adsorption (CCBA) process converts heavy metals in soils, sediments, and sludges to nonleaching silicates. The process can also oxidize organics in the waste stream and incorporate the ash into the ceramic pellet matrix (see figure below). The solid residual consistency varies from a soil and sand density and size distribution to a controlled size distribution ceramic aggregate form. The residue can be placed back in its original location or used as a substitute for conventional aggregate. The process uses clays with specific cation exchange capacity as sites for physical and chemical bonding of heavy metals to the clay.

The process is designed for continuous flow. The input sludge and soil stream are carefully ratioed with specific clays and then mixed in a high-intensity mechanical mixer. The mixture is then densified and formed into green or unfired pellets of a desired size. The green pellets are then direct-fired in a rotary kiln

for approximately 30 minutes. The pellet temperature slowly rises to 2,000°F, converting the fired pellet to the ceramic state. Organics on the pellet's surface are oxidized, and organics inside the pellet are pyrolyzed as the temperature rises. As the pellets reach 2,000°F, the available silica sites in the clay chemically react with the heavy metals in the soil and sludge to form the final metal silicate product.

The process residue is an inert ceramic product, free of organics, with metal silicates providing a molecular bonding structure that precludes leaching. The kiln off-gas is processed in an afterburner and wet scrub system before it is released into the atmosphere. Excess scrub solution is recycled to the front-end mixing process.



Coordinate, Chemical Bonding, and Adsorption (CCBA) Process

### **WASTE APPLICABILITY:**

The CCBA process has been demonstrated commercially on metal hydroxide sludges at a throughput of 70 wet tons per month, based on an 8-hour day, for a 25 percent solid feed. This process can treat wastewater sludges, sediments, and soils contaminated with most mixed organic and heavy metal wastes.

### **STATUS:**

The CCBA process was accepted into the SITE Emerging Technology Program in January 1991. Under this program, the CCBA technology has been modified to include soils contaminated with both heavy metals and most organics. The SITE studies were completed at a pilot facility with a capacity of 10 pounds per hour. Proof tests using contaminated soil have been completed. The Emerging Technology Report, Emerging Technology Summary, and Emerging Technology Bulletin are available from EPA.

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**WESTERN RESEARCH INSTITUTE  
(Contained Recovery of Oily Wastes)**

**TECHNOLOGY DESCRIPTION:**

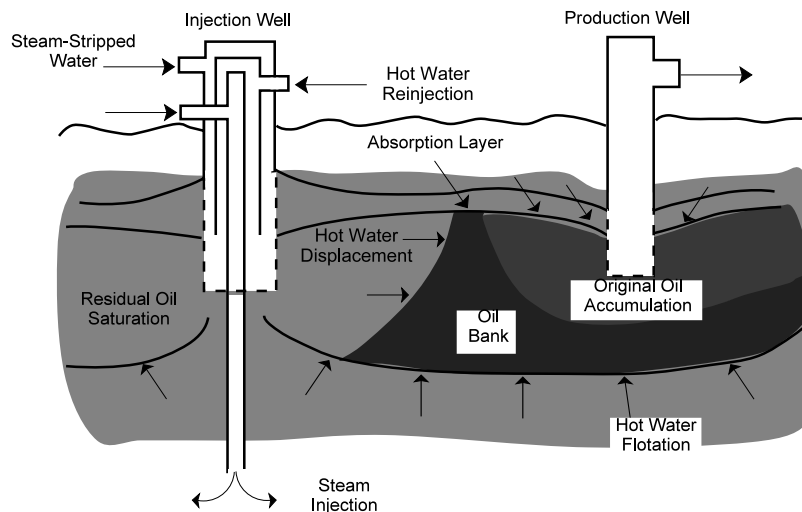
The contained recovery of oily wastes (CROW<sup>®</sup>) process recovers oily wastes from the ground by adapting a technology used for secondary petroleum recovery and primary production of heavy oil and tar sand bitumen. Steam or hot water displacement, with or without the use of chemicals such as surfactants or mobility control chemicals, moves accumulated oily wastes and water to production wells for aboveground treatment.

Injection and production wells are first installed in soil contaminated with oily wastes (see figure below). If contamination has penetrated into or below the aquifer, low-quality steam can be injected below the organic liquids to dislodge and sweep them upward into the more permeable aquifer soil regions. Hot water is injected above the impermeable regions to heat and mobilize the oily waste accumulation. The mobilized wastes are then recovered by hot water displacement.

When the organic wastes are displaced, organic liquid saturation in the subsurface pore space increases, forming a free-fluid bank. The hot water injection displaces the free-fluid bank to the production well. Behind the free-fluid bank, the contaminant saturation is reduced to an immobile residual saturation in the subsurface pore space. The extracted contaminant and water are treated for reuse or discharge.

During treatment, all mobilized organic liquids and water-soluble contaminants are contained within the original boundaries of waste accumulation. Hazardous materials are contained laterally by groundwater isolation and vertically by organic liquid flotation. Excess water is treated in compliance with discharge regulations.

The CROW<sup>®</sup> process removes the mobile portions of contaminant accumulations; stops the downward and lateral migration of organic contaminants; immobilizes any remaining organic wastes as a residual saturation; and reduces the volume, mobility, and toxicity of the



CROW<sup>®</sup> Subsurface Development

contaminants. The process can be used for shallow and deep areas, and can recover light and dense nonaqueous phase liquids. The system uses readily available mobile equipment. Contaminant removal can be increased by adding small quantities of selected biodegradable chemicals in the hot water injection.

In situ biological treatment may follow the displacement, which continues until groundwater contaminants are no longer detected in water samples from the site.

### **WASTE APPLICABILITY:**

The CROW<sup>®</sup> process can be applied to manufactured gas plant sites, wood-treating sites, petroleum-refining facilities, and other areas with soils and aquifers containing light to dense organic liquids such as coal tars, pentachlorophenol (PCP) solutions, chlorinated solvents, creosote, and petroleum by-products. Depth to the contamination is not a limiting factor.

### **STATUS:**

The CROW<sup>®</sup> process was tested in the laboratory and at the pilot-scale level under the SITE Emerging Technology Program (ETP). The process demonstrated the effectiveness of hot water displacement and the benefits of including chemicals with the hot water. Based on results from the ETP, the CROW<sup>®</sup> process was invited to participate in the SITE Demonstration Program. The process was demonstrated at the Pennsylvania Power and Light (PP&L) Brodhead Creek Superfund site at Stroudsburg, Pennsylvania.

The site contained an area with high concentrations of by-products from past operations. The demonstration began in July 1995; field work was completed in June 1996. Closure of the site was completed in late 1998.

The CROW<sup>®</sup> process was applied to a tar holder at a former MGP site in Columbia, Pennsylvania. The work was completed in 1998.

A pilot-scale demonstration was completed at an active wood treatment site in Minnesota. Over 80 percent of nonaqueous-phase liquids were removed in the pilot test, as predicted by treatability studies, and PCP concentrations decreased 500 percent. The full-scale, multiphase remediation is presently underway. Results indicate that organic removal is greater than twice that of pump-and-treat. The project is operating within the constraints of an active facility.

### **FOR FURTHER INFORMATION:**

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**ZENON ENVIRONMENTAL INC.  
(Cross-Flow Pervaporation System)**

**TECHNOLOGY DESCRIPTION:**

The ZENON Environmental Inc. (ZENON), cross-flow pervaporation technology is a membrane-based process that removes volatile organic compounds (VOC) from aqueous matrices. The technology uses an organophilic membrane made of nonporous silicone rubber, which is permeable to organic compounds, and highly resistant to degradation.

In a typical field application, contaminated water is pumped from an equalization tank through a prefilter to remove debris and silt particles, and then into a heat exchanger that raises the water temperature to about 165°F (75°C). The heated water then flows into a pervaporation module containing the organophilic membranes. The composition of the membranes causes organics in solution to adsorb to them. A vacuum applied to the system causes the organics to diffuse through the membranes and move out of the pervaporation module. This material is then passed through a condenser generating a highly concentrated liquid called permeate. Treated water exits the pervaporation module and is discharged from the system. The permeate separates into aqueous and organic phases. Aqueous phase permeate is sent back

to the pervaporation module for further treatment, while the organic phase permeate is discharged to a receiving vessel.

Because emissions are vented from the system downstream of the condenser, organics are kept in solution, thus minimizing air releases. The condensed organic materials represent only a small fraction of the initial wastewater volume and may be subsequently disposed of at significant cost savings. This process may also treat industrial waste streams and recover organics for later use.

**WASTE APPLICABILITY:**

Pervaporation can be applied to aqueous waste streams such as groundwater, lagoons, leachate, and rinse waters that are contaminated with VOCs such as solvents, degreasers, and gasoline. The technology is applicable to the types of aqueous wastes treated by carbon adsorption, air stripping, and steam stripping.



ZENON Cross-Flow Pervaporation System

## **STATUS:**

This technology was accepted into the SITE Emerging Technology Program (ETP) in January 1989. The Emerging Technology Report (EPA/540/F-93/503), which details results from the ETP evaluation, is available from EPA. Based on results from the ETP, ZENON was invited to demonstrate the technology in the SITE Demonstration Program. A pilot-scale pervaporation system, built by ZENON for Environment Canada's Emergencies Engineering Division, was tested over a 2-year period (see photograph on previous page). During the second year, testing was carried out over several months at a petroleum hydrocarbon-contaminated site in Ontario, Canada.

A full-scale SITE demonstration took place in February 1995 at a former waste disposal area at Naval Air Station North Island in San Diego, California. The demonstration was conducted as a cooperative effort among EPA, ZENON, the Naval Environmental Leadership Program, Environment Canada, and the Ontario Ministry of Environment and Energy.

Organics were the primary groundwater contaminant at the site, and trichloroethene (TCE) was selected as the contaminant of concern for the demonstration. The Demonstration Bulletin (EPA/540/MR- 95/511) and Demonstration Capsule (EPA/540/R-95/511a) are available from EPA.

## **DEMONSTRATION RESULTS:**

Analysis of demonstration samples indicate that the ZENON pervaporation system was about 98 percent effective in removing TCE from groundwater. The system achieved this removal efficiency with TCE influent concentrations of up to 250 parts per million at a flow rate of 10 gallons per minute (gpm) or less. Treatment efficiency remained fairly consistent throughout the demonstration; however, the treatment efficiency decreased at various times due to mineral scaling problems.

## **FOR FURTHER INFORMATION:**

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