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Fifth Forum on Innovative Hazardous Waste Treatment Technologies: Domestic and International

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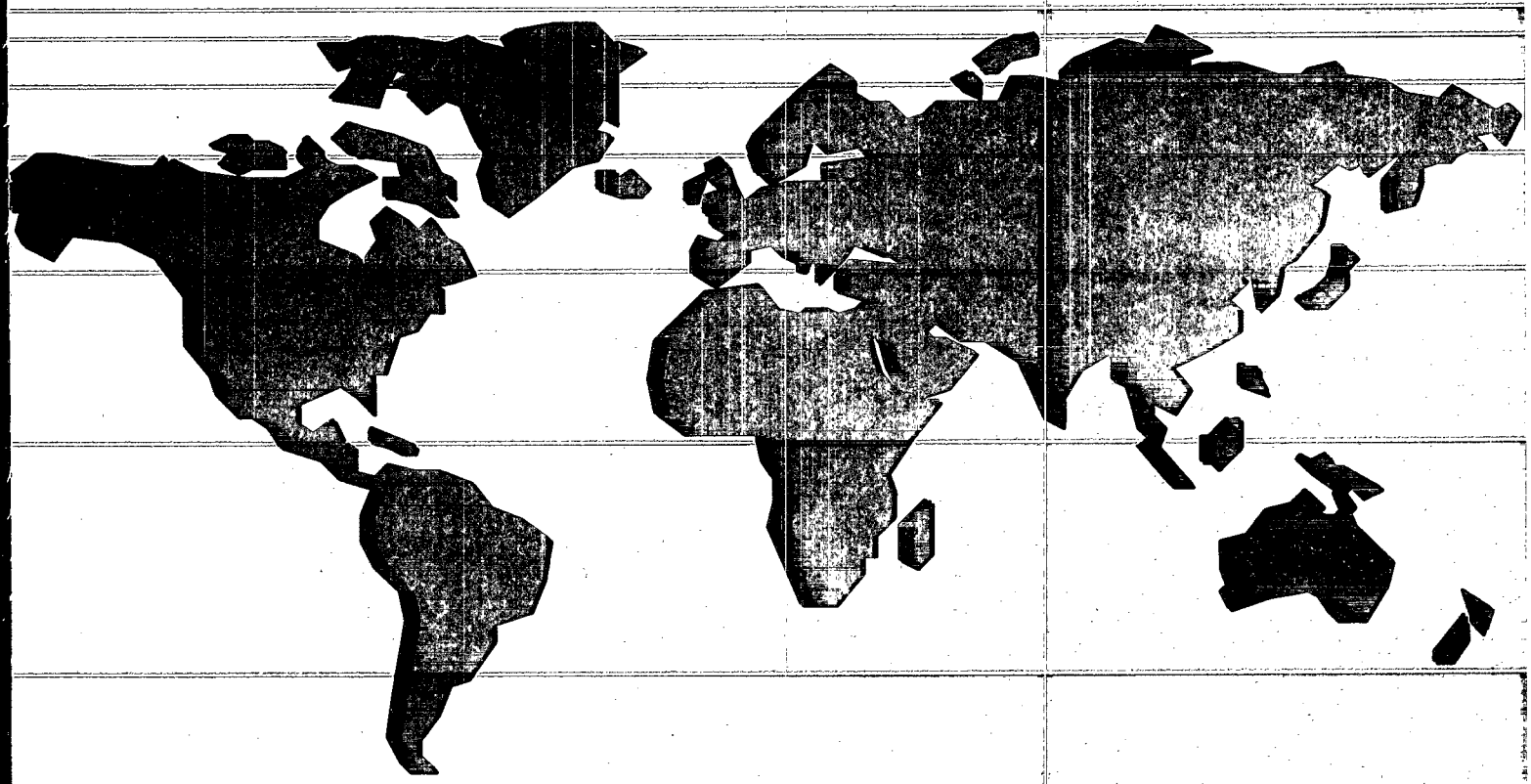

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May 1994

ABSTRACT PROCEEDINGS

FIFTH FORUM ON INNOVATIVE HAZARDOUS WASTE TREATMENT TECHNOLOGIES: DOMESTIC AND INTERNATIONAL

Chicago, Illinois
May 3-5, 1994

TECHNOLOGY INNOVATION OFFICE
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ABSTRACT

On May 3-5, 1994, the U.S. Environmental Protection Agency's Technology Innovation Office and Risk Reduction Engineering Laboratory hosted an international conference in Chicago, Illinois to exchange solutions to hazardous waste treatment problems. During this conference, the *Fifth Forum on Innovative Hazardous Waste Treatment Technologies: Domestic and International*, scientists and engineers representing government agencies, industry, and academia attended over 40 technical presentations and case studies describing domestic and international technologies for the treatment of waste, sludges, and contaminated soils at uncontrolled hazardous waste disposal sites. A Session was also held on opportunities in research and commercialization, which included presentations on export assistance programs and partnerships with EPA in developing innovative technologies. Over 70 posters were on display.

This compendium includes the abstracts of the presentations from the conference and many of the posters that were on display. The abstracts are published as received from the individual authors and their institutions.

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RADIO FREQUENCY HEATING

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INTRODUCTION

The in situ radio frequency (RF) heating process utilizes electromagnetic energy in the radio frequency band to heat soil rapidly. The process can be used to heat the soil to a temperature range of 150-250°C. The contaminants are vaporized and/or boiled out along with water vapor formed by the boiling of native soil moisture. The gases and vapors formed upon heating the soil are recovered and treated on site.

In situ heating is performed by energizing an array of electrodes emplaced in bore holes drilled through the soil. The process can be used for the removal of organic chemicals which exhibit reasonable vapor pressure (about 10 mm of Hg) in the treatment temperature range. The chemical contaminants are removed from the soil as vapors along with steam and air.

The feasibility of the in situ RF soil decontamination process was first demonstrated for petroleum hydrocarbons at a site of a jet fuel spill (1). In this field experiment approximately 500 cu. ft. of sandy soil was heated to a temperature range of 150-160°C. It was demonstrated that 94 to 99 percent of the aliphatic and aromatic hydrocarbons present in the spill site were removed (1). The second demonstration, performed at Rocky Mountain Arsenal (RMA), showed that pesticides contained in clayey soil can be thermally decomposed and removed. The total concentration of pesticides was reduced from an initial value of about 5,000 ppm to a final value of about 50 ppm (2). The third demonstration was conducted at the Kelly AFB during the summer of 1993. A petroleum contaminated site consisting of clay and cobble was successfully heated to the target temperature.

In various laboratory feasibility studies, the treatment conditions for the removal of the following contaminants has been established: perchloroethylene and chlorobenzene from sandy soil (3), jet fuel from clayey soil (4), PCBs from sandy/clayey soils (3,6), phenanthrene, pentachlorophenol and phenol from sandy/clayey soils (5) and creosote from clayey soil (6). All of these studies except the one with jet fuel and creosote were done with clean soils which were spiked with the contaminants in the laboratory.

METHODOLOGY

The RF soil decontamination process heats an appropriate volume of soil in situ to temperatures of 150° to 250°C by means of an electrode array inserted in bore holes drilled through the soil. Selected electrodes are specially designed to permit the application of RF power while collecting vapors by application of a vacuum down hole. Figure 1 is an artist's illustration of the process. The vapor collection system is an integral part of the electrode array since vapor collection points are physically integrated and embedded in the array. A vapor containment barrier is used to prevent fugitive

emissions, and provides thermal insulation to prevent excessive cooling of the near surface zones. Gases and vapors rising up to the heated soil surface are also collected at the surface by means of horizontal collection lines placed below the vapor barrier. These lines are also connected to the vacuum system. Power to the electrode array is provided by means of a power amplifier designed to generate electromagnetic energy in the frequency range of 1 to 10 MHz. The actual frequency used depends upon the volume and depth of the treated soil, and the dielectric properties of the soil. A power transmission system is needed to provide power to the array. It consists of coaxial cables and a matching network.

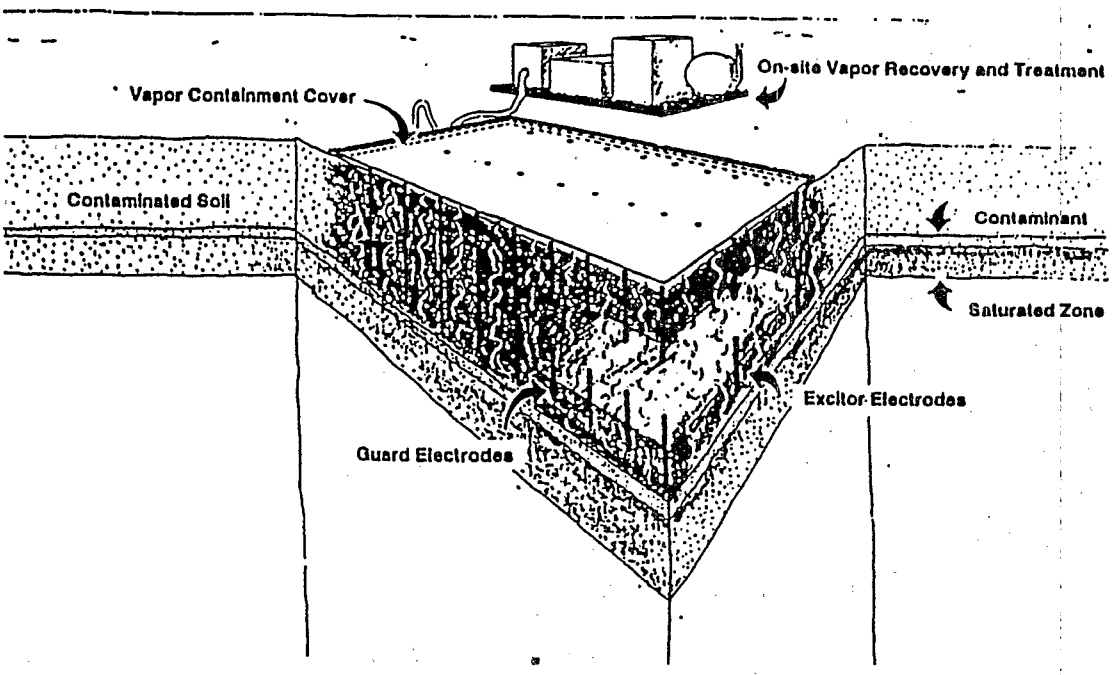

Figure 1. Radio Frequency In Situ Heating Process

Prior laboratory and field experiments (1-9) have shown that high boiling contaminants can be boiled out of the soil at much lower temperatures than their actual boiling point. This occurs due to two reasons: first, the presence of an autogenously established steam sweep helps to improve vaporization rate of such high boiling materials; second, the long residence time in situ permits significant removal, albeit at a rate which is slower than that obtainable in above ground thermal treatment systems. Another phenomenon which operates during in situ heating is the development of effective permeability to gas flow. The increase in permeability is confined to the heated zone, thus creating a preferred path of gas and vapor flow towards the soil surface.

There are several important advantages of the in situ RF soil decontamination process. These are: true in situ treatment minimizes earth removal, excavation etc., thereby minimizing attendant hazards related to odors, fugitive emissions and dust. Only 0.5 to 1 percent of the treated volume will

require removal for the formation of the electrode bore holes. A concentrated gas stream containing air, water and contaminant vapors is produced which is treated on site, and the process equipment may be trailer mounted and mobile.

Some of the limitations of the process are: unable to treat metals, salts, and inorganic pollutants; if large buried metal objects are present in portions of the treatment zone then the applicability of the process may be limited to zones free of such objects. In its current state of development the process is applicable for the treatment of a contiguous volume of soil extending downward from the surface. Methods to heat selected layers of soil at depth are under development.

RESULTS

Laboratory Studies

Several laboratory treatability studies on various types of soils and contaminants have been performed. These studies were done to determine the optimum temperature and treatment time for different types of contaminants found in different soil types. The treatability studies have focussed on chlorinated solvents, volatile aromatic hydrocarbons such as benzene, toluene, etc. (BTEX), petroleum hydrocarbons (TPH), phenols, chlorinated biphenyls (PCBs), and polynuclear aromatic hydrocarbons (PAHs).

The laboratory treatability studies showed that organic contaminants can be removed from soil at temperatures that are considerably below the normal boiling point of the pure contaminants. A summary of the treatability studies is published elsewhere (7). In most instances, it was possible to reduce the concentration of the contaminants by more than 90%. Temperatures of 200°C or more were necessary to remove high boiling point compounds such as PAHs and Aroclor 1242.

Field Experiment at Volk ANGB

The first field experiment was performed at a former fire training pit located on Volk Air National Guard Base (ANGB) in Camp Douglas, Wisconsin to show the feasibility of the in situ RF soil decontamination process. In this field experiment 500 cu. ft. of sandy soil was heated to an average depth of 7 feet. The area of the heated zone was 72 sq. ft. The soil in the site was approximately 98 % silica sand which had been contaminated with JP-4 jet fuel was spilled during routine fire training exercises conducted at the site. The soil was heated to a temperature range of 150-160°C in approximately 8 days with a 40 kW RF power source. It was maintained at the treatment temperature for a period of 4 days.

Numerous soil samples were obtained from the test volume and the soil in the immediate surrounding vicinity. Pre and post test soil samples were analyzed to determine the percentage removal of the aliphatic and aromatic hydrocarbons present in the soil. It was shown that greater than 99 percent of the volatile hydrocarbons and 94 to 99 percent of the semivolatile hydrocarbons were removed from the site. Hexadecane, with a normal boiling point of 289° C, was used as a target compound to represent the semivolatile aliphatic compounds. On an average 83 percent removal of hexadecane was achieved.

During the course of heating, a tracer injection study was performed to determine the flow of soil fluids. Approximately 2.5 g of Halon 2402 (a liquid at ambient temperature) was injected at a depth of 6 ft, and at a distance of 4 ft outside the heated zone. The hot gases leaving the treatment zone were sampled and analyzed for the presence of the tracer. The tracer was detected in the hot gases approximately 100 minutes after the tracer was injected into the soil.

Soil samples obtained from the immediate surrounding vicinity of the heated zone indicated a net loss of contaminants. Together with the results of the tracer study, it was concluded that no net outward migration of the contaminants occurred during the experiment.

Field Experiment at RMA

A second field experiment was successfully completed on Basin F soil at the Rocky Mountain Arsenal. The pilot test demonstrated the ability of the RF heating technology to heat Basin F soil to over 250°C, and in the process reduce organochloro pesticide (OCP) concentrations near to or below Preliminary Remediation Goals. Table 1 compares the removal of OCPs with two proposed remediation goals. Aldrin and dieldrin achieved the 10^{-4} biological worker goal, but not the 10^{-6} worker goal. Endrin achieved both goals, but isodrin achieved neither. OCP destruction efficiencies in the soil heated to 250°C or higher were 97 to 99%, from initial concentrations which were up to 5,000 milligrams per kilogram (mg/kg) (8).

Table 1. FINAL CONCENTRATIONS OF COMPOUNDS VERSUS SOIL TEMPERATURE

Parameter	200-250°C		250-300°C		>300°C		Preliminary Remediation Goals (4)	
	Concentration (mg/kg)	Standard Deviation	Concentration (mg/kg)	Standard Deviation	Concentration (mg/kg)	Standard Deviation	10^{-4} Biological Worker (mg/kg)	10^{-4} Biological Worker (mg/kg)
Aldrin	0.97	1.0	31	40	1.8	3.1	56	0.56
Dieldrin	0.59	0.35	8.0	8.0	1.1	1.5	40	0.40
Endrin	1.7	2.0	5.6	5.3	1.0	1.5	17	17
Isodrin	1.3	-	48	62	49	90	3.6	3.6
DMMP	0.0034	0.0012	0.0028	0.0016	0.0028	0.0019	-	-
DMPA	0.13	0.0	0.022	0.036	0.40	0.89	-	-
TOC	2.1%	1.8%	3.4%	1.7%	2.6%	1.5%	-	-
TOX	360	520	180	110	110	25	-	-

The vapors produced during heating were treated in a vapor treatment system which removed both the semi-volatile and volatile organic contaminants, and the condensate was stored for later treatment and disposal.

A conceptual design has been prepared for treatment of Basin F by RF heating. [9] The cost is complicated by the presence of a 5-ft deep clay cap. If this is considered to be contaminated, then it must be treated. Furthermore basin F was divided into two zones, a deep zone (15 ft) and a shallow zone (10 ft). The present worth cost to treat the shallow zones to 250°C was $43 million, or $110 per ton of soil treated, or $221/ton of contaminated soil treated. The present worth cost for the deep zone was $19 million, or $102/ton of soil treated, or $153/ton of contaminated soil treated. If the cap can be scraped away before treatment, these costs will be less.

SITE Demonstration at Kelly AFB

An additional demonstration of the technology was conducted under the EPA SITE program at Kelly AFB during the summer of 1993. Approximately 100 cubic yards of clayey soil-containing cobbles and contaminated with petroleum fractions was heated to a depth of about 20 ft. Ground water level at

the site was relatively shallow. Dewatering wells were used to continuously pump water and to attempt to minimize water intrusion into the test volume. Soil was heated to temperatures of more than 100°C over 60 days. Effluents containing steam, air and hydrocarbons were collected and disposed using a flare. Soils samples were obtained prior to and after the demonstration and the contaminant concentration data is currently not available. Details of the contaminant removal data and technology assessment will be published later.

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FOR MORE INFORMATION

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THERMAL DESORPTION OF COAL-TAR CONTAMINATED SOIL FROM MANUFACTURED GAS PLANTS

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INTRODUCTION

Clean Berkshires, Inc. (CBI) conducted a full-scale demonstration test of its thermal desorption technology on coal-tar contaminated soils as part of a Research and Development Program conducted by Niagara Mohawk Power Corporation and supported by the EPA SITE program.

Niagara Mohawk is taking a proactive role in remediating its Manufactured Gas Plant (MGP) sites by experimenting with alternative technologies at the Harbor Point Site in Utica, NY. CBI's Thermal Desorption System (TDS) was chosen through national competition as the first technology to be demonstrated. The TDS proved to be effective in remediating soils contaminated with polynuclear aromatic hydrocarbons (PAHs), volatile organic compounds (VOCs) and cyanide.

THE CLEAN BERKSHIRES THERMAL DESORPTION SYSTEM

The Clean Berkshires transportable Thermal Desorption System (TDS) is based on rotary kiln technology to decontaminate soils. The thermal treatment process involves two steps: volatilization of contaminants followed by gas treatment. During the volatilization step, contaminated materials are exposed to high temperatures in a co-current flow rotary desorber, causing contaminants to volatilize to gas phase. The clean soils are then discharged and stockpiled for testing. The gas stream passes to the downstream pollution control equipment, where contaminants are destroyed prior to release to the atmosphere.

The TDS is a full-scale remediation system available for large commercial applications. The system is of modular design and can be transported and mobilized on-site within two to three months. Its compact design requires only a 100' x 150' footprint.

The TDS consists of a series of separate components, linked together and centrally controlled by an operator in the process control room. The system includes of the following components:

- Computer controlled feed system
- Rotary kiln drum volatilizer
- Cyclone
- Afterburner
- Quench tower
- Baghouse
- ID fan and Exhaust Stack
- Multi-stage dust suppression system
- Process control room

If necessary, the TDS may be adapted to include a scrubber system for treatment of specific contaminants (e.g., HCl).

The process begins when prepared soils are loaded into the cold feed bin of the feed system. The Variable Drive Feed System includes four 20-ton storage bins which provide temporary storage for the waste feed materials. Material that is fed to the Kiln will come from a stockpile which has been tested to determine the average contaminant concentration.

A feed belt at the base of the bin delivers soil to an incline conveyor belt that leads to the Kiln. The incline conveyor belt is equipped with a weigh scale, displayed in the Control Trailer, where the Plant Operator controls the feed rate.

Soil is fed from the incline conveyor belt into the Kiln, where the contaminants are thermally transferred from the soil into the gas stream. This thermal transfer takes place as the soils and contaminants are exposed to heat from the direct fire burner located at the feed end of the Kiln. The Kiln burner can be fired with either No. 2 fuel oil or natural gas. Quick moisture removal permits longer soil residence times at optimum volatilization temperatures. The Kiln burner firing rate can be varied according to desired soil exit temperatures. The Kiln and burner system can support soil exit temperatures ranging from 300°F to 1000°F. Special steel alloys are used to line the Kiln, providing for a wide range of soil exit temperatures without the use of refractory.

The Kiln is inclined and rotates to convey the soils from the feed end to the discharge end. The parallel flow of soils and gases in the Kiln results in desired heat exchange between the two media. Parallel flow also ensures that all airborne dust particles are thoroughly decontaminated because they have traveled the length of the Kiln.

The transfer of contaminants into the gas phase is driven by three factors: turbulence, temperature and residence time. Turbulence is provided by the rotation of the Kiln, which exposes greater surface area to the hot gases for improved volatilization. Soil exit temperature is controlled by the firing rate of the burner. Residence time is a function of the incline angle and rotation speed of the Kiln. Residence time may be varied from five to ten minutes to ensure that soils achieve desired temperature exposure. Decontaminated soils exit the Kiln and are transported to the Soil Discharge Cooler (SDC). The SDC is the first stage in the Multi-stage Dust Suppression System.

The Multi-stage Dust Suppression System consists of a series of specially designed components in which the soil is mixed with residual particulate matter removed from the gas stream and a controlled volume of water. Water is sprayed onto and blended into the soil, which both cools the soil and controls fugitive dust. Soil is discharged from a radial stacking conveyor and stored temporarily prior to testing. Treated soils are sampled and analyzed to confirm cleanup.

Heated gases which cause the volatilization of contaminants travel simultaneously and co-currently with soils. The entire system, from the Kiln to the Induced Draft Fan, operates under negative pressure. Negative pressure prevents fugitive emissions of gases and particulate from the system to the atmosphere.

Gases are first drawn from the Kiln through ductwork into the Cyclone. Within the Cyclone, large particulate matter, entrained in the gas stream, is removed by centrifugal force. The particulate matter is discharged through the base of the Cyclone to the Multi-stage Dust Suppression System. Gases and remaining fine particulate exiting the Cyclone are drawn by the Induced Draft Fan through ductwork into the Afterburner.

The Afterburner subjects the contaminated gases to very high temperatures to destroy the contaminants entrained in the gas stream. The Afterburner is designed to achieve 99.99% Destruction and Removal Efficiency (DRE). As in the Kiln, destruction of contaminants in the Afterburner is a factor of turbulence, temperature, and residence time. Turbulence is created by tangential entry of the gases into the swirling flame of the Afterburner. This enhances the mixing of the contaminated gases around the flame. Temperature and residence time of the gases are controlled by the burner firing rate and the volume of air flow. A No. 2 fuel oil or natural gas fired burner generates the flame that produces the high temperatures for destroying contaminants in the process gases.

Exit gas temperatures from the Afterburner can range from 1400°F to 2000°F. At all times, the Afterburner operates at a temperature sufficiently high to destroy contaminants in the process gases. Real-time data is monitored to ensure that adequate destruction takes place.

Gases are drawn by the Induced Draft Fan from the Afterburner through a refractory lined duct to the Quench tower. The purpose of the Quench is to cool the process gases prior to entering the Baghouse. Gases pass through highly atomized water mists in the Quench. Cooling the gases reduces their velocity, causes additional particulate drop out, and protects the Baghouse from excessive temperature. As in the Cyclone, particulate matter that drops out of the gas stream in the Quench is discharged from the bottom of this component into the Multi-stage Dust Suppression System. The gases continue through ductwork into the Baghouse.

The Baghouse is a dry filtering device that consists of a series of fourteen compartments, each of which contains forty eight Triloft filtering bags. Gases are drawn from the exterior surface of the bags to the interior surface, leaving any remaining particles and dust on the outside surface of the bags. Particulate released from the bag cleaning process falls to the hopper auger and is transported through a rotary air lock to the Multi-stage Dust Suppression System.

The Induced Draft Fan is the prime mover of gases through the system. Gases are pulled from their entry point in the Kiln through to the Induced Draft Fan. Cooled contaminant and particulate free gases are then forced out the exhaust stack. Exhaust stack exit temperatures range from 300°F to 350°F.

METHODOLOGY

The Demonstration included treating four waste streams from four separate areas of the site, including: Coke Plant, Purifier Soils, Harbor Sediments and Water Gas Plant soils.

Approximately 1000 tons of soil from each source area was excavated and transported to an on-site materials processing area. The source materials were then physically processed to achieve a uniform size and contaminant level and were subsequently stored in temporary structures. The materials' consistencies varied from the cohesive Tar Emulsions which formed clumps up to 24" in diameter to the fluid Harbor Sediments and Water Gas Plant materials with moisture contents of up to 30%. Primary contaminants included PAHs, VOCs, cyanide, arsenic and lead. Contaminant levels for each of the source areas were as follows:

TABLE 1. CONTAMINANT LEVELS FOR SOURCE AREA WASTE STREAMS

Waste Stream	Range of Contaminants
Coke Plant	72.8 - 2089.6 ppm total PAH
Purifier Soils	205.2 - 1220.1 ppm total PAH
Harbor Sediments	554.0 - 1879.4 ppm total PAH
Water Gas Plant	1375.0 - 3321.6 ppm total PAH

Thorough materials handling operations allowed each waste stream to be fed through the system. For the purposes of this Demonstration each waste stream was treated separately, however during a full-scale remediation effort, additional drying and blending would assist in combining source materials.

The demonstration included several phases of experimentation to evaluate different operating parameters that produce satisfactory soil cleanup and stack emissions levels. First a Materials Handling Shakedown phase was conducted to preliminarily determine how each waste stream would process through the desorber due to varying soil consistencies and moisture contents.

Next during the Experimental phase, each material was processed at various soil exit temperatures and feed rates while maintaining a constant afterburner temperature to determine optimum operating parameters. Results were analyzed overnight by Atlantic Environmental Services' (AES) on-site screening lab. Confirmatory soil samples taken by Tighe & Bond were sent off-site for more detailed and sensitive analysis. Throughout Experimental tests, TRC Environmental Consultants, Inc. continuously monitored stack emissions for CO, CO_2, O_2, THC, NO_x and SO_2, in addition to analyzing a volumetric sample for cyanide. During a second day of Experimental testing, stack emissions sampling was expanded to include sampling trains for volatiles, semi-volatiles, metals and particulate. Additionally, CBI spiked the soil with naphthalene so that a Destruction and Removal Efficiency (DRE) could be calculated.

The Formal phase consisted of processing the four waste streams in the TDS at the best operating parameters for that waste stream, as determined by the Experimental phase. Three replicate runs were performed for each waste stream during the Formal phase. The EPA SITE program is currently evaluating this phase and will provide independent analysis of the TDS performance. The Formal phase test runs involved sampling and analysis by SAIC and IT Corporation that duplicated tests performed by AES, Tighe & Bond and TRC during the Experimental phase.

RESULTS

Please refer to Table 2, Summary of TDS Parameters and Results during the Harbor Point Demonstration. This table summarizes results of different run parameters, during both the Experimental and Formal phases of the demonstration.

CONCLUSIONS

CBI demonstrated that the TDS effectively remediated MGP wastes including soil contaminated with PAHs, VOCs and cyanide. Throughout the Demonstration, TDS emissions remained within acceptable limits. The TDS decontaminated soil from four different waste streams to below detection limits and achieved DREs of at least 99.99%. Since these contaminants are found at many MGP sites, thermal desorption would be an effective technology for other sites. With minor modifications and material blending, the TDS could successfully process all waste streams found on this and other MGP sites.

FOR MORE INFORMATION

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TABLE 2. SUMMARY OF TDS PARAMETERS AND RESULTS DURING THE HARBOR POINT DEMONSTRATION

Waste Stream	Run Number	Throughput (tons/hour)	Soil Exit Temperature*	Moisture Content‡	Infeed Total PAH‡	Outfeed Total PAH‡	DRE§
Coke Plant							
Experimental Phase	CG-057	13 tph	600°F	15%	2089.55 ppm	0.00 ppm	
	CG-058	18 tph	600°F	16%	539.30 ppm	0.00 ppm	
	CG-059	18 tph	550°F	13%	478.79 ppm	22.23 ppm	
	CG-060†	12 tph	600°F	13%	443.11 ppm	3.55 ppm	99.9980%
Formal Phase	CG-076†	15 tph	600°F	18%	98.10 ppm	0.00 ppm	99.9930%
	CG-077†	15 tph	600°F	18%	99.90 ppm	0.00 ppm	99.9953%
	CG-078†	15 tph	600°F	19%	72.80 ppm	0.00 ppm	99.9978%
Purifier Soils							
Experimental Phase	PS-061	15 tph	600°F	13%	749.46 ppm	33.63 ppm	
	PS-062	15 tph	700°F	18%	825.88 ppm	9.42 ppm	
	PS-063	25 tph	600°F	17%	772.73 ppm	9.54 ppm	
	PS-064	25 tph	550°F	17%	1220.10 ppm	64.55 ppm	
	PS-065†	20 tph	800°F	19%	879.48 ppm	0.00 ppm	99.9983%
Formal Phase	PS-079†	20 tph	850°F	22%	692.00 ppm	0.00 ppm	99.9969%
	PS-080†	20 tph	850°F	23%	243.90 ppm	0.00 ppm	99.9944%
	PS-081†	20 tph	850°F	25%	303.00 ppm	0.00 ppm	99.9958%
Harbor Sediments							
Experimental Phase	HS-088	15 tph	600°F	24%	893.56 ppm	4.92 ppm	
	HS-089	15 tph	700°F	24%	710.13 ppm	4.46 ppm	
	HS-090	15 tph	800°F	19%	849.12 ppm	0.00 ppm	
	HS-091†	17 tph	750°F	28%	893.84 ppm	12.86 ppm	99.9994%
Formal Phase	HS-092†	17 tph	750°F	28%	795.60 ppm	2.23 ppm	99.9991%
	HS-093†	17 tph	750°F	26%	954.00 ppm	3.82 ppm	99.9993%
	HS-094†	17 tph	750°F	28%	812.00 ppm	2.54 ppm	99.9982%
Water Gas							
Experimental Phase	WG-084	14 tph	700°F	21%	2261.02 ppm	3.48 ppm	
	WG-085	17 tph	800°F	13%	1770.70 ppm	0.00 ppm	
	WG-086	18 tph	850°F	16%	2522.68 ppm	0.00 ppm	
	WG-087†	18 tph	800°F	18%	2427.12 ppm	0.00 ppm	99.9985%
Formal Phase	WG-095†	18 tph	800°F	30%	1375.00 ppm	7.29 ppm	99.7218%
	WG-096†	18 tph	800°F	29%	1448.00 ppm	10.14 ppm	99.9935%
	WG-097†	18 tph	800°F	26%	1610.00 ppm	4.93 ppm	99.9987%

* Afterburner exit temperature 1800°F.
† Spiking with naphthalene at 10 lbs/hr.
‡ Experimental phase from results AES's on-site lab with detection limit of 3.00 ppm. Formal phase results from off-site lab with detection limit of 0.200 - 1.000 ppm.
§ Calculated by TRC Environmental Consultants, Inc.

THE ECO LOGIC PROCESS
A GAS PHASE CHEMICAL REDUCTION PROCESS FOR PCB DESTRUCTION

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INTRODUCTION

Since 1986, ECO LOGIC has conducted research with the goal of developing a commercially-viable chemical process for destroying aqueous organic wastes, such as contaminated harbor sediments, landfill soil and leachates, and lagoon sludges and also for processing stored wastes (e.g. contaminated soils, solvents, oils, industrial wastes, pesticides and chemical warfare agents). The process described in this paper was developed with a view to avoiding the expense and technical drawbacks of incinerators, while still providing high destruction efficiencies and waste volume capabilities.

A lab-scale process unit was constructed in 1988 and tested extensively. A mobile pilot-scale plant was completed and commissioned in 1991. It was taken through a preliminary round of tests at Hamilton Harbour, Ontario, where the waste processed was coal-tar-contaminated harbour sediment. In 1992, the same unit was taken through a second round of tests as part of the US Environmental Protection Agency (USEPA) Superfund Innovation Technology Evaluation (SITE) program in Bay City, Michigan. This demonstration was partially funded by the DESRT program, the Ontario Environmental Technologies Program and the Defence Industrial Research Program. In this test program, the pilot-scale unit processed PCBs in aqueous, organic and soil matrices. This paper describes the process reactions and the pilot-scale process unit, and presents the results of pilot-scale testing thus far.

PROCESS CHEMISTRY

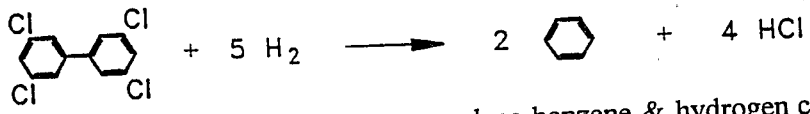
The process involves the gas-phase reduction of organic compounds by hydrogen at temperatures of 850°C or higher. Chlorinated hydrocarbons, such as polychlorinated biphenyls (PCBs) and polychlorinated dibenzo-p-dioxins (dioxins), are chemically reduced to methane and hydrogen chloride (HCl), while non-chlorinated organic contaminants, such as polyaromatic hydrocarbons (PAHs), are reduced to methane and ethylene. The system product gas consists essentially of hydrogen, methane, ethylene, carbon monoxide, and carbon dioxide. The HCl produced is scrubbed out in a caustic scrubber downstream of the process reactor.

Figure 1 shows some of the reduction reactions, including intermediate steps, for the destruction of a variety of contaminants using the ECO LOGIC Process. Unlike oxidation reactions, the efficiency of these reduction reactions is enhanced by the presence of water, which acts as a reducing agent and a source of hydrogen.

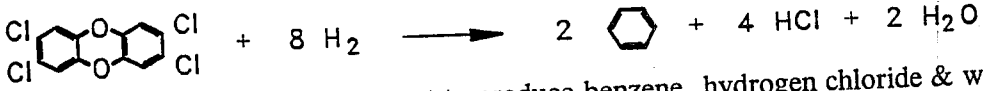
A benefit of using an actively reducing hydrogen atmosphere for the destruction of chlorinated organic compounds, such as PCBs, is that no formation of dioxins or furans occurs. Any dioxins or furans in the waste are also destroyed effectively. The reducing hydrogen atmosphere is maintained at more than 50% hydrogen (dry basis) to prevent formation of PAHs. This makes the scrubbed recirculation gas suitable for continuous monitoring using an on-line chemical ionization mass spectrometer (CIMS). By measuring the concentrations of intermediate reduction products, the CIMS produces a continuous indication of destruction efficiency.

Figure 1

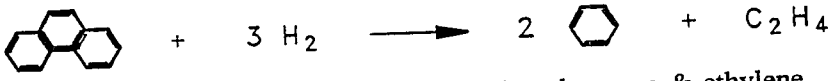
ECO LOGIC PROCESS REACTIONS



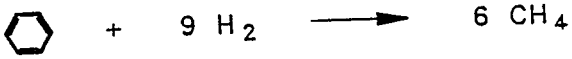
PCB molecule & hydrogen react to produce benzene & hydrogen chloride.



Dioxin molecule & hydrogen react to produce benzene, hydrogen chloride & water.



PAH molecule & hydrogen react to produce benzene & ethylene.



Benzene & hydrogen react to produce methane.

$$C_2H_4 + 2\,H_2 \longrightarrow 2\,CH_4$$

Ethylene & hydrogen react to produce methane.

$$C_nH_{(2n+2)} + (n-1)\,H_2 \longrightarrow n\,CH_4$$

Hydrocarbons & hydrogen react to produce methane.

WATER SHIFT REACTION

$$CH_4 + H_2O \longrightarrow CO + 3H_2$$

Methane & water react to produce carbon monoxide & hydrogen.

Several feed systems are available for various types of wastes, depending on whether watery waste, oil waste, or solid waste is being processed. Watery waste is preheated in a vaporizer using steam from a boiler. The contaminated steam from the vaporizer is metered into the reactor at a rate determined by the process control system. Hot contaminated liquid exits the bottom of the vaporizer at a controlled flowrate and enters the reactor through an atomizing nozzle. Oil waste can be metered directly from drums into the same line using a peristaltic pump.

Solid wastes such as soil or decanted sediment are decontaminated in a thermal desorption unit (TDU) with the contaminants being sent to the reactor through a separate port. The internal workings of the TDU are designed to vaporize all water and organic contaminants in the waste soil/sediment while mechanically working the solids into as fine a mixture as possible. The water vapor and organic contaminants are swept into the reactor by a sidestream of scrubbed recirculation gas.

Solids, such as contaminated electrical equipment, can be thoroughly desorbed using the sequencing batch vaporizer (SBV) chambers. These chambers take advantage of the reheated recirculation gas stream to heat the equipment and carry contaminants into the reactor. The hydrogen atmosphere is non-reactive with most metals, and there are none of the problems with metal oxide formation associated with rotary kilns.

The SBV can also be used for vaporization of drummed solid chemical wastes, such as hexachlorobenzene. Significant stockpiles of "hex wastes" exist and are still being generated as byproducts of chlorinated solvent production. Advantages of vaporizing hex wastes directly from the drum include decreases in worker exposures and fugitive emissions from drum transfer operations, cleaning of the drums in place, and segregation of inorganic contaminants into the existing drums. The SBV has been tested at lab-scale with hex waste samples and PCB-contaminated electrical equipment.

Decant water is the only liquid effluent, and after pH balancing, is suitable for sewer disposal. The amount of effluent is equal to the amount of water in the incoming waste stream, so on-site water treatment is not a costly option if desired. The minor amount of sludge produced can be diverted to the solid waste stream being processed through the TDU.

The cooled and scrubbed product gas is a clean dry mixture of hydrogen, methane, carbon monoxide, and other light hydrocarbons. As earlier indicated, most of the gas is reheated and recirculated back into the reactor, in order to maintain a high concentration of hydrogen in the reactor. A sidestream is drawn off for on-line sampling. Sidestreams can also go to the TDU as a sweep gas, to the SBV as sweep gas, or to a compressor for storage in a tube trailer. Storage of the product gas under pressure permits the analysis of large batches of gas prior to using the gas as fuel and allows the operation of the system in a "stackless" mode. Potential applications for the stored product gas include heating the TDU, steam reformation for optimum hydrogen recovery, and steam/electricity generation.

Throughout waste processing operations, the product gas is sampled continuously using the CIMS. This analyser is capable of accurately monitoring up to 10 organic compounds every few seconds at concentrations ranging from percent levels down to ppb levels. It is used as part of the ECO LOGIC Process to monitor the concentrations of certain compounds indicative of the process destruction efficiency. The compounds selected for monitoring depend on the waste being processed. For example, during PCB processing, monochlorobenzene is typically monitored as an indicator of destruction efficiency. Low levels of this volatile compound indicate that destruction of the PCBs is proceeding to completion. An increase in the monochlorobenzene concentration triggers an alarm in the process control system, and the exceedance of a preset threshold is used to automatically curtail waste input. The CIMS also provides a continuous record of the quality of the product gas being compressed and stored.

TESTING

The pilot-scale process plant was first tested at Hamilton Harbour, Ontario in 1991. The waste processed during those tests was harbour sediment contaminated with coal-tar at concentrations of up to 300 g/kg (dry weight basis). Destruction removal efficiencies (DREs)

of 99.9999% were calculated based on the total organic input and the PAHs analysed in the stack emissions.

A second round of tests of the pilot-scale unit was conducted in 1992 in Bay City, Michigan as part of the USEPA's SITE program. The wastes processed included oily PCB-contaminated water, high-strength PCB oil, and PCB-contaminated soil. Triplicate test runs were planned for each waste type. The results for the test program, confirmed by the USEPA, are shown in Table 1. A SITE Program Project Bulletin for this demonstration was published in September 1993 and a SITE Program Technology Evaluation Report is due in February 1994.

Table 1 USEPA SITE PROGRAM RESULTS

Water/Oil and High-Strength Oil Tests

Run	Waste Type	Contaminant	Concentration (mg/kg)	Target DRE/DE	Achieved
1	Water/Oil	PCBs	4,800	99.9999	Yes
	Tracer	Perchloroethene	4,670	99.99	Yes
2	Water/Oil	PCBs	2,450	99.9999	Yes
	Tracer	Perchloroethene	2,360	99.99	Yes
3	Water/Oil	PCBs	5,950	99.9999	Yes
	Tracer	Perchloroethene	6,100	99.99	Yes
4	Oil	PCBs	254,000	99.9999	Yes
	Tracer	Perchloroethene	33,000	99.99	Yes
5	Oil	PCBs	254,000	99.9999	Yes
	Tracer	Perchloroethene	26,000	99.99	Yes
6	Oil	PCBs	254,000	99.9999	Yes
	Tracer	Perchloroethene	34,000	99.99	Yes

Soil Tests

Run	Waste Type	Contaminant	Concentration (mg/kg)	Desorption Efficiency (%)
1	Soil	PCBs	538	94
	Tracer	HCB	12,400	72
	Tracer	OCDD	0.744	40
2	Soil	PCBs	718	99
	Tracer	HCB	24,800	99.99
	Tracer	OCDD	1.49	99.8

The waste oil was obtained from beneath the Bay City landfill and was analysed to contain 40% PCBs and percent levels of other chlorinated solvents. The contaminated soil was obtained from installation of the sump wells used to collect the oil, and the contaminated water was groundwater from the landfill. The test matrix called for three water/oil tests, three oil tests, and three soil tests.

The water/oil tests were to be nominally 4000 mg/kg PCBs, based on injecting the water and oil in a 100:1 ratio through the atomizing nozzle. As well, perchloroethene was added as a tracer compound. The oil tests were designed to process the high-strength oil at higher throughputs while demonstrating the ability to compress and store the product gas generated. Steam was added through a separate port, but liquid water was not co-injected with the PCB oil. Again, perchloroethene was added as a tracer compound. After oil waste processing, the stored gas was directed to the boiler for about 24 hours, and stack testing by the USEPA sub-contractor was conducted. The target DRE for the PCBs was 99.9999%, and this was achieved for all six tests. The target destruction efficiency (DE) for the perchloroethene was 99.99% and this was also achieved for all six tests. The SITE program analytical results for the

input concentrations of the water/oil mixture and the high-strength oil are shown in Table 1.

Soils with various contamination levels were mixed to produce a relatively homogeneous quantity of soil with a nominal 1000 mg/kg PCB concentration. The soil test runs were delayed until construction and commissioning of the new TDU was completed. During the first TDU test, contaminated soil was processed with a desorption efficiency of 94%, resulting in a processed soil PCB concentration of 30 mg/kg. This result was encouraging for a first run, but the desorbed soil was still above disposal guidelines. The waste soil residence time inside the TDU was increased for the second run, and a desorption removal efficiency of 99% was achieved according to SITE program results. A duplicate sample analysed on site by ECO LOGIC showed a PCB concentration of 0.6 mg/kg, which would correspond to a 99.9% desorption efficiency. The tracer compound used for the soil tests was hexachlorobenzene (HCB), which was spiked at significantly higher concentrations than the PCBs. The hexachlorobenzene was also contaminated with significant levels of octachlorodibenzo-p-dioxin (OCDD). The desorption efficiencies achieved for the HCB and OCDD for Test 2 were 99.99% and 99.8%, respectively. Due to TSCA permit restrictions, only two runs were performed for the third test condition. It should be noted that the performance of the TDU is independent of the destruction process. The reactor destruction efficiencies for the desorbed contaminants were high for both TDU runs.

An additional component of the test program was a 72-hour endurance test aimed at demonstrating the continuous operation capabilities of the ECO LOGIC Process. The equipment operated perfectly and the 72-hour test was concluded successfully.

CURRENT STATUS

ECO LOGIC has applied to the Ontario Ministry of the Environment for a technology approval for the existing pilot-scale unit for the destruction of PCB askarel fluids. This approval is currently underway.

The existing pilot-scale unit can compete economically for the destruction for high-strength wastes. It must be made clear that ECO LOGIC offers total destruction of PCBs and PCB-contaminated equipment, and that the owner of the PCBs is not left with any liability. ECO LOGIC is currently seeking commercial contracts.

To compete economically for the destruction of environmental wastes, such as PCB-contaminated soils and sediments, a full-scale hazardous waste destructor is required. The full-scale destructor is currently being designed and will have a nominal throughput capacity of 100 tonnes per day for soils at a cost of approximately $400 per tonne. ECO LOGIC is planning to construct a full-scale destruction system this spring which should be ready for operation by June 1994.

ECO LOGIC has also entered into a joint venture agreement for the Australian market and the existing pilot-scale destructor is scheduled to go to Australia in late 1994 for demonstration projects in that country.

Treatability studies using ECO LOGIC's lab-scale destruction system are continuing. The lab-scale equipment includes a TDU sized for processing 10 litres of soil or sediment, and an SBV suitable for processing samples of chemical wastes or contaminated electrical equipment. Clients find that treatability studies are a cost-effective method for determining the applicability and effectiveness of the ECO LOGIC Process to their waste problems.

The ECO LOGIC Process is a proven technology for the destruction of high-strength PCB oil wastes and is suitable for the destruction of askarel fluids used in electrical equipment and PCBs or chlorinated dioxins in soils. ECO LOGIC offers a cost-effective alternative to incineration. It can be permitted to provide a complete on-site destruction service for the owners of hazardous organic wastes.

ADVANCED WASTE MANAGEMENT
INDIRECT THERMAL TREATMENT TECHNOLOGIES

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PCS PROCESS METHOLOGY AND TECHNOLOGY DESCRIPTION:

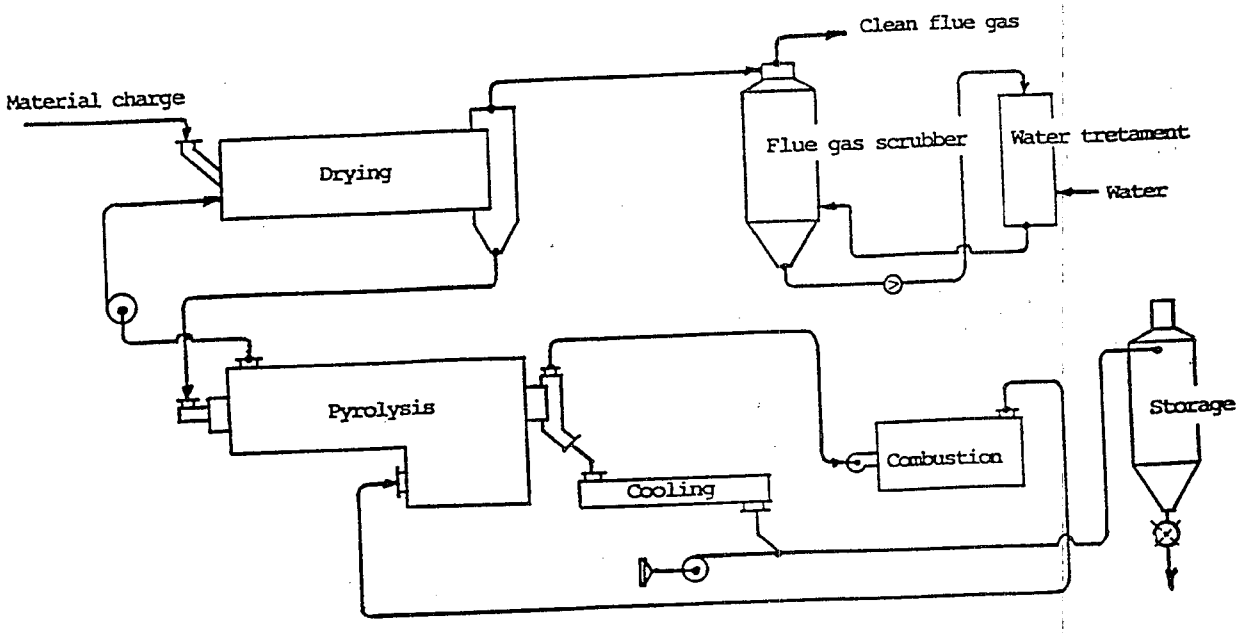
THE PROBLEM: Waste has no chemical formula. Most solid hazardous and non-hazardous waste, including the selected types as well, is of a complex chemical and physical nature with extremely non homogeneous composition and structure. The destruction therefore poses complex technical and cost efficiency problems, especially at the off gas treatment.

THE SOLUTION: The PCS indirect thermal treatment technology uses Flash Pyrolysis to decompose organic and inorganic solid hazardous and solid waste by multiple and separate stage process. Flash Pyrolysis is not an incineration, it is a thermal decomposition process without oxygen in reductive environment, which eliminates the possibility of dioxin or dibenzofuran formation.

The term "Pyrolysis" refers to reductive thermal treatment, indirect heat up, dry distillation and the gas-out process of the organic and/or inorganic material.

The term "Flash" refers to a very fast process of gas-out. The time factor is of great technical importance concerning this process.

The term Product Control Systems "PCS" refers to the indirect thermal treatment family with main components being: the indirect heated rotary reactor which is the heart of the technology, indirectly cooled solid material cooler and the indirectly cooled scrubber. The PCS technology is complete in the sense that the technology starts with raw material input and provides a complete solution treatment process including; material transportation systems, closed drying, Flash Pyrolysis reactor, gas-vapour combustion chamber, water treatment, Honeywell automatization and other auxiliary equipments.



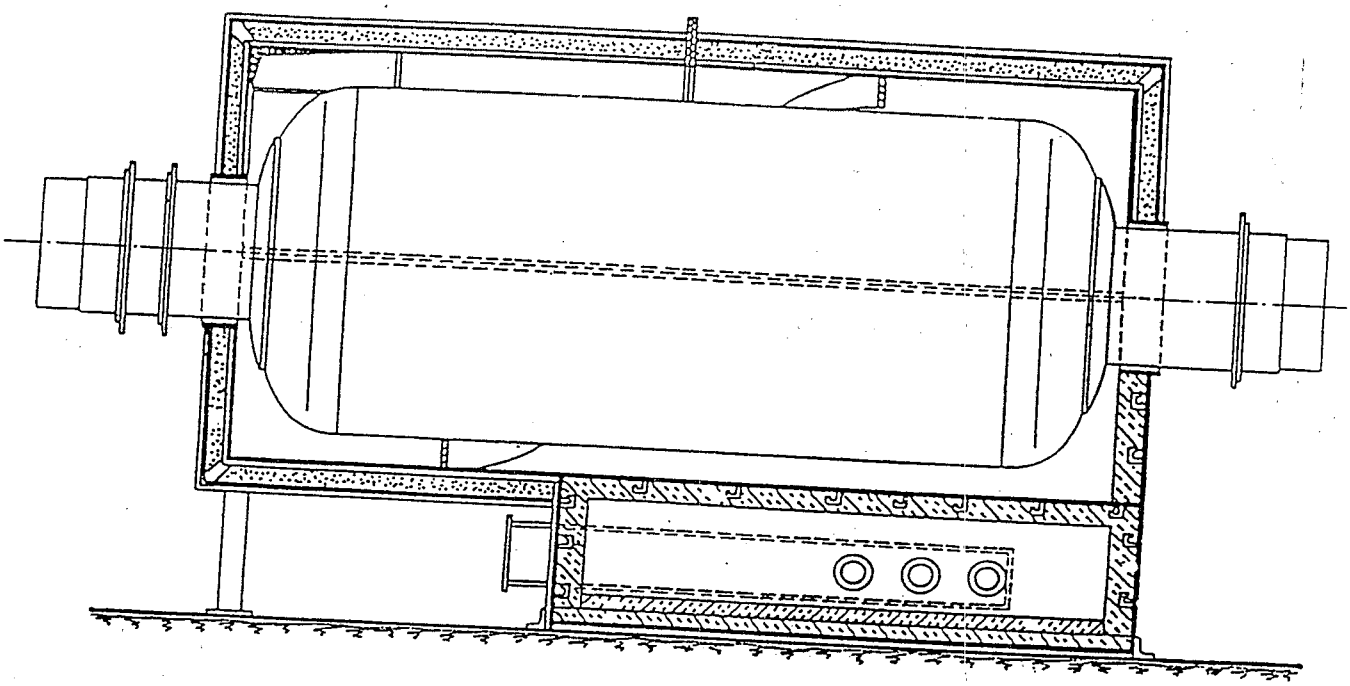
The main component of the PCS process is its use of a specially designed, indirectly fired rotary reactor in which waste in a reductive environment is partially vaporised and/or gas-out in low vacuum (0-50 Pascal or 0.00725 PSI) between the temperature ranges of 450°C - 1,000°C degrees Celsius [°C] (850°F - 1,850°F, degrees Fahrenheit [°F]).

The waste is first reduced by a homogenizer mill to less than 5 mm (< 0.2 inches) prior to entering the dryer. Operating at 400 °C (752 °F), the directly fired closed dryer lowers the moisture content of the waste from 45 % to less than 15 %. The dried waste is conveyed into the rotary reactor where it is indirectly flash pyrolysed. The residence time is approximately one hour. Generally, most heavy metals and high boiling point organic compounds will remain in the solid phase while volatile organic compounds, halogens and some volatile metals, such as mercury, will be concentrated into the pyrolysis gas-vapour phase.

PYROLYSIS GAS-VAPOUR PHASE from the reductive decomposing process is directly combusted at a minimum 1,250 °C (2,300 °F) 2 sec. residence time, fast cooled and heat from its flue gas is recovered. Even though it is generally experienced that dioxin and furan gases are not created in a reductive environment and, theoretically, the pyrolysis gas-vapour phase does not contain dioxin-furan gases, these gases are still to be treated as gases containing dioxins-furans. The remaining gas is cleansed in a high capture efficient, indirectly cooled, wet gas scrubber prior to discharge. Scrubber process water is cleansed prior to discharge and the precipitate from the water treatment, including neutralised salt, is reintroduced into the system.

SOLID PHASE is indirectly cooled and discharged for utilisation. The basic material usually is of mixed organic and/or inorganic origin and/or contains heavy metals. Solid end product, containing pure carbon, is utilised for energy production and the ash mixed with inorganics is conditioned into an unleachable water resistant form of low volume for final disposal. If the basic material is of pure organic origin, the solid end product is Pure Activated Carbon powder which is utilised as a filtration material.

PCS PROCESS REACTOR AND ITS OPERATION:



The reactor rotates around its symmetric axle, is horizontally arranged and cylindrically formed with no refractory line installed inside. The high quality steel mantel is heated from outside through the lined combustion chamber. Inside the reactor body, blades promote the transportation of the material. The reactor is a permanently working vessel; the basic material enters in at the input-end while the out-gassed solid material and the pyrolysis gas-vapour phase are discharged at the output end, separately from each other.

The main features of the PCS Flash Pyrolysis reactor:

1. Indirect heat transfer through the mantel to the ground material with extended surface area.
2. Permanent operation and homogenised material throughput.
3. Special sealings to provide guaranteed closed operation.
4. Automatic process control of the operation.
5. Low vacuum provides for a high security factor during the operation.
6. Practical and not complicated end user friendly construction.
7. Synchronised auxiliary installations.

The required amount of energy input is basically supplied from hot flue gases. These are produced in the combustion chamber for direct incineration of the pyrolysis gas vapours and heats the reactor body from outside the mantel. Heat transfer happens indirectly through the mantel to the material. The heating is nothing more than the transfer of the energy content of a hot medium to a cooler medium.

The heat transfer contains three phases:

Primarily: Energy transfer from heat under the material in the rotary kiln. The material, which is ground down to a maximum dimension of 5 mm, (0.25 inches) to have extended surface area, is permanently mixed, which mixing process is promoted by the blades inside the reactor body. The heated material is to be permanently replaced by cooler materials again and again. Therefore the thermal conductivity of the solid waste material is of less importance and can be within a wider range. This is a very important and vital technical factor, particularly in relation to the solid wastes which are usually bad thermal conductors and are of extremely mixed physical and chemical character.

Secondarily: Radiation heat transfer from the inner top surface of the reactor body.

Tertiary: Over the temperature of 275 °C (530 °F) an exothermic reaction starts during the decomposition of the material.

It is to be noted, that the basic pyrolysis process is of endothermic character. Reactions at temperatures of 275 °C (530 °F), and over, become exothermic. The exothermic process is a slow process. Therefore the extended pyrolysis gas-vapour production will not result in an explosive production of gas vapours. Even if such theoretically explosive production of pyrolysis gas-vapours happens, the size of the reactor's inner space, the reductive environment and the adjustable permanent vacuum control compensate the action.

The thermal engineering design of the reactor is related to the throughput capacity of the reactor and the extremely qualitative variations of the input material. No matter if the basic material is of organic, inorganic and/or mixed character, the chemical components will be separated at a certain treatment temperature if the boiling point of the components are under 1,000 °C, (1,850 °F). The pyrolysis reactions are not only a sequenced series of reactions, but parallel series of reactions as well, with different activities of energy. To provide a successful Flash Pyrolysis process, three different factors are needed: (1)material, which is thermally decomposable, (2)high enough temperature, that the waste material pass the complicated decomposition phases, (3) enough reaction time. The general technical concept is: concerning solid hazardous waste treatment the material is to be processed at approx. 600°C (1,112 °F) and concerning manufacturing of Pure Activated Carbon the material is to be processed up to 1,000°C (1,850°F).

There are five well distinguished phases concerning the dry distillation process inside the reactor:

1. Warm up phase: up to 150°C-160 °C (300°F-320 °F). Characterised by the evacuation of the free and most of the bounded water from the material.

2. Heating up phase: up to 270°C-280 °C (518°F-536 °F). Characterised by heavy discoloration of the material, and the evacuation of the remaining chemically bounded water, with simultaneous development of gasification.

3. Thermal decomposition phase: up to 380°C-400 °C (716°F-752 °F). Characterised by self carbonisation with exothermic chemical reactions and a heavy gasification process.

4. Gas-out phase: up to 500 °C (932 °F). Characterised by the escape of volatile compounds, including the heavy tars, from the material.

5. Stabilisation phase: over 500 °C (932 °F). The solid rest phase of the Flash Pyrolysis process is carbon and/or inorganics including approximately 6-8 % ash and/or the inorganic solid rest products.

PCS PROCESS DEVELOPMENT STATUS:

The PCS technology is at the full scale demonstration and commercialisation phase of the development. The indirect thermal treatment technology concept of the innovative PCS reactor has successfully been proved during the test of the pilot plant. During the past years complete and detailed manufacturing designs have been finalized for preparation of manufacturing of full scale demonstration units with alternative applications:

A. 2 tons/hour input capacity plant for solid hazardous waste treatment.

B. 2 tons/hour input (2,000 tons/year output) capacity plant for high quality Pure Activated Carbon production with twin reactors.

C. 200 kg/hour input capacity plant for treatment of hospital waste.

PCS PROCESS PATENT STATUS:

The PCS method and apparatus innovative technology is recently PCT patent approved world wide: U.S. patent no.: 5,194,069 (Method and Apparatus for Refinement of Organic Material) and 5,261,936 (Gas Treating Apparatus). Additional pending PCT patents: Method and Apparatus for Treatment of Waste Materials and/or Nuclear Contaminated Materials, Thermal Treatment of Materials. Inventor: G. Edward Soméus.

PCS PROCESS PILOT PLANT:

Media Treated: The pilot plant has worked since September 1990 over 2,000 hours testing the following materials: pure wood and straw waste, impregnated wood, heavy metal contaminated wood, furfural, used activated carbon, lignite. Pollutants Treated: All organics, Pentachlorophenol (PCP), Sulphur. Rated throughput: 100 - 250 kg/hour.

Examples for Initial and Final Pollutant Concentrations (FPC):

Wood (acacia lignum) with 7.2 % complex acid content	FPC of acids in cleansed flue gas	not measurable
PCP impregnated wood with 3.0% initial PCP content	FPC of PCP in cleansed flue gas	0.12 mg/m3
Lignite with 3.5 % initial total sulphur content	FPC of SO_2 in cleansed flue gas	10 mg/m3

PCS PROCESS LIMITATIONS:

The PCS technology is limited for: (1)treatment of liquids (water, flammable liquids and solvents), (2)treatment of solid material over 45% moisture content, (3)explosives and/or materials with highly oxidising character under heat treatment, (4)materials which can not be decomposed by thermal treatment at 600 °C (1,112 °F), (5)nuclear waste with high radioactivity, (6)to reach capacity which is limited by the size of the PCS reactor.

PCS PROCESS APPLICATION:

A. Waste-to-Energy:
   1. Solid Hazardous Waste Treatment: Standard input capacity 2 tons/hour (volume approx. 8 m3/hour), 15,000 tons/year.
   2. Clean Coal: Purification of High Sulphur Content Lignite: Standard input capacity 8 tons/hour, 60,000 tons/year.
   3. Hospital Waste Treatment: Standard input capacity 200 kg/hour, 1,240 tons/year.
   4. Mixed and/or Low-grade Selected Household Waste Treatment: Standard input capacity 2 tons/hour, 15,000 tons/year.

B. Waste-to-Pure Activated Carbon:
   Standard input capacity 2 tons/hour, 15,000 tons/year; output 2,000 tons/year (virgin). Regeneration is available.

C. Waste Minimization:
   Treatment of solid low radio-active organic nuclear waste.

PCS PROCESS ECONOMY:

Initial capital cost: (1)Standard version with 2 tons/hour input capacity for solid hazardous waste treatment approx. 3.5 million USD, EXW. (2)Standard version with 2 tons/hour input capacity for solid hazardous waste treatment turn key installed approx. 6.5 million USD, CIF. (3)Standard version with 200 kg/hour input capacity for solid hospital waste treatment approx. 1 million USD, EXW.

Operating and maintenance cost: Average 250 USD/tons (including financial costs)
Amortiserings time: 5 years

RESULTS AND CONCLUSIONS:

Results: that which was recently technically and economically unavailable, is now viable and available reality, even far beyond the year 2000.

Conclusions: (1)safe, advanced and intelligent technology, (2)economical and cost efficient, converts trash into cash, (3)complete solution, no need for post processing, (4)flexible operation and simple maintenance, (5)quality modular design and manufacturing, (6)linkage opportunity to existing large incinerators to improve better technical and economical performance of the incinerator, (7) upgrading of capacity for new and existing installations, (8)training and education opportunity for the end user, (9)neighbourhood and environment harmonised technology with aesthetic outlook, (10)especially suited for local application within small communities to manage locally generated waste stream (decentralised waste management concept).

FOR MORE INFORMATION:

Product Control Ltd.: La Plaiderie, St. Peter Port, Guernsey, C.I., United Kingdom, Tel: (44-481) 726 426, Fax: (44-481) 726 526, Att: Mr. G. Edward Soméus.

BIOREMEDIATION OF SOILS AND SEDIMENTS USING DARAMEND™

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Grace Dearborn Inc.
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INTRODUCTION

Bioremediation of soils/sediments and wastes containing wood treatment organic chemicals, including creosote and chlorinated phenols (especially pentachlorophenol) and high molecular weight (aliphatic and aromatic) hydrocarbons has been problematic due to the insoluble, hydrophobic nature of the compounds. The presence of these organic compounds in soil can result in the blocking of soil micropores and the coating soil organic matter. This effectively prevents the native microbial biomass from accessing the nutrients, oxygen and biologically available water. Therefore, even in soils containing microorganisms with the enzymatic capacity to degrade the target compounds, the rate and extent of bioremediation can be unsatisfactory.

Daramend bioremediation has overcome these difficulties through the homogeneous incorporation of organic amendments which increase the ability of the contaminated material to supply biologically available water, nitrogen, phosphorous, micronutrients, and oxygen to bacteria and other microorganisms. At the same time, the amendments reduce the acute toxicity of the soil's aqueous phase by transiently adsorbing pollutants and providing surfaces for microbial adhesion and development of biofilms.

The ability to cost-effectively increase the activity of PCP, PAH, and hydrocarbon-degrading bacteria in highly toxic soils and sediments renders Daramend bioremediation applicable to a great number of contaminated sites.

TECHNOLOGY DESCRIPTION

Solid-phase, biodegradable organic amendments are used in Daramend bioremediation in conjunction with low intensity tillage and control of the moisture content of the material being treated. These amendments are selected for each individual soil based on their specific physical and chemical properties, including particle size distribution, nutrient profile, and nutrient release kinetics. The rate of bioremediation of the soil is increased through modification of the local environmental conditions of the soil undergoing treatment.

Extensive laboratory studies with a wide range of soils containing organic chemicals have proven Daramend effective in enhancing the target compound degradation rates. Concentrations of pentachlorophenol (PCP) of up to 2170 mg/kg have existed in soils which were effectively treated using Daramend. In addition, residual concentrations 0.7 mg PCP/kg have been obtained.

Equally important is the types of soil which have been effectively treated using Daramend. Laboratory and field pilot scale demonstrations have been performed using all types of soil from a sandy loam to a clay based soil. Sediments dredged from harbours and wood chips are also among some of the types of media successfully treated using Daramend.

PILOT SCALE DEMONSTRATIONS

Wood Treatment Soils

An industrial wood preserving site in Ontario, Canada was the location for the pilot scale demonstration of Daramend. This site is situated approximately 1 km upstream of the mouth of a river. Wood products were treated exclusively with creosote at this site from the early 1900's to mid 1960's. Since then both creosote and pentachlorophenol (PCP) were used until the treatment facility was shut down in 1992. This site is presently used to store lumber which has been treated elsewhere.

The practice of storing treated wood directly on the soil surface has led to the deposition of both chlorophenols and PAHs. The selection of sites for the demonstration project therefore required that a thorough site investigation be undertaken to determine the spacial distribution of chlorinated phenols and polynuclear aromatic hydrocarbons (PAHs).

An initial site investigation/soil characterization study was undertaken in April 1991 for the pilot scale demonstration work. This investigation identified areas of substantial concentrations of PCP in order to test the effectiveness of the technology.

The pilot scale demonstration performed at this site involved soil containing 702, 1442 and 7000 mg/kg of chlorophenols, PAHs and total petroleum hydrocarbons (TPH), respectively. Excavated soil was treated on-site in a confined treatment area. A liner system was used to ensure control of any leachate or runoff generated during the demonstration.

The excavated soil was transported to the treatment area, deposited to a uniform depth of 0.45 m, and homogenized by tilling. The purpose of tillage is to reduce variation in the soil's physical and chemical properties (e.g. small regions of very high contaminant concentration which may inhibit biodegradation of the target compounds) and to uniformly distribute the appropriate organic amendments.

The soil was then treated with the appropriate organic amendments to a depth of 0.45 m. This is the maximum depth to which the solid-phase organic amendment(s) can be incorporated in a homogeneous manner. During the remediation process, soil moisture content was maintained within a specific range to facilitate rapid growth of a large and active microbial population. Diffusion of oxygen through the soil matrix to microbially active microsites where biodegradation occurs can be limited by excessive moisture. Conversely an inadequate supply of biologically available water will also inhibit biodegradation. Bench scale treatabilities were used to determine both the optimal soil moisture content and the most effective organic amendment(s).

The soil was tilled on a regular schedule to increase diffusion of oxygen to microsites and to re-distribute water in treatment zones.

The chlorophenol concentrations in the soil were reduced from 702 mg/kg to 4 mg/kg in 345 days(Figure 1), total PAH concentrations were reduced from 1442 to 36 mg/kg in 209 days (Figure 2). Residual TPH concentrations went from 7000 mg/kg to 34 mg/kg in the first 182 days. In all cases the control zones experienced low or no reduction in concentrations of chlorophenols, PAHs or TPH.

It is also important to note that even the most recalcitrant higher molecular weight PAH's were reduced to below the Canadian Council of Ministers of Environment (1991) guidelines for industrial soils. An example of the reductions seen is presented in Figure 3.

The soil from the pilot scale demonstration was subjected to toxicity testing by an independent laboratory. The untreated soil had a 100% mortality rate for earthworms, and 0% seed germination for lettuce, radish and oats. The Daramend treated soil had a 0% mortality rate for earthworms and showed 88% seed germination for radishes, 93.3% for oats and 46.7% for lettuce. Lettuce is one of the most environmentally sensitive plants and even the control showed only 88% seed germination.

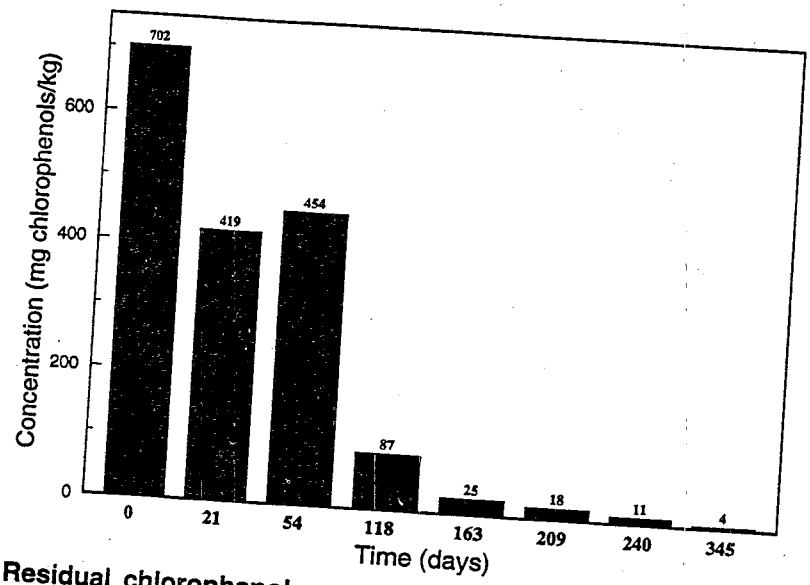

Figure 1: **Residual chlorophenol concentrations during pilot scale ex-situ (on site) Daramend bioremediation of industrial wood preserving site soil.**

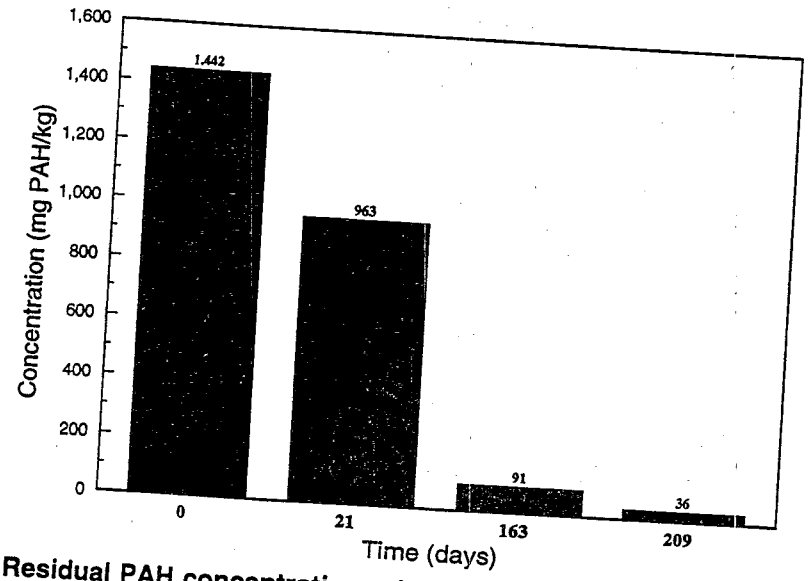

Figure 2: **Residual PAH concentrations during pilot scale ex-situ (on site) Daramend bioremediation of industrial wood preserving site soil.**

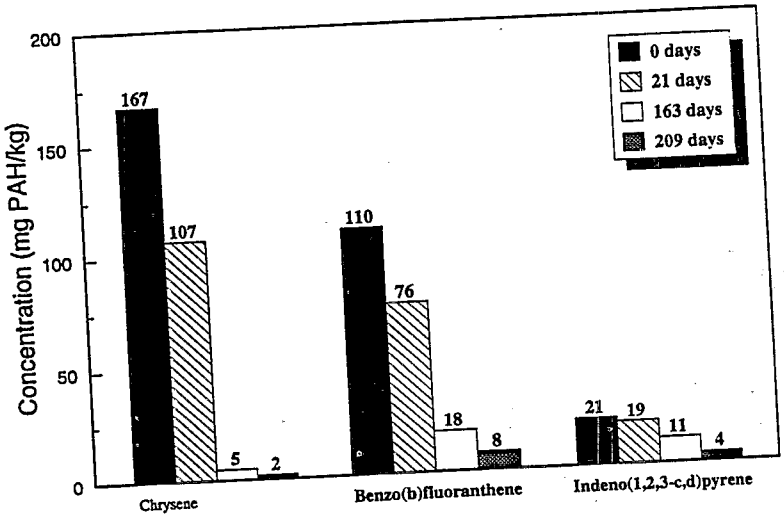

Figure 3: **Residual PAH concentrations during pilot scale ex-situ (on site) Daramend bioremediation of industrial wood preserving site soil.**

Sediment- Ex-Situ Application

This pilot scale demonstration utilized approximately 90 tonnes of sediment dredged from Hamilton Harbour (Ontario). The treatment area consisted of two double layers of sand and high density polyethylene. The purpose of this liner system was to prevent migration of target compounds from the sediment to the surrounding soil. The treatment area was covered with a steel/polyethylene structure to prevent contact between the sediment and normal precipitation patterns. This was done to ensure control of sediment moisture and temperature.

The sediments were treated in the same manner as the soil in the first pilot scale demonstration. The high water content of sediments has traditionally prevented the use of bioremediation and the pilot was performed to demonstrate that low cost bioremediation of sediments was possible. Control of moisture content in sediments can be facilitated with the use of a bulking agent.

Composite samples were taken from each of five subplots within the treatment area to determine the untreated sediment initial PAH concentrations. The average PAH concentration from all the composite samples was 1150 mg/kg total PAH. Concentrations of the 16 priority PAHs ranged from 5 to 720 mg/kg.

Data from pilot-scale Daramend bioremediation of dredged sediments from Hamilton Harbour is presented in Figure 4. At 312 days a total reduction of 90% was achieved.

Full-Scale Demonstration:- Ex-Situ and In-Situ Applications

The wood treatment site used in the pilot scale demonstration is the location for the full scale demonstration. The ex-situ (on-site) portion of this demonstration is being audited under the US EPA SITE demonstration program.

Initial concentration of chlorophenols in the soil chosen for the ex-situ demonstration was approximately 127 mg chlorophenols/kg. The concentrations are the average composite samples from each of twenty three subplots within the areas treated. The ex-situ portion of the full-scale demonstration has been initiated. Baseline and time zero sampling has been performed by the SITE auditors. A full EPA SITE demonstration report is expected to be published in late 1994.

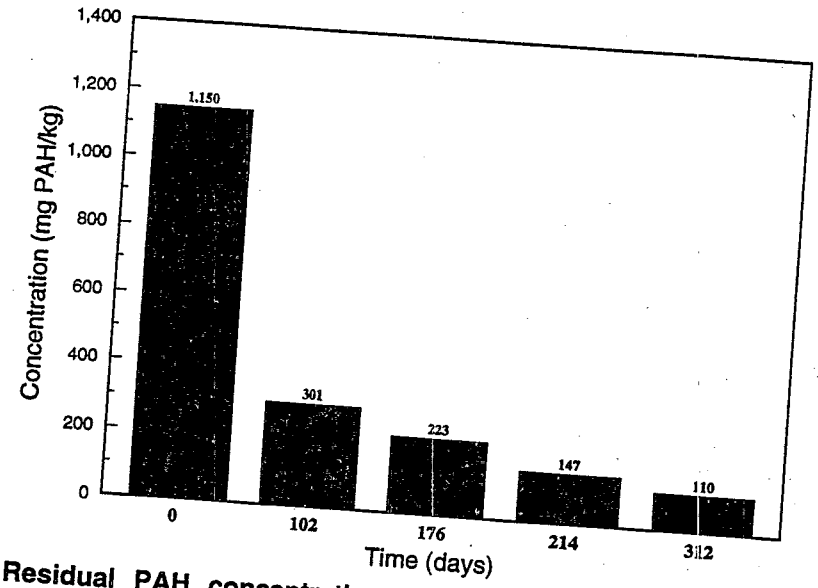

Figure 4: **Residual PAH concentrations in dredged sediments during Daramend bioremediation.**

COMMERCIAL SITES

Daramend is currently being used as a commercial treatment technology at three sites in Canada and one in the United States. The size of the areas being treated is quite varied, with some in more of a pilot scale clean-up rather than a full site remediation. This is one of the strengths of the technology, in that as much or as little of the site can be cleaned up at a time as determined by the economic realities of the company.

The sites undergoing commercial treatment include two containing wood treatment chemicals: a clay soil and the other a site containing wood chips, and one containing pesticides.

BIODEGRADATION OF DINOSEB USING THE SIMPLOT PROCESS

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INTRODUCTION

The J.R. Simplot Company process hereafter referred to as the Simplot process was developed to remediate soils contaminated with nitroaromatic compounds. Initial studies and method development was performed by Dr.'s Ronald L. and Don L. Crawford at the University of Idaho. In this demonstration the compound of interest was dinoseb (2-*sec*-butyl-4,6-dinitrophenol), an herbicide used on potatoes and legumes before being banned . This technology completely degrades the dinoseb without the formation of toxic intermediates. The Simplot process is also effective on other nitroaromatics such as TNT, RDX and HMX.

The Simplot process utilizes anaerobic conditions to facilitate the degradation of dinoseb. This is achieved by mixing a carbon source (potato byproduct) and a buffer with the contaminated soil. The aerobic bacteria utilize this carbon source and create the anaerobic condition needed to degrade the dinoseb. The microorganisms are often indigenous to the site which is being remediated. If necessary bacteria can be provided to enhance degradation of the compound.

METHODOLOGY

The Simplot process consists of a bioreactor equipped with agitation and monitoring equipment. Excavation, screening, homogenization and loading equipment are required for loading the reactor. During treatment, continuous onsite personnel are not needed. For small contamination sites, small portable bioreactors can be used. At larger contaminated sites, modular bioreactors can be erected with minimal effort.

The Simplot process is dependant on pH, redox potential, and temperature. The pH range for effective degradation is between 7.5 and 8.0. This range is maintained by the addition of acids or buffers. Trials at Ellensburg showed that once the process is started, pH targets were achievable. A redox potential of -200 mV is required to maintain anaerobic conditions. This redox potential is achieved when aerobic bacteria consume the oxygen from the soil and water fractions. During agitation (liquid lancing) of the reactor, the solid phase is recontacted with the liquid. This is accomplished without rasing the redox potential by submerging the pump inlet well below the surface of the liquid. Periodic lancing of the reactor provides sufficient contact between the liquid and soil phases. Treatability studies have shown that semi-static or static systems will achieve acceptable results when soil, water, and carbon sources are well mixed during the loading of the bioreactor.

Temperature can also influence the successful operation of the bioreactor. During treatability studies it was determined that a reaction temperature between 35 and 37°C was optimal. We determined at Ellensburg that a reaction temperature of 18°C was sufficient.

For this demonstration, the soil was screened to 0.5 inches, where the oversized materials were placed in a pile for further processing and cleaning and the properly sized materials were placed in a stock pile for addition to the bioreactor. The bioreactor was filled with the amount of water and buffer needed for the 40 cubic yards of contaminated soils. The carbon source was added to the soil as it was placed into the bioreactor. Once the bioreactor was filled, the inoculant was added allowing the system to be started.

RESULTS

The Simplot process was able to reduce the concentration of dinoseb in the soil to below analytical detection limits within 23 days. The mean concentration of dinoseb in the 40 yards of soil placed into the bioreactor was 28 ppm. It was estimated that cold weather would slow the reaction so midpoint samples were to be taken at 23 days. The samples at the midpoint showed that the dinoseb had been degraded.

The analytical detection limit was 0.015 mg/Kg. With removal of the dinoseb to below detection limits, the removal efficiency was greater than 99.88%. The remediated soil was demonstrated to be clean to the Washington Department of Environmental Quality (DEQ). The State of Washington is one of the states that allows cleaned soils to be returned to the ground after being listed in the Resource Conservation and Recovery Act (RCRA). Since the soil was clean, it was placed back on site in an area that was not contaminated as clean useful soil.

CONCLUSIONS

Based on experience and data generated in the demonstrations of the Simplot process, the following conclusions have been drawn:

1) The Simplot process can reduce the level of dinoseb in the soil by greater than 99.88%. The final post treatment samples were degraded to less than the analytical detection limit of 0.015 mg/KG.

2) Complete anaerobic biodegradation of dinoseb can be achieved without the formation of toxic intermediates.

3) The Simplot process can degrade dinoseb at temperatures much lower than optimal for most bioremediation technologies. Degradation of dinoseb was demonstrated at 18°C.

4) Treatability studies and the test at Ellensburg, WA have shown that continuous mixing is not required. Periodic mixing of the soil and recontacting the muds with the liquid is sufficient.

5) The Simplot process works in the presence of other commonly found contaminates on agricultural sites. On the Ellensburg site the soil was co-contaminated with 2,6-dichloro-4-nitroaniline (nitroaniline); parathion; malathion; 4,4'-DDT; atrazine; chlordane and endosulfan.

6) The Simplot process can be used in a wide variety of soil types. The soil type will determine the amount of soil processing required before placement in the bioreactor. Soils containing large rocks and debris will need to be separated. The oversized material is then cleaned of surface contamination. The cleaning liquid is added to the bioreactor.

7) The Simplot process is estimated to be less than 1/2 the cost of incineration. The cost is

site specific and will need to be determined by treatability studies.

The Simplot process is a cost effective alternative to other processes for the decontamination of dinoseb for any size site. The process has no air emissions in the form of particulates during remediation. The Simplot process allows cleaned soils to be returned to site in states that allow RCRA listed 40 CFR Part 261 Subpart D wastes to be returned to site. Soils will be rich in organic carbon, minerals, and have a high nutritional value. This treatment can be completed in less than one season, with no liability for shipping contaminated soils off site.

BIOLOGICAL SLURRY TREATMENT AS PART OF AN INNER CITY MODEL REMEDIATION PROJECT OF A 10.000 M³ SOIL CONTAMINATED WITH METHYLATED PHENOLES UNDERNEATH THE GOLDBEKHAUS IN HAMBURG, GERMANY

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INTRODUCTION

With regard to growing environmental concern and limited space in Hamburg as the second largest city in Germany, the city and the state of Hamburg have taken significant action to overcome problems caused by closed hazardous waste sites, industrial landfills and old chemical production sites.

The total volume spent for evaluation, remediation and incapsulation reaches a yearly total of US $ 35 million, not included research and pilot plants.

HANSATEC is a Hamburg based company specialized in biological and physical soil treatment both on-site and off-site with a 32.000 square feet treatment facility.

Linked to a group with several environmental activities in the port of Hamburg, HANSATEC received a US $ 8 million contract for the incapsulated removal, transportation and treatment of a highly contaminated slurry, produced during in-situ soil washing system SOILCRETE by company KELLER GRUNDBAU at the GOLDBEKHAUS - site.

The Remediation Site

During the years 1889 until 1963 the company Schülke & Mayr produced the desinfectant SAGROTAN ® on a 25,000 square feet industrial site. Located close to a scenic channel of the river Alster, surrounded by early 1900's buildings in a preferred living area this site and the old production facilities have become a cultural center for the quarter. Meanwhile the buildings are classified as historical monuments

In 1985 the first surveys and chemical evaluation were carried out after indications of contamination occured. During the next three years further studies provided more geological and chemical data and resulted ultimately in a final remediation conception.

THE CONTAMINATION

Due to a well defined production process of the desinfectant facility the contaminants are well known and identified as

1. Phenol
2. Methylated Phenols
3. Dimethylphenol

Substance	Water Solubility	Vapor Pressure	Legal Standard	Toxicity - Fish -	Toxicity - Bacteria -
Phenol	8.4 g/100 ml	0.2 hPa	100 ppm	5 mg/l	350 mg/l
Methylphenol	2.5 g/100 ml	0.05 hPa	5 ppm	15 mg/l	100 mg/l
Dimethylphenol	--	--	10 ppm	10 mg/l	130 mg/l

It is shown that these contaminants not only have a very high emission potential but also a high toxicity to humans (nervous and intestial systems) connected with a high skin-permeation capability.

For this reason a completely incapsulated system for any treatment on-site and a high standard of workers' protection is required during remediation work.

RESULTS OF SITE EVALUATION

Due to the geological situation a total of 80 - 100 t of contaminants are spread in some 10,000 m³ of soil. The maximum concentration in a tourbe-layer is described with 63,000 mg/kg. The maximum depth in which the standard value of 20 mg/kg is exceeded is 18 m below surface.

To a very small amount PAH and heavy metals are found - due to the old heating facility for the factory.

During WW II the chemical laboratory was used for experiments with chemical weapons. Prior to any remediation work the area had to be cleared by a special department of the City of Hamburg.

BIOLOGICAL DEGRADATION STUDIES

According to literature the contaminants are potentially biodegradable, whereas the inhibitory concentration for microbiological growth too low for technical treatment units in this case.

Due to this fact, a population of highly resistant microorganisms with sufficient degradation capabilities was isolated from the site, selected for external fermentation (only organisms identified and classified as being non pathogenic to humans and aquatic system were chosen for bioaugmentation) and provided as a freeze-dried concentrate.

The optimum degradation parameters were checked in a laboratory set-up as follows:

Experimental Material and Methods

500 grams of homogenized waste material and 200 grams of water were filled into a 1 liter column. 5 ml of a nutrient solution (equivilent to 150 mg N/l and 75 mg P/l and a buffer solution (pH 7) was added. Air was pumped onto the column at 500 ml/min. In order to calculate the "stripping effect" a 3 M NaOH-solution was used in a gas washing bottle. Temperature was held constantly at 25° C.

The contaminants are detected by HPLC - analysis.

As a screening the determination of Phenols according to DIN 38409 H16 (KOH extraction, colormetric determination) is used

TECHNICAL CONCEPTION

After almost three years of pre-investigations the remediation concept was as follows:

I.Removal of soil from the site by modified SOILCRETE® technique by KELLER GRUNDBAU.

A 15 cm concrete layer is built as a coverage for the site to allow equipment moving, clean working area and most effective sealing of the drilling equipment.

A so called preventer is mounted onto the concrete layer.

A special drilling device is brought down to the desired depth - according to contamination spreading. After reaching the end depth a 400 bar high pressure water injector rotates and is slowly removed to the surface. By this technique a 1.5 m diameter column is created with the loosened soil material and water.

Right after this process a "contractors device" is brought down and the "column" is refilled with concrete pumped in with 10 bar. The contaminated soil/water slurry will be completely exchanged and leaves the preventer.

II. Handling and Transport of Slurry

A combined pneumatic system "sucks" material out of the preventer by vacuum of -0.9 bar and an air flow of 1500 m³/h into a storage tank, out of which the material is pneumatically transfered onto a sieving machine. A 4 " pump pumps the slurry into specially equipped barches, each holding 75 m³.

Removal and Transportation in Numbers

contaminated soil	:	14,800 cubic yards
surface of contaminated soil	:	1,400 sqft.
maximum depth	:	59 ft
maximum concentration	:	63,000 mg/kg phenolic substances
number of drilling units	:	2
number of vaccum units	:	3
number of barches	:	4
holding capacity	:	98 cubic yards
begin/end of operation	:	7/28/92 - 10/27/93
average production	:	112 cubic yards/day

maximum production	:	234 cubic yards/day
distance from remediation site to external treatment site	:	11 miles
number of transports	:	426

EXTERNAL TREATMENT

The material is pumped over 85 m from the barches - the landing station is located on a tidal canal of the Elbe river in the port of Hamburg - into the treatment facility. A high perfomance dredging-pump together with a 9 bar high pressure flushing system is used to operate the system with the required security. Prior to biological treatment the material has to be separated into different fractions listed as follows:

Material	Separation Unit	Treatment
gravel 2 - 8 mm	sieve with flushing device	target value is reached
sand 25 µm - 2 mm	screw classifier	landfarming
fine sand 150 µm - 500 µm	derrick-machine	landfarming
organics and minerals 63 µm - 100 µm	belt press	landfarming with inoculation
water, organics and minerals < 63 µm	bioreactor	neutralisation inoculation of adapted micro-organisms

EXTERNAL TREATMENT IN NUMBERS

area of treatment facility:

machinery:	1,568 sq.yd
landfarming area	4,312 sq.yd
infrastructure	392 sq.yd
total	6,272 sq.yd

electrical installation	195 kw
personnel:	5

COSTS

transportation	DM 80.00 per m³ (~ US$ 45.00)
separation/biological treatment	DM 200.00 per m³ (~ US$ 115.00)
workers protection fees (according to German guide line ZH 1/183)	DM 30.00 per m³ (~ US$ 18.00)
recycling of treated material	DM 25.00 per m³ (~ US$ 14.00)

CONCLUSIONS:

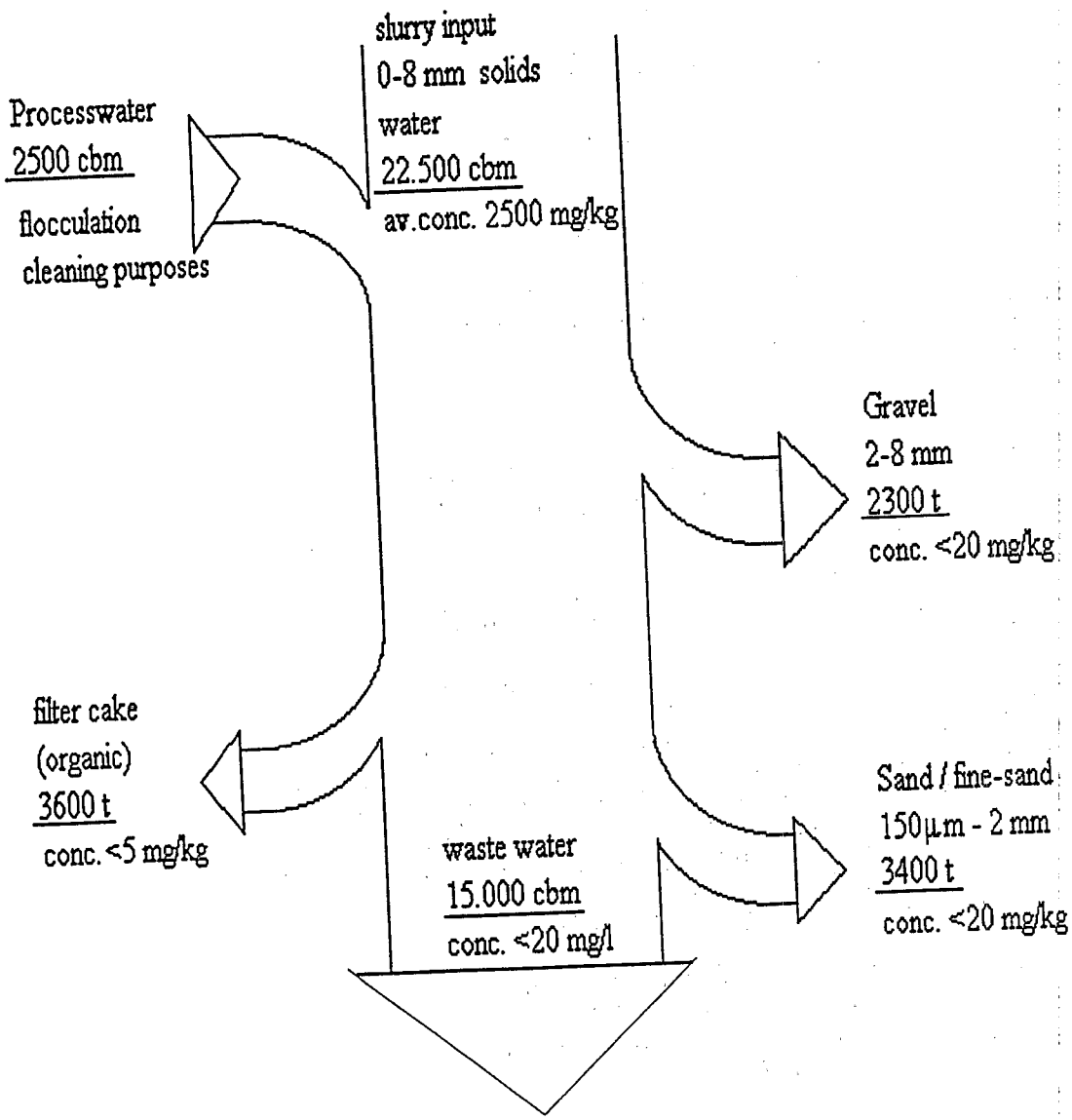
A cost effective and innovative technology was developped and introduced to meet the following requirements of the City of Hamburg:

- removal (completely incapsulated) of heavily contaminated soil underneath existing buildings, while full range of activities in a neighboring cultur center took place in a distance of less than 65 ft;
- total information of the public about every step of remediation;
- environmental friendly transportation of the contaminated material;
- full biological clean-ups;
- 100% recycling of treated material;
- continous monitoring of gaseous contaminants in treatment facility and on-site.

After 244 work days some 23,000 m³ of material was treated successfully. By means of a specially adapted population of microorganisms even chemicals designed for desinfectant purposes were degraded down to background levels.

A heavy duty separation technique as pre-treatment insured optimum biological conditons and a well defined marketable recycling material.

Mass balance
(external treatment)



BTEX, MINERAL OIL, AND PESTICIDES REMEDIATIONS USING THE UVB TECHNOLOGY

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Eric J. Klingel, IEG Technologies Corp., 1833 D Crossbeam Drive, Charlotte, NC 28217, USA, Tel.: (704)357-6090
Eduard J. Alesi, IEG Technologie GmbH, Dettinger Str. 148B, D-73230 Kirchheim/Teck, Germany, Tel.: +49(7021)861293

INTRODUCTION

Vertical circulation flows around wells with two screen sections in one aquifer, so called "Vacuum Vaporizer Wells" (German abbr.: UVB), have become increasingly important for aquifer remediation. Originally this idea was used only for in situ remediation of aquifers from strippable contaminants. For the patented UVB technique, special wells with two screen sections, one at the aquifer bottom and one at the groundwater surface or below an aquitard, are employed (Figure 1). The groundwater moves vertically within the well. The contaminated water enters the well at the bottom and the stripped or treated water leaves at the top or vice versa. In the vicinity of the well a vertical flow circulation is created.

The groundwater statistically passes the well casing several times where it can be treated with suitable measures depending on the contamination before it finally leaves the sphere of influence of the UVB (Figure 2). Thus, the groundwater surrounding the well and finally the aquifer material regarding this zone is remediated. The generated groundwater circulation determines the sphere of influence of a well and is overlapped with the natural groundwater flow (1).

METHODOLOGY

For in situ bioremediation of hydrocarbons essentially oxygen is needed. The in situ stripping process with air by an UVB (Figure 1a) provides oxygen saturation. While the groundwater quantity captured by a well remains nearly constant, the quantity of circulating water around the UVB can be extremely enhanced by a stronger pump in the well casing. Thus, the amount of oxygen supplied for in situ bioremediation can be considerably increased with nearly no additional costs. Carbon dioxide as a by-product is removed from the groundwater by the same stripping process, so the pH-value cannot drop producing new problems otherwise. For hydrocarbons lighter than water (LNAPL), especially when they are found in phase, a downward operating UVB (Figure 1a) is normally used: The contaminated water enters the well through the upper screen and the treated groundwater leaves the well through the lower one. Volatile stripped contaminants in the off-gas are eliminated by using e.g. activated carbon or biofilters. At those sites often an UVB technique is used which combines vapor extraction with the stripping process; thus lots of oxygen are supplied to the vapor zone and capillary fringe for biodegrading processes. To enhance in situ biodegradation additional nutrients, and, if necessary, further electron acceptors can in principle be added in the well casing just before the stripping unit to get an optimal mixing; up to now additions have not been used, however. The bioprocesses occur in the well casing and in the aquifer surrounding the well (2).

A special bioreactor or other technologies have been or can be installed within the well casing between the lower and upper screens to treat special contaminants as e.g. pesticides or nitrate (Figure 1b). These in situ techniques can be combined with in situ stripping to eliminate the biogas produced (e.g. CO_2 or N_2) or to introduce oxygen (2).

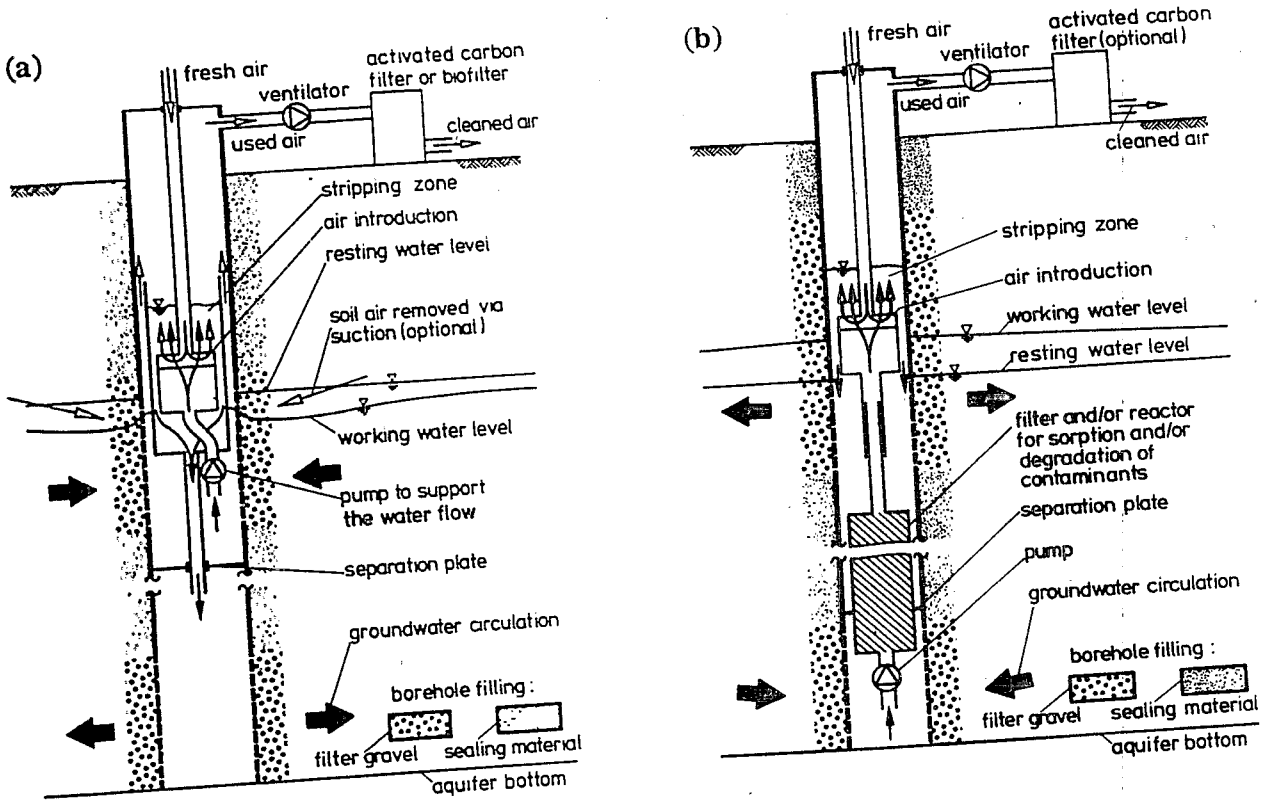

Figure 1. UVB technique combining in situ stripping and enhanced in situ bioremediation: (a) downward operation for LNAPL (e.g. BTEX, mineral oil, phenol, kerosene), and (b) using special reactor within the well casing to eliminate e.g. pesticides, nitrate

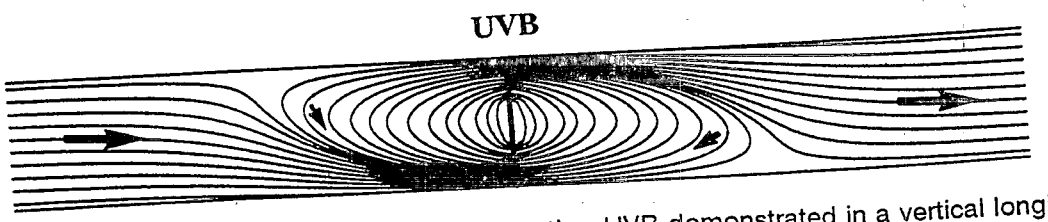

Figure 2. Streamlines around an upward operating UVB demonstrated in a vertical longitudinal section parallel to the natural groundwater flow

RESULTS

Case 1: BTEX and Mineral Oil in Berlin, Germany

The UVB technology combining in situ stripping and enhanced in situ bioremediation (Figure 1a) was installed in Berlin, Germany, and has successfully remediated a site contaminated with BTEX, styrene, and mineral oil hydrocarbons. The spill was caused by a leaking storage tank. Some feasibly removable soil was excavated from the unsaturated zone and transported to a landfill. The concentration of BTEX and styrene in the groundwater at the beginning of remediation was 280 mg/L and of mineral oil hydrocarbons was 1 mg/L.

At the site sandy gravel dominates from 3.9 m to about 10.6 m below the soil surface; however, clayey silt as well as fine organic-rich layers and occasional stones form intermittent horizontal layers. At around 10.6 m, gray clayey marls make up an impermeable layer. The unconfined saturated aquifer has a thickness of about 6.5 m; the groundwater table lies at around 4 m below the ground surface. With a hydraulic gradient of 0.08% and a hydraulic conductivity of 3.1 x 10^{-3} m/sec, groundwater flows at a rate of 1.1 m/day. Pore space in the sandy gravel is 0.2.

Two UVBs were installed to remediate the groundwater and vadose zone at the site. The source area of the contamination was just upstream of UVB 1. Because free product of LNAPL was found on the groundwater surface, both UVBs operate downward (Figure 1a).

After some tests the operation of UVB 1 started on June 19, 1991 and of UVB 2, which is located 40 m downstream of UVB 1, on October 22, 1991. The operation was stopped on February 8, 1993 when for some time the contaminant concentrations of the groundwater was below detection limits in all monitoring tubs. A renewed monitoring of the groundwater on September 21, 1993 gave maximum concentration values of 0.73 mg/L for BTEX and styrene and of 0.63 mg/L for mineral oil in the shallow monitoring tube of UVB 1. All the other monitoring tubes showed non detectable values. So UVB 2 was removed. The operation of UVB 1 was again started on October 20, 1993. Five following groundwater monitorings resulted in non detectable concentration values each. So UVB 1 was finally stopped in January 1994. The locally found concentration values in September 1993 are supposed to stem from the capillary fringe upstream from UVB 1. The paper presents the measured data of removed hydrocarbons as well as the concentrations of hydrocarbons, oxygen, and the pH values in the groundwater influenced by the operation of the UVBs.

Case 2: BTEX and IPE in Troutman (Piedmont region), North Carolina

At a retail gasoline facility in the Piedmont physio graphic region in west central North Carolina total BTEX and isopropylether (IPE) concentrations (prior to activation of an UVB system) were found up to 1.72 mg/L and 2.6 mg/L. At this site hydrocarbons, only dissolved in groundwater, were detected over the entire aquifer thickness and no phase was found. Therefore an upward operating UVB system (2) was installed. Depth to groundwater is 13.7 m and the hydraulic conductivity is approximately 1.3 10^{-5} m/sec. Regolith (saprolite) consisting mainly of clayey silt reaches to a depth of 22.9 m over lying fractured bedrock. A Soil Vacuum Extraction (SVE) system previously operated at this site. The SVE system was deactivated after seven months of operation in May 1992 after VOC removal rates (i.e. off-gas concentrations) decreased to 0.45 to 0.68 kg/day.

Dissolved petroleum hydrocarbon constituents have historically been present in all of the original five monitoring wells. Two additional monitoring wells were installed after UVB system activation on September 17, 1992 to better define both the lateral and vertical extent of petroleum hydrocarbons present in groundwater. Vertical hydrocarbon extent is being monitored through a monitoring well completed in bedrock, which is located cross gradient to the UVB system. It was sampled on December 18, 1992 and February 11, 1993 and laboratory analysis indicate below detection limits for BTEX and IPE.

The capture zone of the UVB system was calculated to encompass the area with dissolved BTEX and IPE. The initial hydrocarbon removal rate (i.e. off-gas) was 15.6 kg/day. Removal rates have ranged from 0.45 to 10.4 kg/day during the first 93 days of operation since activation. The stripping reactor is operating at an 83% to 97% stripping efficiency. A significant decrease in the concentration of dissolved BTEX and IPE in the center of the plume (3 m from the UVB well) has been observed through the initial 474 days of operation, reducing maximum concentrations from 1.72 mg/L and 2.6 mg/L prior to activation to values of 0.004 to 0.11 mg/L and 0.48 to 1.2 mg/L. In also comparing BTEX and IPE concentrations in the other monitoring wells besides the latter one, it appears that the extent

of the dissolved phase plume is diminishing. The paper will discuss the well operation and the measured results.

Case 3: Pilot test for pesticides in Germany

A specially designed well based on the UVB technology of Figure 1b was used in a pilot study for a biological and physical in situ remediation of triazines (3). During reloading and rinsing out of the storage tanks, pesticides seeped into soil and groundwater. Downgradient of this source area, where the UVB is located, the contaminated groundwater flows into the remediation well through the lower screen section and is pumped through the activated carbon filter within the well casing and up to the reactor situated aboveground for this pilot study. Here oxygen saturation takes place by the standard UVB technique (Figure 1b). Activated carbon is used to adsorb the triazines; the carbon also serves as backing and growth material for microorganisms that exist in the groundwater. Before the pilot test began, triazine metabolites were detected in the groundwater. Thus, contaminant-adapted microorganisms were present and already degraded some triazines. Typical factors limiting the biological degradation rate include low triazine concentrations in the aquifer and low absolute numbers of microorganisms in the groundwater. By allowing both the contaminants and the microorganisms to accumulate within the biofilter, these limitations can be overcome. Sufficient oxygen for the degradation is available because of the oxygen saturation of the groundwater. Thus, the activated carbon unit need not to be renewed often. The collected field data and experiences obtained from this pilot test verify that the UVB with a biofilter within the well casing can be successfully applied to triazine contamination in groundwater. The paper will discuss the findings and monitoring results during the pilot test.

CONCLUSIONS

Three case studies demonstrate that in situ groundwater and aquifer remediations can be successfully realized in a reasonable time. The used UVB techniques have the advantage that vertical circulation flows around wells with two screen sections includes the total aquifer thickness as well as an extended horizontal sphere of influence and transport contaminated groundwater in a continuous process through the well casing where it can be treated with suitable in situ treatment techniques. Depending on the found contaminants these techniques are in the case of BTEX, mineral oil and IPE the elimination of all strippable compounds by in situ stripping in a vacuum and simultaneous supply with oxygen as an electron acceptor for enhancing biodegrading processes as well as removal of degradation products (CO_2). The biodegradation takes place in the well casing and in the aquifer surrounding the well. The production of biomass was detected in the well but bioclogging was no limiting factor of the bioremediation.

In case of pesticides a reactor filled with activated carbon has been installed within the casing of the UVB beside the usual stripping unit to deliver oxygen saturation in the total sphere of influence of the well. The sorption processes on the activated carbon supplies the desired concentration of pesticides (and of microbes), which is, beside suitable milieu conditions (e.g. sufficient 0_2), the basis for the degradation in case of a plume remediation with maximum triazine concentrations of only 3 µg/L.

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CONTROLLING FUGITIVE EMISSIONS FROM EXCAVATION OF CONTAMINATED SOIL: A CASE STUDY

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INTRODUCTION

When site conditions necessitate the excavation and on-site treatment of soil contaminated with volatile organic compounds (VOCs), unintentional releases of these VOCs to the atmosphere can cause serious problems. While on-site personnel can be trained and outfitted with safety equipment to minimize exposure to airborne contaminants during remediation, surrounding civilian populations are at risk. In addition to the short-term effects of VOC exposure like nausea and headache, there can be long-term health risks, including increased incidence of cancer. Additionally, even if there is no direct exposure to humans, emitting untreated VOCs directly to the atmosphere degrades the general air quality. Every pound of VOC that is lost from the soil at a site cleanup as fugitive emissions represents a simple trade-off of soil contamination for air contamination.

At the Basket Creek Surface Impoundment Site in Douglasville, Georgia the EPA Region IV Superfund removal program was faced with a challenging situation. The site was contaminated during the 1960's when it was used for the illegal disposal of hazardous waste. An intermittent stream bed was dammed with soil to form a small impoundment. Liquid hazardous waste was dumped into the impoundment over a number of years. In 1970 the impoundment was covered with soil. While no cleanup took place over the ensuing years, a community of eighteen homes developed within a one-half mile radius of the site.

EPA initiated action under the Superfund program in April of 1991. Sampling of soil from the surface impoundment indicated very high concentrations of VOCs and elevated concentrations of heavy metals. Soil sample results from the most contaminated area are as follows:

Contaminant	Concentration (ppm)
Mercury	390
Lead	9,400
Trichloroethylene	8,600
Toluene	220,000
Methyl Isobutyl Ketone	66,000
Methyl Ethyl Ketone	23,000

METHODOLOGY

Based on economic considerations, the decision was made to evaluate the feasibility of on-site treatment of the contaminated soil. Treatability studies were conducted for two on-site treatment technologies, in-situ vapor extraction and low temperature thermal desorption. In-situ vapor extraction was ruled out because of the low permeability of the contaminated soil. During the low temperature thermal treatment treatability study, the treatability sample ignited during a simulation of conditions in the primary chamber of a thermal desorber. This indicated that the soil was too highly contaminated with VOCs to safely treat with on-site low temperature thermal treatment. At this point a decision was made to excavate the soil from the impoundment, process the soil through a power screen, and stockpile the soil on site. Treatment options could then be evaluated based on the homogeneous mixture of contaminated soil in the stockpile.

Calculations were made to estimate the quantity of VOCs that would be released to the atmosphere from the excavation, screening, and stockpiling operations. Experience with methane emissions from coal seams in the mining industry was used to calculate VOC emission rates. The calculated maximum quantity of VOCs potentially released from the operations as fugitive emissions was estimated at 1,800 pounds per day. Depending on weather conditions, these emissions posed potential health risks for local residents and posed a threat to general air quality. At this point a decision was made to investigate the possibility of utilizing engineering controls to minimize fugitive emissions. The outcome of this investigation was the development of a workplan which involved the following components:

- construction of an enclosure large enough to cover the impoundment area and a stockpile area

- development of an air handling system capable of exhausting a sufficient quantity of contaminated air to maintain a safe working environment in the building

- installation of a thermal oxidizer (fume incinerator) to thermally destroy the VOCs in the air stream exhausted from the building

- installation of an ex situ vapor extraction system designed to remove VOCs from the stockpiled soil

Implementation of this workplan began in March of 1992 with the erection of a metal, pre-fabricated building measuring 60 feet wide by 120 feet long by 26 feet tall. This was followed by installation of the air handling equipment which included three 1,200 cfm (cubic feet per minute) vacuum pumps for the vapor

extraction system, an 8,000 cfm induced draft blower for exhausting the building air, a baghouse (dust collector) for removing particulate from the air stream, and duct work to connect the components. An 8,000 cfm capacity thermal oxidizer was leased to treat the contaminated air stream.

In October of 1992 a full system test was completed in conjunction with a trial burn on the thermal oxidizer. Contaminated soil was exposed with a trackhoe and the soil was stirred to liberate VOCs which were routed to the thermal oxidizer. The Environmental Response Team of EPA conducted the trial burn. The thermal oxidizer demonstrated greater than 99% removal efficiency (maximum inlet concentration of 1,378 ppm and maximum outlet concentration of 7.5 ppm) on a total hydrocarbon basis. Mass emission rates were calculated for VOCs, semi-VOCs, and dioxin/furan and reported to the Agency for Toxic Substances and Disease Registry (ATSDR). ATSDR determined that the predicted emissions from the thermal oxidizer would not pose a threat to public health.

Full scale operations commenced on November 20, 1992. Excavation of the area of contamination (60 feet wide by 80 feet long and up to 14 feet deep) was accomplished by dividing it into ten-foot by ten-foot grids. Excavation was limited to individual grids to limit the surface area of exposed soil. As VOCs were liberated during the excavation process, they were collected by the air handling system and routed through the duct work and into the thermal oxidizer where the VOCs were oxidized at 1,600 degrees F. After a grid was excavated and the contaminated soil screened and stockpiled, confirmatory samples were collected. If the sample result indicated that the removal action levels had been reached, the grid was backfilled and the next grid was opened. The air handling and treatment system operated at all times while excavation operations were ongoing. As the stockpile was built, slotted plastic well screen was arrayed in the pile. These horizontal vapor extraction wells (seventeen wells total) were connected to three manifolds outside of the building. A vacuum pump provided the vacuum pressure for each manifold. These manifold pipes (six-inch plastic pipe) then fed into the main duct (24-inch galvanized steel) just before the inlet to the thermal oxidizer. As the stockpile increased in size, the individual vapor extraction wells were extended by adding ten foot sections of well screen.

The controls put in place to limit fugitive emissions, while preventing off-site exposures, created additional concerns for on-site worker safety. The most critical safety concern was the potential to develop an explosive atmosphere within the enclosure. Because it was not practical to eliminate all ignition sources inside the enclosure, the emphasis was placed on controlling and monitoring the concentration of combustible gas. The key to controlling the concentration of VOCs in the air was the air exhaust system. By removing the VOCs as they were emitted from the soil, VOCs were prevented from dispersing

throughout the enclosure airspace. Vacuum ducts were placed at the excavation and on the power screen because these were sources of VOCs. Additionally, the vapor extraction wells in the stockpile limited off-gassing of VOCs from the stockpiled soil.

VOC concentration in the building air was monitored at all times while excavation was taking place. A Combustible Gas Indicator was used to monitor the concentration of combustible gas in the airspace. A limit of 10% of the Lower Explosive Limit (LEL) was set as an automatic cease-work condition. A Photo-Ionization Detector (PID) was used to monitor airborne contaminants on a total hydrocarbon basis. A limit of 500 ppm hydrocarbons in air was set as a cease-work condition. In addition to the atmosphere within the enclosure, another important safety concern was the potential to develop an explosive atmosphere in the air handling duct work, both inside and outside the enclosure. A limit of 20% of the LEL was set for all components of the air handling system, including the vapor extraction piping, the flexible duct, and the steel duct.

RESULTS

The Basket Creek Surface Impoundment cleanup was a success on two levels. Most importantly, it achieved the goal of cleaning up the site through the removal and treatment of the contaminated soil. A second important achievement was the demonstration that fugitive emissions from VOC contaminated sites can be virtually eliminated.

During the four month long excavation phase of the project, approximately 2,000 tons of contaminated soil was removed from the former impoundment and placed on the stockpile. Over that period approximately 70,000 pounds of VOCs (primarily toluene, methyl ethyl ketone, and methyl isobutyl ketone) were removed from the soil. The primary mechanism for VOC removal was the vapor extraction system in the soil stockpile. Specifically, 75% to 80% of the VOC removal took place in the stockpile vapor extraction system. The remaining removal consisted of VOCs liberated during the excavation and materials handling processes. All of the recovered VOCs were routed to the thermal oxidizer for treatment. The vapor extraction system was operated for three weeks after excavation was complete. Sampling of the stockpiled soil then demonstrated that the soil was no longer a regulated waste and it was subsequently disposed of off-site at minimal cost. VOC removal during excavation and in the vapor extraction system resulted in total VOCs in the soil being reduced from approximately 30,000 ppm to less than 350 ppm.

A secondary objective of the project was to demonstrate that fugitive emissions can be controlled, even when excavating and handling soil contaminated with extremely volatile contaminants. A rigorous air monitoring and sampling protocol was implemented to evaluate the effectiveness of the fugitive emission control system. Based on the fact that no VOCs were detected during

hourly air monitoring surveys around the perimeter of the enclosure and the fact that no VOCs were detected in off-site high volume air samples, it is apparent that the control system was effective. This is particularly significant in light of the fact that airborne concentrations of VOCs inside the enclosure occasionally approached 500 ppm and regularly ranged between 200 and 400 ppm.

CONCLUSIONS

The total cost of the project was approximately $2.2 million. This cost is significantly higher than a conventional excavation and disposal project. Most of the extra costs were associated with the engineering controls employed to capture and destroy the fugitive emissions. These capital costs, approximately $1 million, include the enclosure, the vapor extraction system, the particulate filter, the induced draft blower, the thermal oxidizer, and all of the duct work and piping to connect the different parts of the system. The $1 million includes the cost to buy or lease the equipment plus the labor cost involved with fabricating the system. One important consideration is the fact that these are fixed costs which are incurred regardless of the quantity of soil treated. Because of the relatively small quantity of soil involved at the site, significant diseconomies of scale were encountered.

The fact that uncontrolled hazardous waste sites pose a long-term threat to public health and the environment through the contamination of important natural resources such as groundwater and surface water is well established. However, the short-term risks associated with cleaning up these sites are not nearly so well understood. The additional costs of the Basket Creek project associated with collecting and treating fugitive emissions were incurred so that these short-term "remediation risks" could be minimized. The purpose of the Basket Creek project was to demonstrate that the available technology is capable of achieving total fugitive emission control. This successful demonstration now provides site managers with another tool to use for managing short-term remediation risks. A system like the one employed at Basket Creek is most applicable where high concentrations of VOCs are found in a relatively small area. However, a portable system that could be moved from one area of contamination to another might be practical for larger sites.

REMEDIATION OF AN AREA CONTAINING CHEMICAL WARFARE AGENTS

WOLFGANG P.W. SPYRA

Abstract

A very unique remidiation of a contaminated site is introduced. The former German Army Gas Laboratory was situated in the Spandau Citadel in Berlin from 1936 till the end of World War II. Major research work for a chemical warfare was done there, as

- Developing and testing protective equipment
- Experiments in the field of detoxification
- Developing and testing chemical warfare agents
- Evaluating caputured chemical warfare agents and detoxicants
- Subjective experiments with human being and animals
- Developing methods for producing the blood and nerve agents up to "Sarin"
- Developing substitute raw materials
- Laboration of munition

This means that a lot of different and very unusual hazards could be there like tear gas, sternutators, blister agents, nerve agents and others more.

The primal cause to become attention on that problem was an incident which happened in 1983 when civil workers during reconstruction works at the fortification released a chemical substance from a discovered bottle. This bottle caused the suspicion of nerve agents because an enzyme test was positive.

By intensive investigations evaluation of files and questioning of coeval witnesses it was possible to determe that this discovery was not made be coincidence but because of the great number and varity of recoveries it was considered to be a part of unsystematic deposits of chernicals and top chemical warfare agents from World War II.

At the end of this investigations there was the decision that this area has to be remidate. A recovery strategy was developed. In order to obtain the Basis for the recovery strategy, hazardons situations head to be classifid into 3 remediation categories.

Before starting the remidiation procedure different preinvestigations must be made as

- Ferromagnetic investigations
- Evaluation of pictures of the British Royal Air Force
- Test of soil for toxic substances, etc.

to identify potential areas of danger.

The concept for warding of hazards provides for the creation of a danger area which is exclusively meant for personnel tasked with the prevention of danger. Beyond this area the residual risk can be compared to the hazards to which all citizens to varying dagrees may be exposed.

Three mainpoints made the conception difficult. First it was diffrend to obtain literature on chemical warfare gents, specially on those used in World War II.

This military waste, which does not exclude chemical warfare agents, the radius of the danger zone has to be assumed at 500 m, given that no large-calibre ammunition has to be expected. With respect to the citadel the situation around the point of dankger is as follows:
100.000 people live within the compass of 2.5 km. In the immediate vicinity of 500 meters there is a traffic junction of both the public transportation and the individual traffic.

The size of this danger area is determined by the hazard. The following criteria are applied to determe the degree of hazardousness:

- released amount of chemical warfare agent
- dangerousness of the relcared chemical warfare agent
- how was the agent released
- weather conditions
- effective protective measures

For safety reasons a danger zone has to be defined on principal as such during recovery work. This zone must be adequate in view of the potential hazards key substances and quantities were determined by orientation on toxic, chemical and physical properties of the suspect substances and the degree of protection we found suitable

200 g Tabun
200 g Hydrocyanic acid
500 g Phosgene

The recovery of chemical warfare agents principally bears the risk of selting free these highly toxic chemicals.
Thus all measures are devised in a way to ensure that

- no warfare agent are set free
- in case they are set free the source of the harmful substance is to be sealed immedeately, and
- the released warfare agent is bond.

The used recovery techniques varied from mechanical procedures to the treatment of archeology finds.

As a summary it can be said that for remediation measures the state of aggregation, solid, liquid or gaseous, as well as vapor preasure and the enthalpy of vaporization of chemicals require special consideration and aspect of on - the - job safety.

Low temperatures are favorable for the recovery because chemicals have less vapor pressures than at higher temperatures. This reduces concentrations of the toxicants in the atmosphere.

For physical reasons the minimum temperature for recovery work is the freezing point of water (T = Grad Celsius) because water is used to mininize the danger. The maximum temperature depends on the maximum stress human beings can be exposed to, as they cannot bear over a longer period of time a temperature higher than their interior body temperatur of 38 Grad Celsius.

This report introduces an integral concept for the remediation of extremely dangerous areas in densely populated housing areas, which apart from meeting technical and engineering requirements considers also socio-political and social aspects.

The comprehensive preparation and enforcement of the those measures required approx. 13.4 mio DM for personnel and approx. 11.1 mio DM for material and investments. Thus the recovery costs per m^3 searched soil amount to 4,000 DM. Based on experiences and on the fact that existing facilities can be used again it has to be assumed that future recovery project will cost much more less.

The remediation works in form of a partial remediation of the Citadel (3,000 square meter, depth down to 6 m) were already concluded after 1 1/2 year of recovery time instead of the planned four years while the "normal life" at the citadel could be maintained to a limited extent. Recovery material consisting of 70.000 kg soil mainly contaminated with arsenic componends like Lewisite I, II and III but also pure chemical warfare agents are waiting to be disposed of. Chemical warfare agents of all classification were found, except from nerve agents. In detail those are: eye-irritants, sternutators, pulmonary agents and skin irritants.

A disposal of the material is complicated at the moment. The only incineration plant for chemical warfare agent in Germany, operated under the responsibility of the Federal Ministry for Defense, is not functioning at present. But even when it will be operating again, the question has to be asked when Berlin will be able to dispose of its recovered harmful substances: too many finds are made nationwide and the capacity of the plant is too limited to cope with the destruction of chemical warfare agents.

TECHNOLOGY FOR HAZARDOUS GASEOUS POLLUTANTS TREATMENT BY DOUBLE ELECTRON BEAM GAS EXCITATION

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INTRODUCTION

The hazardous wastes in the forms of liquids, gases and solids are produced by industry. Especially harmful for a man and environment are pollutants which are dispersed, out of control, often many kilometers from the source. Even the concentration of these pollutants in the waste stream is very low (ppm's) the total amount of hazardous waste emitted may reach thousends tons annualy.

Presently, no doubt, most harmful for a man and environment are acidic pollutants SO_2 and NO_x emitted during fossile fuels combustion. The amounts of these compounds emitted in Poland, where coal is mostly used as a primary energy source, reach 4 and 1.5 million tons SO_2 and NO_x annualy. The above numbers for the USA are 27 and 19 respectively.

The other gaseous pollutants emitted by industry to atmosphere are volatile organic compounds (VOC). The off-gases obtained during remediation of soil of ground water (vacuum or air stripping) contain these compounds as well.

PROCESS DESCRIPTION

An electron beam accelerator is a basic tool used in a process. High energy electrons form large numbers of ion pairs and exited molecules along their paths. These cause fast reactions of reactive components, mostly undesirable hazardous components of gaseous mixture.

The products of reaction are neutralized (in the case of SO_2 and NO_x, $H2SO_4$ and HNO_3 are formed which react with ammonia) or decomposed. The solid products (ammonia sulfate and nitrate) are then collected and used as a fertilizer.

The process has been successfuly applied for flue gas treatment at power plants (SO_2, NO_x) [1,2,3,4], waste incinerator (SO_2, NO_x, HCl, dioxines), tunnels (NO_x) [5] and other industrial and soil remedition off-gases (VOC) [6,7].

The biggest industrial plant for electron beam flue gas treatment is in operation in Poland [8]. 20000 Nm^3 /h of flue gases is treated with removal efficiency of 90% for SO_2 and 80% NO_x. New technical solutions has been applied for the first time (double and longitiudal irradiation, new window construction, new type humidifier etc.) leading to the reduction of energy consumption (9 kJ/kg of gas) and solving other operational problems [9].
The scheme of industrial pilot plant is given in Fig.1.

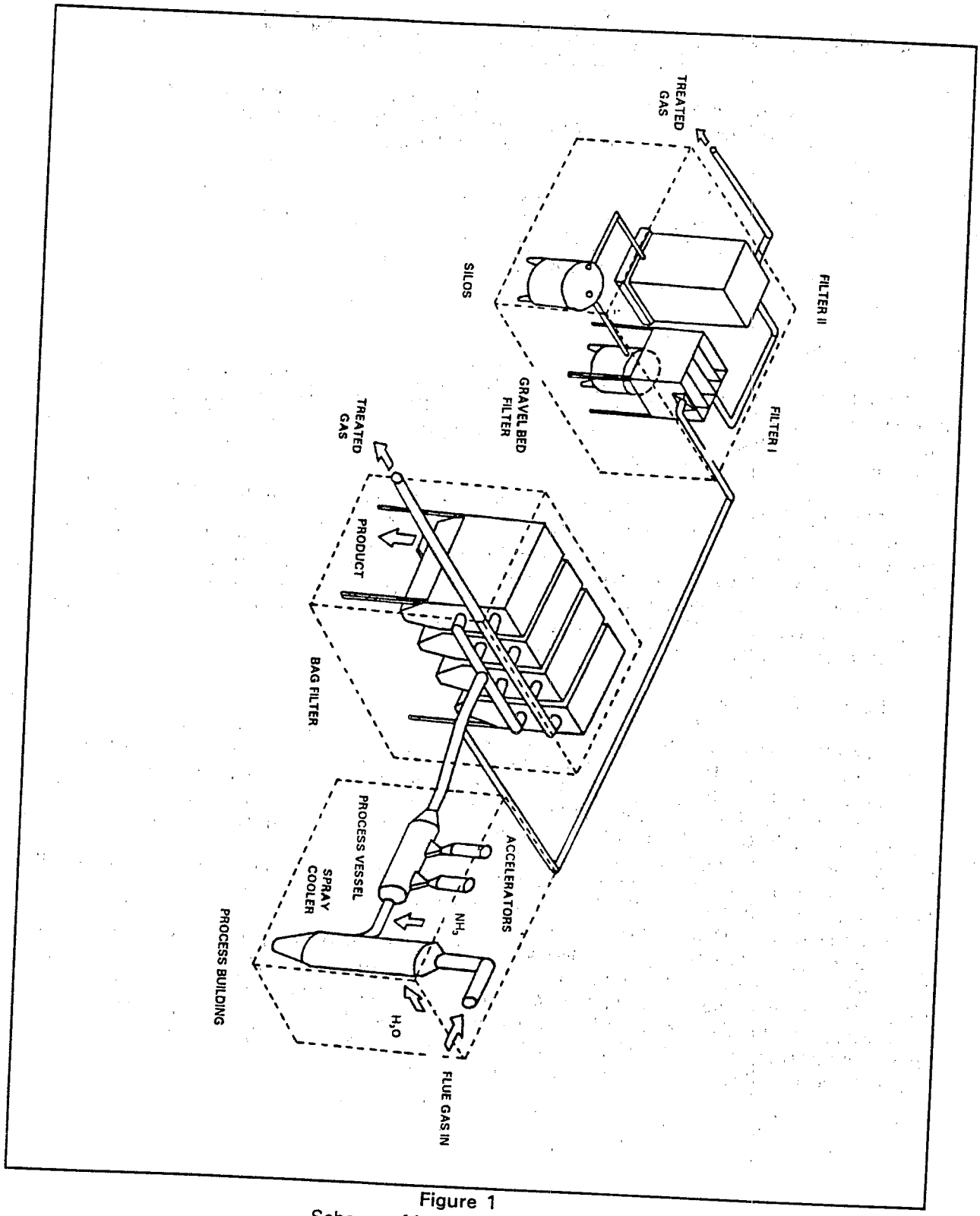

Figure 1
Scheme of industrial pilot plant.

EB/MW COMBINED PROCESS

The experimental set up for investigation of hazardous waste removal from gaseous phase has been built on the base of electron accelerator and two independent microwave generators in Institute of Nuclear Chemistry and Technology [10]. That allows to investigate a combined removal concept based on the simultaneous use the electron beam and streams of microwave energy to produce cold plasma in reaction vessel.

The reaction vessel was constructed as a cylinder. The microwave streams are propagated axially. The electron beam introduces reaction volume perpendicularly to the axis of the vessel. It passes titanium foil window. More then 75% of microwave energy is concentrated in discharge volume according to estimation. The inlet and outlet of the stream of the gas are mounted on wall side of the vessel. The stream of the gas can flow directly or can be formed orbicularly.

The preliminary experiments show that is possible to find such condition with, where the efficiencies of the removal processes caused by simultaneous use the electron beam and microwave energy increased total efficiency of the removal process to compare with separate ones what would make possible to obtain the technical and economical advantages of this combined method.

This reactor is especially useful for decomposition of gaseous, liquid and solid hazardous wastes (organic and inorganic). Liquids and solids have to be feeded to the reactor in dispersed forms (aerosol).

INDUSTRIAL PLANT DESIGN

The planned industrial plant will be constructed at the Electric Power Station Pomorzany, Szczecin. The demonstration plant will treat flue gases from combined power/heat block consisting of two Benson type boilers of 56 MW electrical and additionaly 40 MW power each.

The 270 000 Nm^3/h flue gases (half of the amount produced by block) will be treated with removal efficiency of 90% for SO_2 and 70% for NO_x. This enables to meet Polish regulations which will be imposed in 1997.

The scheme of the plant is given is in Fig.2. Two accelerators units of 600 kW each will be used and each unit consists of two accelerator heads what enables application of the double gas irradiation principle.

CONCLUSIONS

The extensive research on eb flue gas treatment technology has been performed in Poland since 1985. The positive results obtained in two consecutive stages - at laboratory unit and, subsequently, at industrial pilot plant have led to preparation of full scale industrial project.

Feasibility study prepared has shown economical and technical advantage of the process over conventional technology (FGD plus SCR).

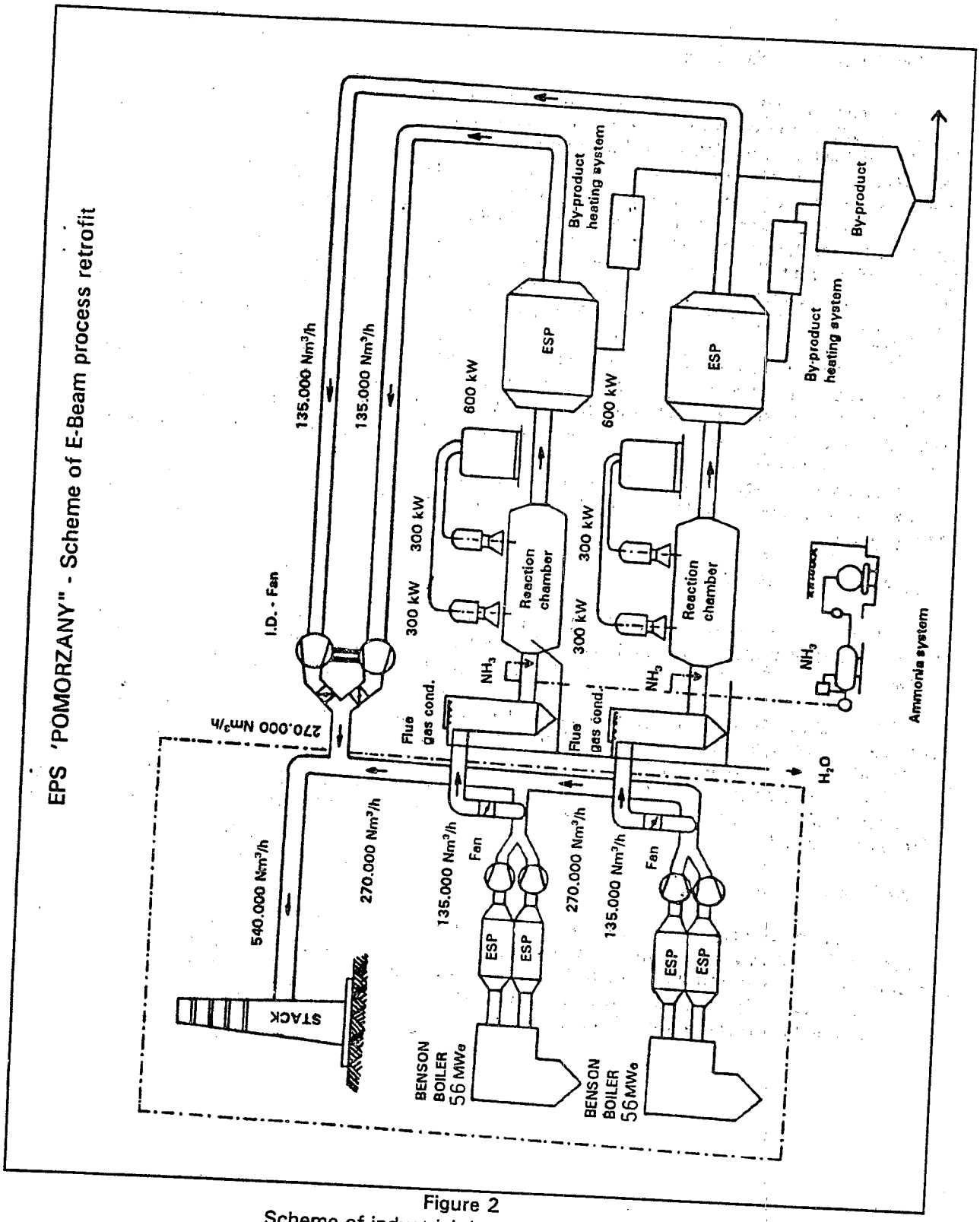

Figure 2
Scheme of industrial demonstration plant.

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INSTALLATION FOR SEWAGE SLUDGE HYGIENIZATION BY ELECTRON BEAM APPLICATION

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INTRODUCTION

Many kinds of hazardous wastes are presently produced by men and environmental pollution has become more and more serious problem in industrialized countries. Different methods of disposing or recycling must be applied depending on the specifity of the wastes, for instance, chemical wastes from industry, agricultural wastes from big farms, biological wastes from sewage treatment plants, hospitals and international airport. In some cases combustion is the only safe method of neutralization, however, recycling of wastes after specific treatment is usually considered as the best method of their disposal.

The main danger caused by hospital, airport and sewage treatment plant is sanitary one. All methods of destroying microorganisms and parasites (and their eggs) may be suitable for the elimination of that danger. In some cases hazardous wastes of organic origin make the problem, too.A lot of investigations have been done to solve the problem of wastes. It appears that irradiation is one of the methods of treatment which makes the wastes harmless and enables their recycling (1-3, and references therein).

Sludges collected in municipal sewage treatment plant contain organic and inorganic components valuable for the agriculture, and their beneficial use is possible but after effective hygienization. Investigations performed in many countries show conclusively that sewage sludges not overcharged much by heavy metals, while treated with gamma rays or electron beam (EB) are sanitary safe and can be used with good result as soil fertilizer.

GENERAL OUTLINE OF THE PROCESS

Experiments which have been performed in our Institutes proved that irradiation with 10 MeV EB decreases bacteria content in the sludges to the safe level (including Mycrobacterium tuberculosis) and kills all parasites and their ova.

Preliminary tests on the effect of EB treated sludges on the growth and yield of vegetables in pot cultures showed significant positive effect of sludge addition compared to plants grown on untreated soil.

On the basis of experiments mentioned above the installation has been designed for the sewage station in Polish city Otwock. Scheme of installation for sewage sludge hygienization with electron beam, and vertical and horizontal projection of radiation processing unit are shown on figures 1 and 2, respectively. Dewatered sludges (containing about 30% of dry metter) are spreaded on the transporter and disinfected by electron irradiation with a dose of 5 kGy. Capacity of the installation is 70 tons of sludges (day what corresponds to about 48000 m) day of sewage. Capital costs of irradiation processing unit is 4.0 million US dollars, what mainly depends on the cost of accelerator and its building.

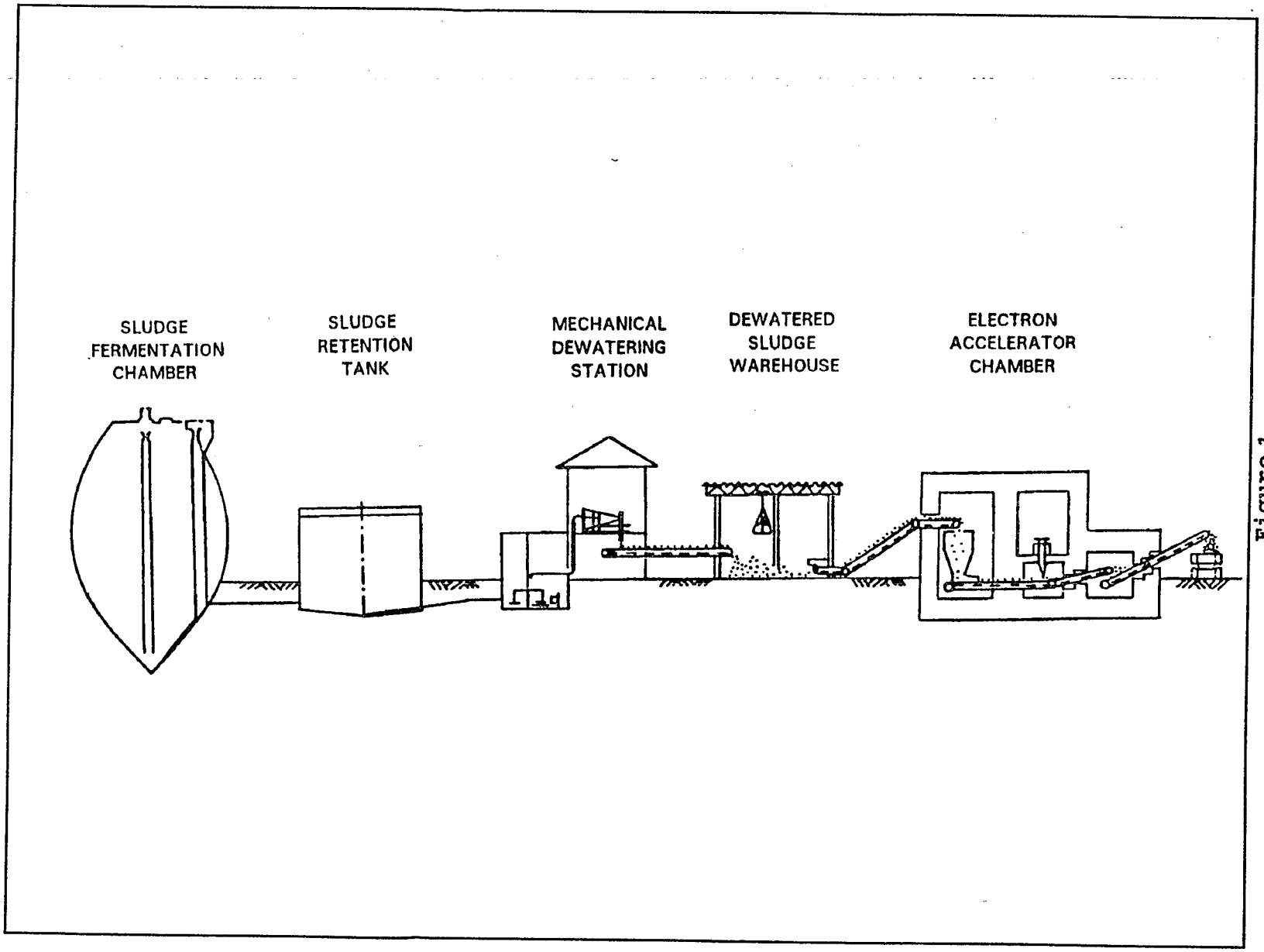

Figure 1
Scheme of installation for sewage sludge hygienization with electron beam.

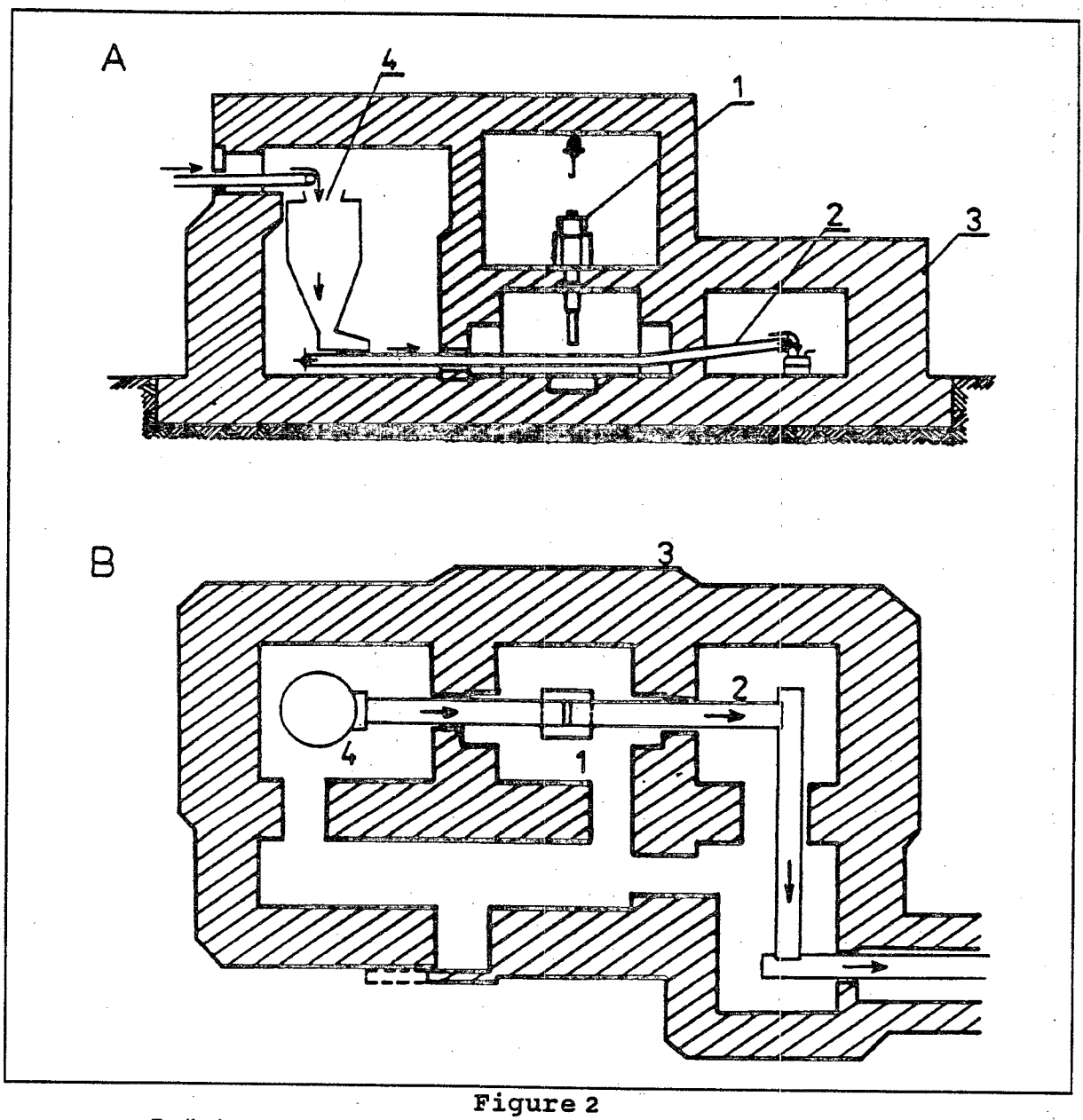

Figure 2
Radiation processing unit.A-vertical projection, B-horizontal projection

1-electron accelerator, 2-conveyor, 3-shielding walls, 4-dewatered sewage sludges feeder.

Hygienized with EB sewage sludges can be spreaded on the soil (as fertilizer) immediately after leaving the installation and no place for long storage of these sludges is needed, in the contrary to conventional methods applied recently in sewage stations.

RADIATION PROCESSING UNIT

Construction and equipment costs:	
- dewatered sludge warehouse	0.4 Mio USD
- centrifugal machine	0.15
- building for accelerator and auxiliary equipment	1.6
- electron accelerator of 10 MeV, 15 kW	1.0
- water cooling system (closed cycle)	0.2
- disinfected sludge warehouse	0.15
- conveyors	0.3
- roads, squares, illumination	0.2
Plant parameters:	
- building area	752 m^2
- usable area	1150 m^2
- cubature	7000 m^3
- power installed	300 kW
- water consumption	0.3 m^3 /day
Manpower:	
- one shift operation	7 persons
- two shift operation	12 persons
Performance:	
- capacity of communal liquid waste	48000 m^3 /day
- capacity of dewatered sludges	70 t/day
- dose	5 kGy
- two shift operation	3840 h/year

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SOIL WASHING, FROM CHARACTERIZATION TO TAILOR-MADE FLOW DIAGRAMS, RESULTS OF FULL-SCALE INSTALLATIONS

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1. INTRODUCTION

The principle of soil washing technology is to concentrate the contaminants in a small residual fraction by separation. The soil is mixed with water into a slurry and then several separation/classification-technologies are used to remove the contaminants such as screening, hydrocycloning, gravity separation and froth flotation. The sand product can be reused, the residue has to be landfilled or treated. Soil washing is applicable to a wide variety of contaminations such as heavy metals, Polycyclic Aromatic Hydrocarbons (PAH), mineral oils, pesticides, cyanides and others.

The objectives of soil washing are two fold. The first is to decrease the level of the concentration of contaminant. The second is to decrease the quantity of the concentrated residue. Often these two objectives interfere. Adding an extra separation step will create more residue, not adding a step means a higher concentration of contaminant in the product.

In designing a soil washing process it is important to understand in what form the contaminant is present within the contaminated soil. This characterization is the key to find an optimum in the two objectives; the lowest concentration of contaminant in the product and a minimal quantity of residue.

2. METHODOLOGY

The characterizing of contaminated soil consists of a characterization of the contaminant and a characterization of the soil. In the dutch legislation the standards for the contaminants are made referring to their chemical form (like benzo(a)pyrene) or to their absolute concentration (like total lead). The physical form in which the contaminant occurs within the soil is still not clear when the concentration is known. Determination of this physical form is the objective of the characterization.

2.1. Contaminant-characterization

In general there are four main physical forms in which a contaminant can occur in the soil.

- Particles that have a high concentration of contaminant. These particles can be pure contaminant, like lead-dust or pesticide pellets, or not pure, like tar particles or slags.
- Coatings of contaminants on the sand particles.

An example is the lead-coating that often is found on shooting range sand.

- Water soluble components. Since soil contains 10-20 % of water, the pollution of the water will also pollute the soil. Phenol is a good example for this type of contaminant, but also some metal-salts are soluble enough to give significant soil contamination.
- Contaminants that adsorb to the soil. Adsorption is possible whenever the contaminant is (slightly) water soluble. From the water phase the contaminant adsorbs to a place with a higher binding energy. In this way the contaminant can migrate from one soil fraction to another. Almost all contaminants show this adsorption-behaviour. Very often absorption takes place onto the fine clay-fraction and onto organic material.

The actual contamination in a soil is often a combination of more characterization-types. All kinds of contaminants occur in the soil, and every contaminant can have different occurrence. The first step for a proper characterization consists of evaluation of the historical information available concerning the source of the contamination. Examples for common sources are: chemical industry-calamities and spillage, gasoline-station-spillage, use of slag-material in road-construction, hunting and waste-dumping. After the initial contamination of the soil, the physical occurrence of the contaminant can and can change, for example because of the adsorption-processes.

The above mentioned historical analysis gives a prediction in what physical form the contaminants are present but needs to be confirmed by soil characterization. This physical and chemical analysis includes wet screening, Scanning Electron Microscopy (SEM), stereomicroscope, density separation and absolute chemical analyses.

As an example the physical and chemical form of some contaminations are related to the four characterization-types in table 1.

TABLE 1. SOME EXAMPLES OF DIFFERENT PHYSICAL OCCURRENCE OF THE SAME CONTAMINANT

	Particles	Coating	Water	Adsorbed
Lead	dust	shooting range sand	leadchloride	at clay
Benzo(a)pyrene	slags	tars	low conc.	at clay
Arsenic	fungicide powder	--	as complexes	organic mat.

2.2. Soil-characterization

The characterization of the soil is very straight-forward. Important factors are the particle size distribution, the organic matter content and the calciumcarbonate content.
This physical characterization is important for the amount of residue that the process will generate. Also a large content of certain fractions like the sludge, the organic matter or the oversize can cause operating problems in the process.

2.3. Conclusion

A combination of the soil- and the contaminant characterization is the best starting point for developing a successful soil washing process. The effort that is put into the characterization phase will result in lower concentrations contaminant in the clean sand product, lower production costs and lower quantities of residue. This way the environmental and the commercial efficiencies are optimized. Heidemij has a large experience in translating the characterization to a real-scale soil washing process. The translation-path is visualised in figure 1.

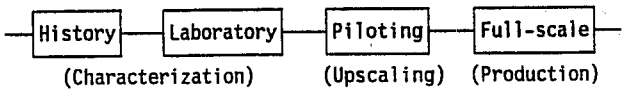

FIGURE 1. Linking characterization and full-scale soil washing.

3. RESULTS

3.1. Introduction

In each case study presented, the characterization results as well as the actual process used are explained. The projects are realised with a capacity that varies between 15 and 40 tonnes/hour. The product sand in all projects was reused. The residual sludge and oversize are landfilled or treated with other technologies.

Special attention is paid to the contamination level of the soil before and after soil washing. The efficiency for each component is presented. These efficiencies are, of course, only valid in relation with the described project.

3.2. Case studies

3.2.1. Case study 1.

Characterization. In this case study the soil was contaminated with dredged sediment that was landfilled. The sediment was contaminated with cadmium coming from industrial activities, metallurgical as well as phosphate-processing. The concentration of cadmium was 8-18 ppm.

The relation between particle size and contaminant-concentration is shown in Fig 2. This figure was assembled from concentration analysis data derived from samples with a different content of fines.

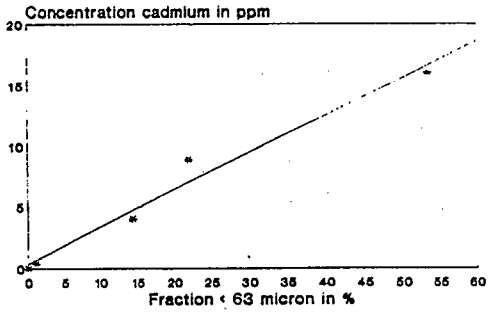

FIGURE 2. Relation fines content and cadmium-concentration for case study 1.

There is a clear relation between fines-content (defined as fraction smaller then 63 μm) and cadmium-concentration. In this case the contaminant appears to be associated only with the fines.
The cadmium might be readsorbed to the fine particles.

Process. The soil was wet screened to separate the coarse particles (clay lumps, gravel, waste material). After wet screening the fines were separated from the sand fraction using hydrocyclones. The fines were removed almost completely. The sand product was reused at a residual cadmium concentration of 0.4 - 0.8 ppm (removal efficiency approx. 95%). Figure 3 shows the schematic flow diagram.

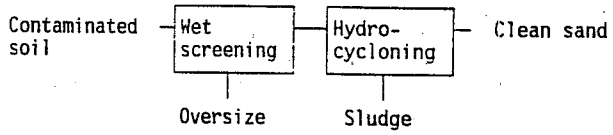

FIGURE 3. Schematic flow diagram case study 1.

3.2.2. Case study 2.

Characterization. Shooting at clay-doves with lead-pellets (usually 1.1-1.3 mm) contaminated surface soils over a large area. The top-layer of the soil was contaminated with lead shot, but the pellets also leached out due to acid rain. The leachate readsorbed to the soil, specifically to the clay fraction and the organic matter. The pellets also disintegrated due to mechanical forces and corrosion. Therefore also lead-slices with a diameter smaller then 1.0 mm were found. Figure 4 shows the relation between lead-content and particle size. In the plus 1,000 μm fractions the lead content varied between 5,000 ppm and 200,000 ppm. Higher concentrations than 5,000 ppm are not presented in the graph.

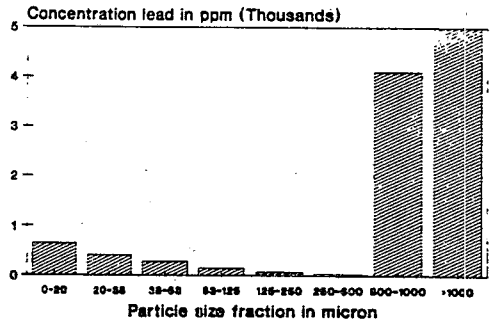

FIGURE 4. Distribution of lead over the size fractions.

The lowest concentration of lead is found in the 63-600 μm fraction, which is also the main soil size fraction.

Process. The soil with an input lead concentration of 1,000-5,000 ppm was first wet screened to remove oversize material. In a next screening step the soil was screened at 600 μm to remove the lead pellets. The clay fraction was separated by use of hydrocyclones. The remaining soil was scrubbed and leached with slightly acidic solution and finally dewatered. The sand product contained 50-60 ppm lead (removal efficiency approx. 98%).
The schematic flow diagram is presented in figure 5.

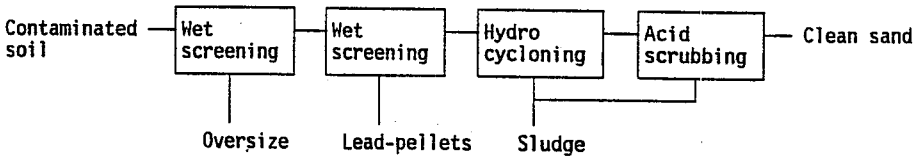

FIGURE 5. Schematic flow diagram case study 2.

3.2.3 . Case study 3.

Characterization. The historical analysis of this case study showed that the soil was contaminated with slag-residue produced from metallurgical industrial activities. The slag material was easily visible in the soil and appeared to be lighter than sand. They were also disintegrated and leached-out to the groundwater.

Soil samples were wet screened and in the different size-fractions the contamination-content was analyzed. There turned out to be a clear correlation between the three contaminants. This indicates that the characterization of the three different contaminants are the same, except for the fines, where the relation was different probably due to different solubilities of the metal-salts. The results are shown in figure 6.

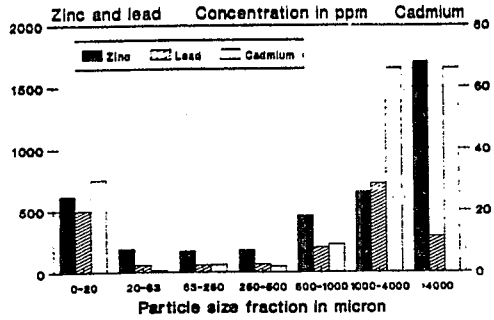

FIGURE 6. Relation cadmium, lead and zinc content as a function of particle size.

The sand fraction (38-2,000 μm) was analyzed with Scanning Electron Microscopical analysis to identify the physical form of the heavy metal contaminants present. The condensed results of this analyses are shown in table 2.

TABLE 2. ELEMENTAL COMPOSITION OF CONTAMINANTS AS IDENTIFIED BY SEM-ANALYSIS.

Elemental analysis	Mineralogical description
Zn, Si, (Fe, K, Al)	Zn on silicate matrix
Zn, C, (Ca, Al, Si, Fe, Pb)	Zn on organic matrix
Zn, O, Si	pure ZnO with Si
Zn, Pb, Al, Si	Zn/Pb on Al/Si-matrix
Zn, S, Si, O	Zn-sulfide on SiO_2 matrix
Pb, S	Pb-sulfide
Zn, S	Zn-sulfide

It was frequently found that zinc and lead contaminants were present in the form of different discrete particles in a "free" form or attached to organic (slag) material. From the mineralogical analysis it appeared that a great variety of zinc and lead containing compounds were present.

The presence of non-discrete zinc and lead within slag particles could not be detected by the SEM-analysis technique but chemical analysis showed that these slag particles also contained high concentrations zinc and lead in their structure.

The great variety of mineralogical forms in which zinc and lead were found is typical for thermal processes that produce slag materials and can be directly related to the original source of the contamination: pyro-metallurgical industrial processes.

Process. The soil was screened to remove oversize material and large slag-particles. Hydrocyclones were used to remove the fine particles. The low-density slag-particles were removed by gravity separation, other slag-particles were removed by froth-flotation. The concentration of the contaminants are listed in table 3. Figure 7 shows the flow diagram.

TABLE 3. CONTAMINATION LEVELS IN PPM OF INPUT AND OUTPUT OF CASE STUDY 3.

	Lead	Cadmium	Zinc
Input	140-611	5-17	640-2822
Output	60	1.3	200
Efficiency (%)	57-90	74-92	69-93

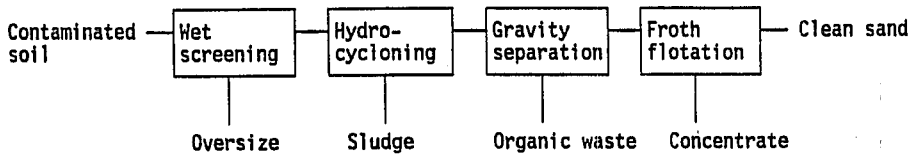

FIGURE 7. Schematic flow diagram case study 3.

3.2.4. Case study 4.

Characterization. The soil in this case study is contaminated with coal-ashes containing Polycyclic Aromatic Hydrocarbons (PAH). There is a side-contamination of copper, lead and zinc due to traffic emissions and other urban activities. This case study focuses on the PAH-occurrence and process performance because PAH was the critical contaminant. In The Netherlands it is common to use a selection of ten types of PAH as a total PAH-content. This so called 10-PAH-content is used in this study. The PAH-content averaged 85 ppm.

Figure 8 shows the distribution of the PAH over the size fractions. The size distribution of the sand is also presented.

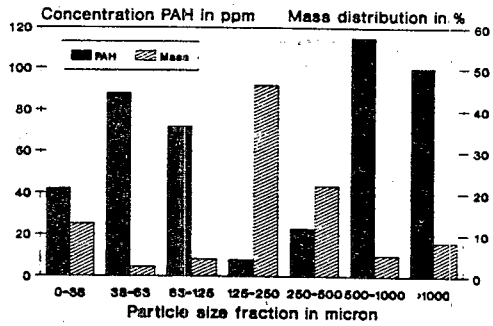

FIGURE 8. Distribution of total-PAH over the size fractions for case study 4.

The PAH-concentration is the lowest in the main size fractions. The readsorbtion to the fines is not very large, but still important.

Process. The coarse particles were removed by wet screening. Special attention was paid to the hydrocycloning because of the high efficiency required. It was necessary to remove practically all the fines. The PAH-containing low-density particles were removed in gravity separation step. Other PAH-containing particles were removed by froth-flotation. Figure 9 shows the flow diagram of the used process. The concentration of the PAH is also given after each treatment step.

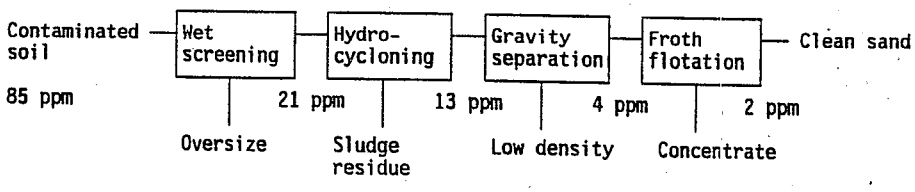

FIGURE 9. Schematic flow diagram case study 4 with total-PAH concentration.

The overall removal efficiency for PAH was 98%. The side contaminants were also removed to satisfactory levels.

4. CONCLUSIONS

Based on a good characterization of the soil and the contaminant it is possible to design optimized tailor-made flow diagrams. The characterization starts with a historical analysis and is completed with an extensive chemical and physical characterization.

For the case studies presented it was shown that differences in the physical occurrence of the soil and the contaminants resulted into different optimized flow diagrams. The case studies presented indeed have different flow diagrams. The difference in flow diagrams sometimes meant little adjustments in the process, in other cases it was also necessary to redesign the installation completely.

For the case studies presented removal efficiencies higher than 90% were achieved. These removal efficiencies are typical for soil washing. In each project the sand was treated to a contaminant level that made reuse possible.

The fundamental approach from characterization to tailor-made flow diagrams lead to optimum results in the realisation of soil washing projects. Using this concept of tailor-made flow diagrams, Heidemij has successfully treated more than 200,000 tonnes of contaminated soil.

SOIL WASHING AND TERRAMET™ LEAD LEACHING/RECOVERY PROCESS AT THE TWIN CITIES ARMY AMMUNITION PLANT

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INTRODUCTION

COGNIS and Bescorp have successfully combined acid extraction (TerraMet™ metal leaching/recovery process) with soil washing to remove eight heavy metals from contaminated soil at Site F, an ammunition test burning area, at the Twin Cities Army Ammunition Plant (TCAAP) in New Brighton, MN. Eight heavy metals, primarily lead and copper, were treated to the RCRA cleanup criteria of background, in addition to live and spent ordnance removal. This represents the most ambitious metal clean up ever undertaken. The lead contamination was a result of particulate lead, ranging in size from 6" chunks to 400 mesh particles, as well as ionic lead adsorbed onto soil particles. The lead concentration was lowered from an initial 3,000 - 6,000 ppm to the state cleanup criteria of < 300 ppm. All the excavated soil fractions were treatable and returned to the site. Bescorp's soil washing process generates three fractions: oversize, sand, and fines. The sand is density treated to remove particulate lead and copper. The TerraMet metal extraction process then leaches and recovers heavy metals from the sand and fines fractions with a proprietary aqueous leaching solution. Through the combined density pretreatment and leaching process, both metallic lead fragments and dust as well as soil bound lead salts and oxides have been treated. The lead recovered from the process is recycled at a secondary lead smelter. The TCAAP treatability study and field-scale results will be described.

SOIL WASHING/SOIL LEACHING PROCESS

A flow chart for the COGNIS-Bescorp remediation process is shown in Figure 1. Bescorp was responsible for the physical separation steps, and COGNIS was responsible for the chemical leaching and metal recovery technology. The soil is fed into the trommel where attrition breaks the soil material down into its constituent particles of rock, gravel, sand, silt and clay. The clean oversize rock, gravel and ordnance are rinsed and removed by a 1/4" screen. The oversize is sorted on a conveyer belt and ordnance removed for proper disposal. The clean oversize rock and gravel exits the plant. The sand and silt/clay fines are separated in a patented vertical separation chamber which separates the sand from the fines by hydraulic settling forces. The metal containing fines are swept into a clarifier where they are flocced and allowed to settle. The settled fines are pumped through a series of leaching clarifiers. The leached fines are dewatered and neutralized before being combined with the clean oversize and sand fractions. The sand fraction is run through a mineral jig to remove the bulk of the metallic lead and copper particles, flecks, and dust. The partially cleaned sand fraction is then subjected to counter-current leaching. The leached sand is dewatered and neutralized before being combined with the fines and oversize. The metal loaded leachant is fed into the metal recovery units where the dissolved contaminant metals are reduced out and recovered in metallic form for recycle.

The leaching-metal recovery concept is illustrated in Figure 2. The contaminated soil fraction is contacted with a leaching agent which dissolves a portion of the lead. The lead is removed from the lead-rich leachant in a metal recovery stage. The lead-depleted leachant is then ready for additional

contacting with new soil. The leaching process is conducted in a counter-current fashion to maximize its efficiency. The leaching is controllable so that the lead concentration in the soil is acceptably low. This approach completely recycles the leaching agent. Thus, the metal bearing leachant never leaves the process, no liquid waste streams are generated, and metal recovery can be tailored to the site.

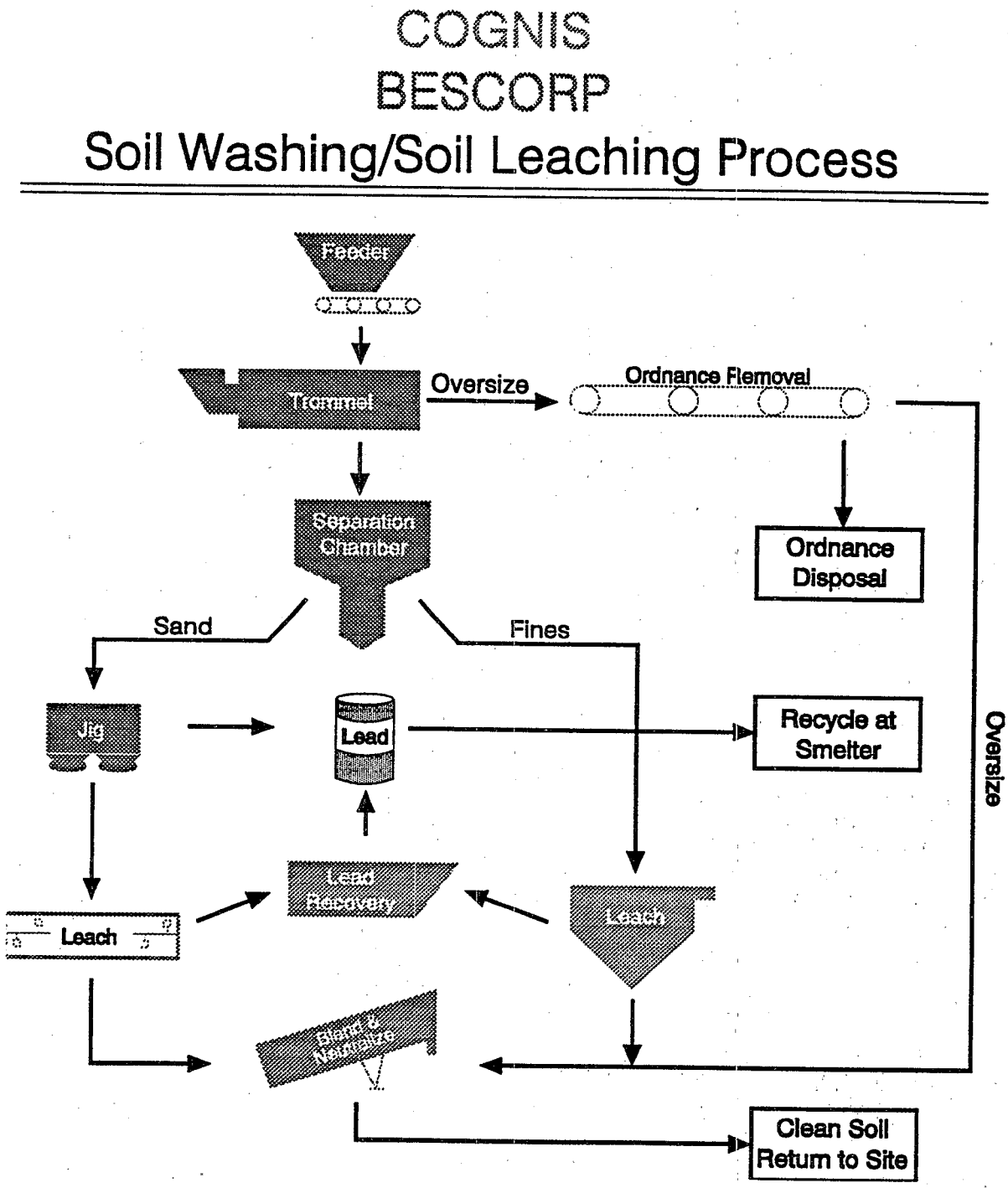

Figure 1. COGNIS and Bescorp Field-Scale Process

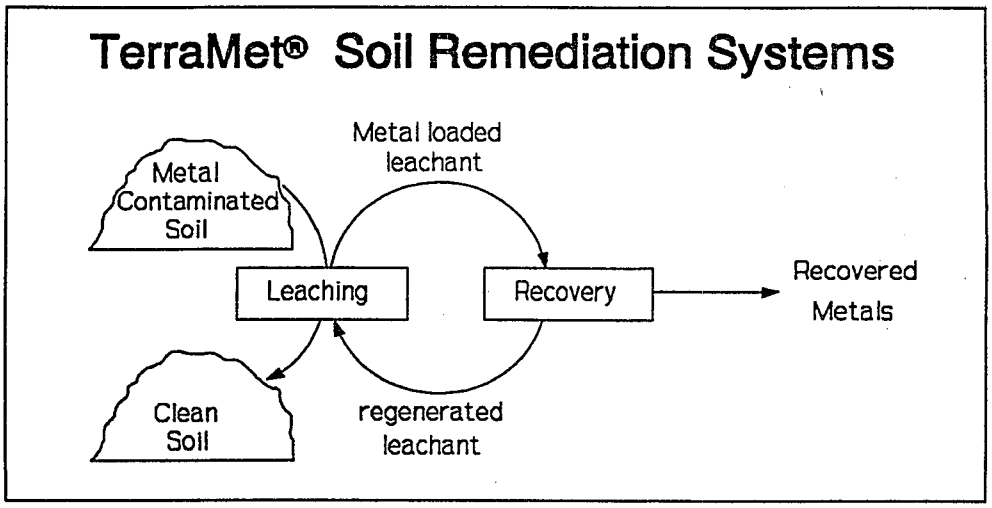

Figure 2. Lead Leaching - Recovery Concept

The preferred recovery process for lead is direct reduction of the dissolved ionic lead to lead metal. Other metal recovery options have been tested, and the most appropriate recovery process for a specific site depends on the leachant required and the amount and type of metals present.

RESULTS

In the treatability study, soil from the ammunition test burning area at TCAAP was studied. At Site F both metallic lead fragments as well as ionic lead were found. Because of the high density of lead relative to most soil constituents, the coupling of soil washing with density separation was a logical pretreatment to leaching. Soil was first size classified to generate a sand fraction which was subjected to density separation using standard mineral processing equipment to remove heavy lead fragments. The results of density separation lowered the lead concentration in the sand significantly (Table 1).

Table 1.
Density Separation of Lead Particles

Particle Size (Mesh size)	Lead Conc. Before & After Density Separation (ppm)					
	Trial 1 Before	Trial 1 After	% Pb Removed	Trial 2 Before	Trial 2 After	% Pb Removed
+8	2050	996	51	NA	NA	NA
+30	4190	389	91	1436	168	88
+50	2410	494	80	1025	187	82
+100	4060	842	79	901	138	85
+200	2900	2960	0	940	416	56
-200	4360	2490	43	679	739	0

Tables 2 and 3 show the results of leaching the fines and density pretreated sand fraction. Leaching the fines was very effective and gave residual lead concentrations of <20 ppm with leachants #2. The results on the sand were equally satisfactory. Residual lead concentration of < 70 ppm was also achieved with leachant #2.

Table 2.
Leaching[1] of TCAAP -200 Mesh Fines

	Cumulative % Pb Leached					Initial[2]	Final[3]
	Leaching Contact #					[Pb]	[Pb]
Leachant	1	2	3	4	5	(ppm)	(ppm)
2	59	90	96	97	97	575	16
2	64	92	97	98	98	608	11

Table 3.
Leaching[1] of TCAAP Density-Pretreated +200 Mesh Sand

	Cumulative % Pb Leached					Initial[2]	Final[3]
	Leaching Contact #					[Pb]	[Pb]
Leachant	1	2	3	4	5	(ppm)	(ppm)
2	49	71	81	85	88	585	69
2	75	87	90	92	93	190	14

[1]Data is from five consecutive contacts of soil samples with leachant.
[2]Based upon the total Pb detected in leachant plus Pb retained in soil as determined by nitric acid digestion.
[3]Based upon EPA acid digestion of treated soil.
[4]Below reporting limit

After the small bench-scale experiments proved the success of the multiple leaching concept, additional larger scale continuous leaching experiments verified the leaching results obtained earlier. The continuous-scale apparatus more closely approximates full-scale treatment. It employs an agitated leaching vessel from which a soil slurry is pumped into a clarifier. The clarifier separates the slurry into a clarified feed at the overflow and a thickened slurry at the underflow. The underflow is continuously returned to the leaching vessel. The overflow is pumped into the metal recovery unit where the lead is removed from the leachant and the lead recovered as solid lead powder. The lead-depleted leachant is then returned to the leaching vessel for continued leaching. After leaching is complete, the soil-leachant slurry is dewatered and neutralized. Thus, the entire leaching, clarification, and metal recovery process operates continuously on the batch of soil in the leaching vessel. Table 4 illustrates typical data on TCAAP soil. Routinely < 100 ppm residual lead and TCLP passage was observed. The lead concentrations shown under the influent and effluent columns are the concentrations of lead in the leachant entering and exiting the metal recovery unit.

Table 4.
CONTINUOUS-SCALE LEACHING EXPERIMENT TCAAP SOIL (DENSITY PRETREATED)

Matrix	Lead Concentration (µg/g)	
	Pre-Leaching	Leached
Soil (Avg)	250 - 350	31.1
Replicate 1		32.6
Replicate 2		28.2
Replicate 3		33.2
Leachate	Influent (µg/mL)	Effluent (µg/mL)
Sample 1	15.4	2.5
Sample 2	10.6	2.1
Sample 3	4.6	1.3
Sample 4	2.5	0.7
Sample 5	1.4	<0.5
Sample 6	0.9	<0.5
Sample 7	0.5	<0.5

CONCLUSIONS

The Bescorp and COGNIS soil washing/soil leaching treatment at TCAAP allows all the excavated soil material to be treated and returned to the site. Particulate metal contaminants are physically separated for recycle, and the ionic metal contaminants are leached and recovered for recycle. The combined plant utilizes full recycle of all aqueous solutions and 1,600 tons of lead-contaminated soil were processed through the full-scale system at TCAAP in mid-September through October, 1993. The project will be completed in the Spring of 1994.

Soil washing/soil leaching has been proven at field-scale, reducing lead to < 300 ppm and seven other heavy metals to background. However, the process is not a generic, fixed process, but one which can be site-specifically tailored to meet the requirements of each site by utilizing the necessary unit operations. Factors such as contaminant type and level, clean up criteria, soil mineralogy, soil particle size distribution, and process throughput all affect processability and cost.

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THE B.E.S.T.® SOLVENT EXTRACTION PROCESS FOR REMEDIATION OF PESTICIDE CONTAMINATED WASTES

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INTRODUCTION

Resources Conservation Company's (RCC) patented B.E.S.T. Solvent Extraction Process is commercially proven, cost effective treatment alternative for remediating pesticide contaminated soils, sludges and sediments. Bench scale and pilot scale treatability test data clearly show that the B.E.S.T. process can effectively remove pesticides from contaminated soils (removal efficiencies >99%) to very low residual pesticide concentrations (<1 ppm). Pesticide compounds removed from soils include: DDT, βBHC (Lindane), Eldrin, Dieldrin, Aldrin, Isodrin, and Toxaphene. Process performance data are provided from sites located in New York, New Jersey, North Carolina, Colorado, California, and The Netherlands.

During the 1960's, the B.E.S.T. process was developed by the Boeing Company for use aboard the manned space station. Building on this early development, RCC has advanced commercialization of the B.E.S.T. process to the point where it is a cost effective treatment alternative for pesticide contaminated soils. Development of the B.E.S.T. process has included extensive laboratory research, bench scale treatability testing, design, construction and operation of three pilot plants and one full scale commercial unit.

This paper discusses the many lessons learned as the B.E.S.T. process was developed as an on-site treatment technology for treating pesticide contaminated soils, sludges and sediments. Laboratory research provided data on the physical and chemical properties of the B.E.S.T. process solvent, triethylamine. Bench scale treatability testing was used to develop a testing protocol that closely predicts full scale process performance. Operation of the first two pilot scale test units provided the necessary data for design of a continuous B.E.S.T. process configuration for treating pumpable wastes, such sewage sludges and petroleum refining oily sludges.

The full scale commercial B.E.S.T. process unit was used to treat 3,700 yd^3 of PCB contaminated oily sludges at the General Refining Superfund site located near Savannah, GA. This unit was configured to treat only pumpable sludges. RCC learned that to effectively remediate hazardous waste sites the process needs to treat both pumpable and non-pumpable wastes (soils). The third pilot scale test unit was designed to operate in batch mode to allow the process to treat both pumpable and non-pumpable wastes (soils). This pilot unit has been used at several sites to demonstrate performance of this process configuration. Last year, RCC successfully completed a Superfund Innovative Technology Evaluation (SITE) demonstration of the B.E.S.T. process with PCB contaminated sediments from the Grand Calumet River. In early 1994, a B.E.S.T. process pilot plant conducted a series of demonstration tests with pesticide contaminated soils at a federal facility in Colorado.

METHODOLOGY

The RCC B.E.S.T. Process is a mobile batch solvent extraction system designed to remove organic contaminants from soils, sludges, and sediments. The B.E.S.T. Process is distinguished from other solvent extraction and related soil washing systems by the use of triethylamine as the extraction

The geometry of the triethylamine molecule is tetrahedral. A nitrogen atom is at the center of a three-sided pyramid; the four points of the structure are occupied by three ethyl functional groups and one electron cloud. This structure gives triethylamine the dual polarity which is responsible for its unique properties.

The property that is the key to the success of triethylamine extraction is the property of inverse immiscibility. At temperatures below 60°F, triethylamine is miscible with water (i.e., triethylamine and water are soluble in each other). Above this temperature, triethylamine and water are only partially miscible. This physical property can be exploited by using cold triethylamine (below 60°F) to solvate oil and water simultaneously.

The B.E.S.T. Process utilizes the physical property of inverse miscibility by mixing the feedstock with chilled triethylamine solvent to create a single-phase extraction liquid. The liquid is a homogeneous solution of triethylamine and the water present in the feedstock. This solution solvates the organic contaminants (such as oils) present in the feedstock and enables the triethylamine to achieve intimate contact with solutes at nearly ambient temperatures and pressures. This allows the B.E.S.T. Process to maintain efficient extraction when handling feed mixtures with high water content. Therefore, by utilizing solvent chilled below 60°F, solids can be dewatered while organic contaminants are simultaneously extracted. Afterwards the remaining organic contaminants can be removed at temperatures above 60°F. In addition to inverse miscibility, characteristics that enhance triethylamine's use in a solvent extraction system include the following:

- A high vapor pressure (therefore the solvent can be recovered from the extract by way of simple steam stripping)
- Formation of a low boiling azeotrope with water (therefore the solvent can be recovered from the extract to very low residual levels)
- A heat of vaporization one-seventh of water (therefore, solvent can be recovered from solids by simple heat with a low energy input)
- Triethylamine is alkaline (pH=10); therefore some heavy metals can be converted to hydroxide form, which precipitate and exit the process with the treated solids.

There are four basic operations involved in the B.E.S.T. process: extraction, solvent recovery and oil polishing, solids drying, and water stripping. The extraction operation for materials having relatively high content is additionally broken down into two types of extraction cycles. The initial primary extraction cycles are termed "cold extractions"; secondary extractions are termed 'warm' and 'hot extractions' depending on the temperature range at which they are conducted.

BENCH SCALE TREATABILITY TEST RESULTS

RCC has conducted several bench scale treatability tests with pesticide contaminated soils, sludges, and sediments. The primary objective of these tests was to determine the feasibility and cost effectiveness of the B.E.S.T. process. RCC's bench scale treatability tests are designed to provide data that closely simulates full scale performance. The data generated by the tests allows RCC to evaluate feasibility of the process and to estimate treatment costs.

The bench scale treatability test objectives are:

- To record observations and data to predict full-scale performance of the B.E.S.T. process treatment train.

- Take samples during simulation of the treatment train and conduct analysis sufficient to determine the removal efficiency of the process for the treatment compounds of concern.

- To calculate the extraction efficiency of target compounds.

Bench-scale treatability testing of the B.E.S.T. process is conducted at RCC's Treatability Test Laboratory located in Bellevue, Washington, USA.

The purpose of the bench-scale treatability testing is to provide guidelines for pilot-scale and full-scale operations. To effectively simulate the B.E.S.T. Process on a small scale, RCC utilizes laboratory equipment resembling pilot and full scale components. The data collected include settling data, compositional data, pH data, and soil agglomeration observations. Settling data are collected to predict the level to which the material would settle and the amount of time required to reach that level. Compositional information is compiled by the RCC laboratory to determine the amount of material to be treated per batch. Observations such as centrifugation performance and soil agglomeration helps the treatment system operator to recognize discrepancies from normal occurrences.

Delta Engineering - The Netherlands
Bench Scale Treatability Test Data

PESTICIDE COMPOUND	FEEDSTOCK (mg/kg)	TREATED SOLIDS (mg/kg)	REMOVAL EFFICIENCY (%)
Aldrin	56	0.1	>99
Dieldrin	150	0.3	>99
Endrin	140	0.02	>99.9
Endrin Ketone	280	0.5	>99.9
Endrin Acetone	70	0.1	>99.9
Isodrin	340	0.28	>99.9

Elf AutoChem Superfund Site - NJ
Bench Scale Treatability Test Data

PESTICIDE COMPOUND	FEEDSTOCK (mg/kg)	TREATED SOLIDS (mg/kg)	REMOVAL EFFICIENCY (%)
β-BHC (Lindane)	10.2	0.09	99
4,4'-DDD	32.6	0.03	99.9
4,4'-DDE	18.0	0.48	97
4,4'-DDT	28.6	0.02	99.9
Dieldrin	4.2	0.09	98

FMC Superfund Site - CA
Bench Scale Treatability Test Data

PESTICIDE COMPOUND	FEEDSTOCK (mg/kg)	TREATED SOLIDS (mg/kg)	REMOVAL EFFICIENCY (%)
Endosulfan	390	<0.02	>99.99
4,4'-DDT	500	0.05	>99
4,4'-DDE	84	0.5	>99
4,4'-DDD	190	0.05	>99.9
Dieldrin	37	<0.02	>99.9
Endrin	140	0.02	>99.9

Federal Facility - CO
Bench Scale Treatability Test Data

PESTICIDE COMPOUND	FEEDSTOCK (mg/kg)	TREATED SOLIDS (mg/kg)	REMOVAL EFFICIENCY (%)
Aldrin	360	0.05	>99.99
DDT	4.2	<0.01	>99.9
Dieldrin	780	0.039	>99.99
Endrin	470	0.04	>99.99
Isodrin	150	0.28	>99.9

Plattsburgh AFB - NY
Bench Scale Treatability Test Data

PESTICIDE COMPOUND	FEEDSTOCK (mg/kg)	TREATED SOLIDS (mg/kg)	REMOVAL EFFICIENCY (%)
4,4-DDT (Composite)	500	0.01	>99.9
4,4'-DDT (Hot Spot)	3900	0.20	>99.9

Hercules 009 Landfill - NC
Bench Scale Treatability Test Data

PESTICIDE COMPOUND	FEEDSTOCK (mg/kg)	TREATED SOLIDS (mg/kg)	REMOVAL EFFICIENCY (%)
Toxaphene	390	1.1	99.7

CONCLUSIONS

The B.E.S.T. Solvent Extraction Process:

- Extracts a wide range of pesticide compounds from soils, sludges and sediments including: Endrin, Aldrin, Isodrin, Dieldrin, DDD, DDE, DDT, Lindane and Toxaphene,
- Removal efficiencies for pesticide compounds is excellent, typically >99%,
- Residual pesticide concentrations in treated solids are very low, typically <1.0 mg/kg,
- Cost effective treatment alternative for treating pesticide contaminated soils, sludges and sediments, typically $125 - $250/ton

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CLEANING ORGANICALLY CONTAMINATED SOIL BY STEAM EXTRACTION - PILOT-SCALE EXPERIMENTS AND IMPLEMENTATION ON AN INDUSTRIAL SCALE -

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1. INTRODUCTION

The findings presented here were compiled by the Institute of Aachen Technical University for Water Management in Residential Areas (ISA) in collaboration with Bonnenberg u. Drescher Ingenieurgesellschaft mbH, Aldenhoven in the context of a research project sponsored by the Federal Ministry for Research and Technology (BMFT).

Public sponsorship of the first-ever industrial-scale implementation of the process by DERA GmbH, Aldenhoven, implemented in the form of a demonstration project, is currently being sought from the BMFT under the auspices of the Federal Environmental Protection Agency, Berlin.

2. PROCESS PRINCIPLES

The elaborated remedial action technique can be classified as a thermophysical process in the low-temperature range (T = 100 to 250°C). Soil cleaning by steam is carried out by steam distillation. This method is the most important special application of carrier distillation. It enables high-boiling substances that are immiscible or difficult to mix with water to be distilled often at the relatively low temperature of 100°C. From a thermodynamic viewpoint the reduction of the boiling point of not easily volatile substances can be explained by the fact that they form a heterogeneous aceotrope in the water mixture (1, 2). When the material is subsequently heated in the mixing apparatus (steaming and jacket heater), "microboiling" takes place inside the pores of the adsorbate. The second mechanism that is effective is the desorption of the contamination from the solid matrix.

Steam extraction offers the following benefits:

- In contrast to processes that use hot air or inert gases, such as N_2, as the heating and transport medium, the use of steam as the carrier gas reduces the boiling point of the contaminants.
- The chosen "ploughshare mixer" type of reactor mechanically generates a fluidized bed, unlike drum-type furnaces or screw conveyors. In conjunction with the disintegration of the soil agglomerations that form by high-speed rotating knife heads, this makes certain of a secondary stripping effect with an optimum flow around the individual grains (Section 3 contains further details on the reactor).
- Vapour that is not entirely saturated with contaminants can easily be recycled by an injector (vapour recirculation).
- Besides disintegrating soil agglomerations, the reactor used for the steam extraction process has an additional conditioning effect: the decontaminated soil can be cooled and wetted by injecting water before it is discharged.
- No catalytic or adsorptive waste air purification is required owing to the complete condensability of the carrier medium. Following mechanical separation of the highly concentrated contaminant

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[1] DERA GmbH, Aldenhoven
[2] Bonnenberg u. Drescher Ing. ges. mbH, Aldenhoven

phase, the condensed contaminated vapours can either be treated before entering the sewerage or subjected to process water treatment and subsequently reused to generate steam (closed cycle, therefore the preferred option).

3. PROCESS IMPLEMENTATION ON PILOT AND INDUSTRIAL SCALE

An intermittent mixer in which a mechanically generated fluidized bed with excellent heat and mass transfer behaviour forms is used for decontaminating soil with steam (3). This setup achieves thorough contact between the steam ($T \leq 160°C$, $p \leq 7$ bar), supplied by a steam generator and injected into the mixer by a steam lance, and the contaminated soil. Previous experiments have demonstrated the major influence exerted by the process temperature on the necessary treatment time. For this reason, the pilot plant is currently equipped with a superheater with an output of up to $T \leq 250$ °C, $p \leq 4$ bar. The contaminated vapours are condensed in a heat exchanger downstream of the reactor, whereby most of the contaminants can be separated from the condensate directly in the form of a floating or sinking, water-insoluble phase. This concentrated contaminant is generally disposed of in existing hazardous waste incineration plants, but it can also be treated in a used-oil recycling facility. During the semi-industrial trials, the aqueous phase was treated by adsorption with active coke and introduced into a communal sewage treatment plant.

Figure 1 is a flowchart depicting the pilot plant set up at the Institute of Aachen Technical University for Water Management in Residential Areas. The mechanical fluidized bed reactor (ploughshare mixer) comprises a cylindrical drum with axial whirler ($n \leq 160$ rpm). Solid agglomerations are disintegrated by a rotating knife head. The form taken by the mechanical fluidized bed in a ploughshare mixer is illustrated on the left of Figure 2. The mixing drum with whirler and radial knife head is shown in the right of the Figure (top view).

The planning and authorization procedure for the first full-scale industrial steam extraction plant, in the form of a mobile facility, is currently under way. The prospects of approval are favourable in the light of the Investment Facilitating Act which came into force in the Federal Republic of Germany on June 1 1993. This envisages a simplified authorization procedure for mobile on-site plants with an operating period of less than 12 months at the same site. Furthermore, the location scheduled for initial operation is a former mine, so that an application can be made for collective authorization under mining law for operation at several such sites.

The plant is scheduled to commence operation in the third quarter of 1994. It will have a throughput of 5.2 to/h with an average soil treatment time of $t = 2$ h (batch operation). This specification implements a scale-up factor of 100 (in comparison: scale-up factor from laboratory to semi-industrial scale = 1000). The ploughshare mixer has a volume of $V = 10$ m^3, is $L = 5.4$ m long and has a diameter of $D = 1.6$ m. With reference to the findings of pilot-scale operation, the mixer will be designed for operation at atmospheric pressure and temperatures up to $T = 250°C$. A steam generator with an output of ≤ 12 to/h will be rented for a transitional period of three years. The waste steam from a domestic refuse incineration plant being built in the vicinity will be used thereafter. The contaminated soil will be delivered in containers and stacked in an intermediate multi-bay store. It will be delivered to the preliminary treatment unit (mechanical screening, comminution) and the steam extraction plant itself by bucket loaders. In contrast to the operating mode of the pilot plant, the contaminated vapours will not be condensed with relatively large amounts of industrial water as a cooling medium, but in several stages. The first condensation stage serves the purpose of preheating the feed water for the steam generator, the second stage comprises a cooling circuit with an uncovered cooling tower, while the third stage simply further reduces the temperature of the effluent, from T = app. 30 °C to T = 15 - 20 °C. Any volatile matter with a condensation temperature of $T < 15$ °C contained in the soil will be removed by active coke as necessary. The highly concentrated contaminant phase is subsequently separated from the

effluent in an oil separator (for thermal disposal or recycling as used oil). This contaminated aqueous condensate can be treated by conventional industrial waste water treatment methods. Owing to the predominantly low solubility products of organically contaminated soil, adsorption processes are most favourable, especially in conjunction with relatively inexpensive lignite coke. This is illustrated by the following approximate calculation:

Two hours of treating a batch (10.4 to) contaminated with 1% diesel oil by weight obtains approx. 15 to of condensate. The theoretical water solubility of diesel fuel cdiesel/water is 20 mg/l. Therefore, 103.7 kg of the total 104 kg of contamination extracted from the soil are present as a skimmable contaminant phase. Only 0.3 kg are dissolved in the waste water. Two-stage coke filtration, each stage having a volume of Vadsorber = 5 m3, is able to adsorb 500 l contaminated oil before the material has to be renewed (assuming a 5 % contaminant load by volume).

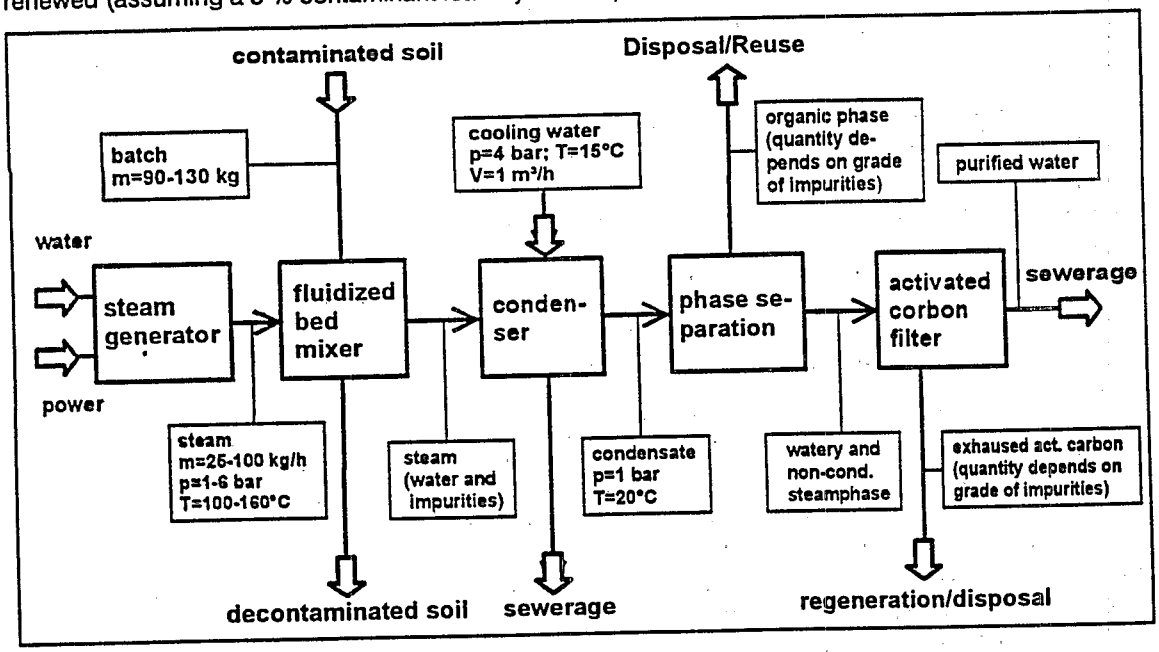

Figure 1: Flowchart of the pilot plant for the steam-extraction of contaminated soil

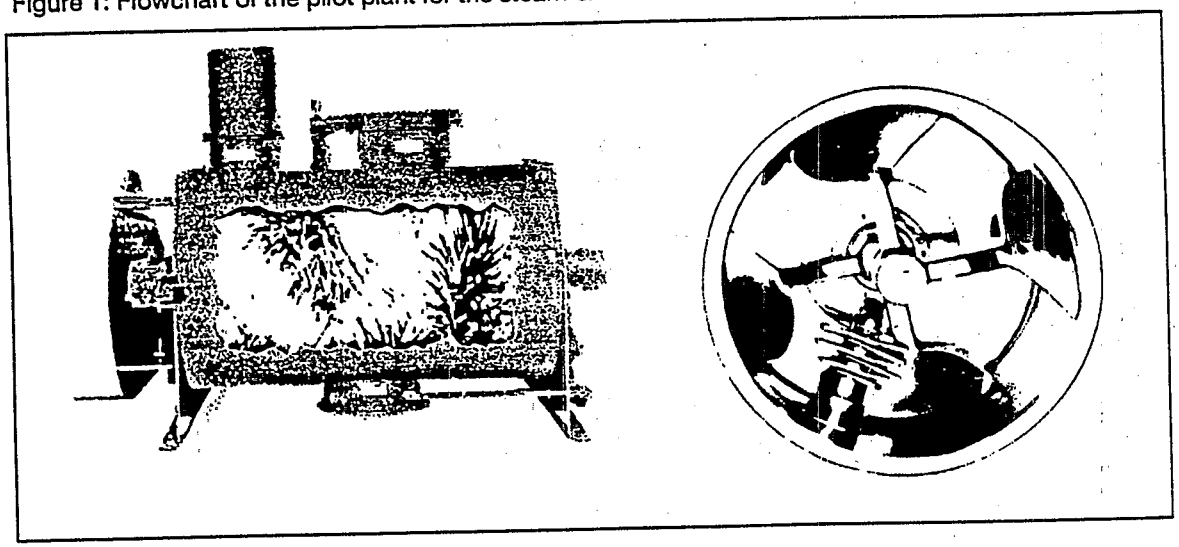

Figure 2: Left: Ploughshare mixer showing the mechanical fluidized bed
Right: Mixer with centrifuge and knife head manufactured by Lödige, Paderborn (4)

This corresponds to a filter life of 1,350 soil batches or 227 working days (two-shift operation). In order to operate as close to the theoretical solubility limit as possible in practice, especially close attention is to be paid to complete phase separation in the industrial-scale configuration (utilizing coalescence separators). No emulsion formation was detected during the pilot-plant trials. As a consequence of the simple method of gravity phase separation in a vessel, however, single drops of diesel oil in the aqueous phase increased the hydrocarbon content to 5 to 10 times the theoretical value.
In the context of the DERA project, the exhausted lignite coke will be disposed of in the hazardous waste incinerator operated by the same company on the same site.

Besides designing effluent treatment provisions with the objective of feeding the cleaned condensate into the municipal sewer system, the technical and economic feasibility of further treating the process water for reuse in steam generation is to be investigated. Owing to the stringent requirements as regards the purity of the boiler feed water, membrane processes may have to be employed here.

4. DECONTAMINATION RESULTS

Table 1 lists the experimental parameters and decontamination results of a number of trials. Note the relatively low process temperatures at which a favourable decontamination efficiency can be achieved. At the conference of experts we will be able to present results that illustrate the influence of higher temperatures (up to $T \leq 250$ °C).

The trials conducted thus far demonstrate that soil polluted with BTX/CHC (chlorinated hydrocarbons) can be thoroughly decontaminated by steam treatment lasting from only 15 minutes to one hour. A higher specific steam consumption is required with highly adsorbent matrices. The influence of adsorptive contaminant binding is more significant with mineral oil hydrocarbons whose COC values are higher than those of volatile substances by several powers of ten. This is illustrated by the reduced efficiency of steam treatment when applied to soil containing clay and silt that is artificially contaminated with diesel oil (decontamination efficiency 96%, cf. Table 1) compared with that obtained when treating predominantly sandy soil by steam extraction (decontamination efficiency > 99%). Both this sandy soil and the soil in Table 1 with hybrid contamination was taken from a thoroughly contaminated site, which was soaked by pollutants over a period of many years. A reduction in the necessary duration of treatment can be anticipated with fine-grained soil owing to the shift in the adsorption/desorption balance at higher process temperatures in conjunction with the very favourable mass transfer conditions in the fluidized bed.

As outlined by the following example, the results obtained with the three PCB-contaminated samples that were treated by steam extraction in the laboratory scale[3] verify the influence of stripping effects. The grit chamber residue treated in a distillation flask with an inserted glass tube acting as a steam lance had an oily or sludgy consistency. It was therefore "boiled" during the steam treatement at temperatures between 100 and 140°C, but drying and swirling were omitted. The PCB decontamination efficiency obtained by this method was 92 %. In contrast, the decontamination efficiency was significantly higher in the case of the "pumice" and "silica sand" batches, which occurred as a loose heap of material in the still and was therefore more effectively enveloped by the injected steam.

[3] For safety reasons; results of pilot-plant trials available at the end of '93

Soil/residue	Contamination		Experimental parameters				Decontamination efficiency [%]
			Mixer [°C]	Batch [kg]	Duration of treatment [min]	Spec. steam consumption mp/mB [-]	
Fine sand 0 - 2 mm	**Volatile substances**	BTX/CHC cocktail *) 1 % by weight	104	110	15	0.14	99.95
Soil with 8 % clay and 22 % silt		BTX/CHC cocktail *) 1 % by weight	100-130	110	60	0.66	99.975
Alumina (exhausted adsorbent, Al_2O_3)		CHC, 4.1 % by weight as EOX	103	100	60	1	99.8
Sandy soil with silty secondary components	**Mineral oil**	Diesel oil contamination HC = 0.16 %	103	90	120	0.53	> 99
Soil with 8 % clay and 22 % silt		Diesel oil contamination *) HC = 1 %	130		150	1.78	96
Sandy soil with silty secondary components	**Hybrid contamination (chlorophenols, HCB, HC)**	HC = 0.85 %, HCB = 320 g/kg as EOX, chloro-phenols*) = 400 g/kg	104	130	120	0.98	99.9
Loess soil (≥ 80 % clay/silt)	**PAH**	(Dimethyl-) Naphalene, Fluorene, Phenanthrene, Acenaphtene, 740 mg/kg	120	89	150	1.7	99
Grit chamber residue	**PCB **)**	14.7 mg/kg	100-140	100 g	180	6 - 7	92
Pumice *)		198.8 mg/kg	100-140	25 g	180	30 - 40	> 99.9
Silica sand *)		60 mg/kg	100-140	100 g	180	0.8 - 2	97 - 98

Table 1: Decontamination results of steam extraction from soil and residues (excerpt)

*) Contaminated artificially **) Laboratory scale

5. PROCESS APPLICATION AREA

In principle, the process can be used with volatile contaminants (chlorinated hydrocarbons, BTX), but especially with contaminants with a higher boiling range that are volatile in steam. The following substance classes of contaminations are considered volatile in steam (1, 5, 6, 7):

- Hydrocarbons and mineral oils (boiling range T_B = 200 to 350 °C)
- Chlorinated aromatic compounds and phenols (T_B = 180 to 350 °C)
- Polycyclic aromatic hydrocarbons (T_B = 270 to 400 °C)
- Polychlorinated biphenyls (T_B = 300 to 410 °C)
- Polychlorinated dibenzodioxins.

Steam extraction reaches its application limits in the presence of extremely high boiling PAHs, such as occur in the form of the tar pitch residue from coal tar processing. While production residues with an volatile contamination spectrum can be advantageously treated, contaminated sites with exclusively volatile contaminations can probably be cleaned less expensively by the in-situ method of soil air extraction.

6. COSTS

Table 2 contains an investment and operating cost estimate for the demonstration plant described in Section 3. The calculation is based on two-shift operation and an assumed relatively small number of operating days, namely 200 a year. This value takes account of down-times that may be necessary owing to technical modification and optimization measures. The investment costs of the machines and equipment are depreciated over three years (usual period for a publicly sponsored R&D project). Besides the principal assemblies, that is the steam generator, ploughshare mixer and condenser, the investment cost of the plant components in the amount of DM 57.2 million (line B.1) also covers the soil pretreatment and steam extraction unit loading equipment, and the treatment facility for the contaminated condensate. The personnel expenses for 3 plant operators per shift, contained under general costs (line C.1), make up some 20 % of the overall capital requirement.
The cost of supplies (line C.2) primarily contain energy costs for steam generation and the procurement of electricity to drive the mechanical fluidized bed reactor; it also contains the cost of industrial water. The cost of residual material disposal embraces the disposal or reprocessing of the oil-contaminated condensate and the regeneration or disposal of the exhausted active coke from the effluent treatment stage.

The most significant cost factor of the new steam extraction process is the general costs (personnel, insurance, maintenance). The investment requirement makes up about one-third of the total budget, while the cost of supplies and residual material disposal accounts for less than 10 %.

A	**Estimates for financing and engineering**				
A.1	Depreciation period		Capacity		
A.2	Machines and equipment	3.0 a	Capacity/h	5.20 t/h	
A.3	Construction engineering	3.0 a	Oper. hours/d	16.00 h/d	
			Capacity/d	62.40 t/d	
			Oper. days/a	200.00 d/a	
			Oper. hours/a	3,200.00 h/a	
			Annual cap.	12,480.00 t/a	
B	**Investment costs**	DM '000	DM '000/a	DM/t	%
B.1	Plant components	5,720	2,091.00	125.66	33.21
B.2	Planing, authorization	320	88.47	5.32	1.41
B.3	Miscellaneous	262	105.42	6.34	1.68
B.4	Σ Investment costs	6,302	2,284.89	137.31	36.29
C	**Operating costs**		DM '000/a	DM/t	%
C.1	General costs (personnel, maintenance etc.)		3,405.76	204.67	54.10
C.2	Cost of supplies, residual material disposal		604.80	36.35	9.63
C.3	Σ Operating costs		4,010.56	241.02	63.71
D	**Total cost of demonstration plant**		6,295.45	378.34	100

Table 2: Cost estimate for the construction and operation of an industrial-scale plant for cleaning organically contaminated soil by steam extraction

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HYDRAULIC FRACTURING TO IMPROVE REMEDIATION OF CONTAMINATED SOIL

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INTRODUCTION

In situ methods of removing contaminants from soil offer cost effectiveness and limit additional exposure to the contaminants. However, those techniques that depend on movement of water or air through the soil are hampered by low permeability at many sites.

Hydraulic fracturing provides the potential of dramatically improving the effectiveness of most remedial technologies that require fluid flow in the subsurface; these include soil vapor extraction (SVE or vapex), bioremediation, soil flushing, and pump and treat. Hydraulic fractures can also be used as *in situ* reservoirs of materials, such as compounds that release oxygen and nutrients, to enhance bioremediation.(1) Fractures can be filled with electrically conductive materials to induce contaminant migration by electroosmosis or electrophoresis or to improve Joule heating, which may increase microorganism populations and metabolic activity, volatilize contaminants, or cause vitrification.

Long recognized as a method of increasing the yields of oil wells, hydraulic fracturing has been adapted for use in the subsurface as a method to enhance environmental remediation. The technology is particularly suited to sites underlain by soils where the lateral component of stress exceeds the vertical stress applied by the weight of the overburden (these soils are termed overconsolidated.) Fractures created in overconsolidated soils tend to propagate in a horizontal to sub horizontal plane, allowing the fractures to reach maximum dimension without intersecting the ground surface. In general, they are 1 to 3 centimeters thick, slightly elongate in plan, asymmetric with respect to their parent borehole, and as much as 14 meters (m) in diameter. This geometry, in most cases, will be the most favorable for *in situ* technologies that utilize vertical wells. Glacial drift of the Midwest and Northeast, swelling clays of the Gulf coast, and similar soils are frequently overconsolidated and suitable for hydraulic fracturing. Depositional stratigraphy may also influence the geometry of fractures, so normally consolidated soils that are strongly bedded may also be amenable to hydraulic fracturing.

The technology is most effectively applied to low permeability (less than 10^{-5} centimeter per second [cm/s]) silts, clays, or rock. By causing a substantial increase in effective permeability, hydraulic fracturing can improve the extent of influence of wells and spatial distribution of *in situ* remediation processes, decrease remediation time, and minimize the number of wells needed for remediation. Indeed, without fractures many sites could not be considered candidates for *in situ* remediation.

Under the auspices of the SITE program, hydraulic fracturing has been demonstrated at three sites.(2) Field studies at the US EPA Center Hill Solid and Hazardous Waste Research facility were conducted to determine the performance of hydraulic fracturing in silty clays. Sand filled hydraulic fractures were also created at a contaminated site in Oak Brook, Illinois (the Oak Brook Site) where SVE is being tested for removal of chlorinated solvents from soil. Another contaminated site in Dayton, Ohio (the Dayton site) was studied to determine the effectiveness of this technology in enhancing bioremediation of petroleum fuels. The demonstrations showed that flow rates through wells completed with hydraulic fractures were 15 to 40 times greater than unfractured wells. Hydraulic fractures extended the zone of influence around wells by a factor of 10 or more. At the Oak Brook site, an order of magnitude increase in contaminant yield was observed.

METHODOLOGY

A hydraulic fracture is created when fluid is pumped into a borehole until a critical pressure is reached and the enveloping soil fractures. Sand-laden slurry is pumped at rates between 60 to 100 liters per minute into the fracture as it propagates away from the borehole. The base fluid in the slurry is a viscous aqueous solution of cross linked guar gum that can easily entrain and transport sand grains. The slurry system also contains enzymes that degrade the guar gum polymer several hours after pumping is completed. The aqueous solution loses viscosity as the gel degrades, drains away, and leaves behind a highly permeable pathway for delivery or recovery of fluids in the subsurface.

Initiation of a horizontal fracture is facilitated by creating fracture nucleation sites, usually at the perimeter of a horizontal disk-shaped void within the soil. The void can be created by rotating a horizontal high pressure jet around the side of a borehole and thereby eroding a notch extending 10 to 15 cm into the wall of the borehole. These operations are commonly executed in an open hole section below casing that has been driven into soil. The lateral pressure of the soil on the outer wall of the casing effectively seals the casing and prevents leakage.

Location and growth of fractures can be monitored during installation by observing the upward displacement of the ground surface with a leveling telescope. The uplift pattern typically appears as a broad, shallow dome several meters in diameter and 1 to 2 cm in altitude. Based on our results, uplift appears to equal the thickness of the shallow, gently dipping fracture.

The equipment necessary for hydraulic fracturing include a mixer for preparing a slurry of several hundred liters of gel and hundreds of kilograms of sand within a few dozen minutes, a pump to inject slurry, and supporting equipment. The equipment used for SITE program demonstrations cost approximately $93,000. This equipment allowed installation of as many as six fractures in a day. Cost of material used in a single fracture varies but typically ranges from $150 to $300.

RESULTS

Demonstrations at three sites have documented the improvement in rates of fluid movement into or out of wells and the expansion of influence of wells that can be accomplished by using hydraulic fractures. These three sites, all underlain by the glacial till that occurs in much of the Midwest, are in Cincinnati and Dayton, Ohio, and Oak Brook, Illinois.

Center Hill Site

This site, an uncontaminated US EPA testing facility in Cincinnati, is underlain by a silty clay with lesser amounts of sand and gravel, the characteristics of soil amenable to hydraulic fracturing. Five wells were installed to compare the differences of fractured and unfractured wells, to determine the effect on performance from venting of the fracture to the surface, and to assess the performance of wells with multiple fractures. Three wells with hydraulic fractures were installed. One well had hydraulic fractures at 1.5 and 3 m below ground surface (bgs). A second well had a single fracture at a depth of 1.5 m that vented to the surface 7 meters (m) from the well. The third well had a single fracture at 1.5 m that remained below the surface. Two conventional wells were screened in unfractured ground. The wells were connected to a vacuum blower that was capable of 300 cm of water of suction. Pneumatic piezometers were installed around the wells to measure suction head in the soil.

Well discharge, as both vapor and liquid flow rate, was an order of magnitude greater for the fractured wells than the unfractured wells.(2) For the fractured wells, rate correlated strongly with precipitation; after heavy rainstorms yields of vapor would decrease, substantial water would be produced over the next few days, and the system would gradually recover. The vented fracture was more responsive to rainfall than the unvented fractures. The conventional wells were unaffected by rain.

Suction head was detectable at greater distance from the wells with fractures than from the wells without. Around the conventional wells, suction was about 3 cm of water at a distance of 1 m. In contrast, the same suction head could be observed 8 m from the fractured wells. Also, suction around the fractured wells was influenced by rainfall events. Suction head would decrease gradually during drying of the soil and increase significantly after heavy precipitation.

Oak Brook Site

Contaminants consisting of trichloroethene (TCE), 1,1,1-trichloroethane (TCA), 1,1-dichloroethane (DCA), tetrachloroethene (PCE), and other solvents are present in silty clay till to depths of 6 m bgs. Hydraulic conductivity varies from 10^{-7} to 10^{-8} cm/s. The low conductivity hinders vapor extraction. In order to improve extraction rates, hydraulic fractures were created at depths of 1.8, 3, and 4.6 m bgs at two locations. Ground surface uplift measurements showed a maximum thickness of 2.5 cm and indicated a lateral extent of about 6 m. Multi-level recovery wells, Wells No. RW3 and RW4, were installed to connect each fracture individually to a two-phase vapor extraction system. The vapor recovery rates from these two wells were compared to rates from similarly screened zones in unfractured Well No. RW2. A multi-level monitoring system consisting of as many as six pneumatic piezometers per borehole was installed at radial distances of 1.5, 3, 4.6, and 7.6 m from each recovery well.

The vapor flow rates and contaminant concentration were measured using variable area flow meters and gas chromatography. Other parameters of interest included water discharge from the vapor extraction system, soil moisture content, and soil vacuum at the recovery wells and the monitoring holes.

Vapor discharge rates from Wells Nos. RW2, RW3, and RW4 are presented in Table 1. The average discharge rates from the fractured wells, RW3 and RW4, were 15 to 20 times greater than unfractured Well No. RW2. Discharge from fractured wells tended to fluctuate, while that for Well No. RW2 was more consistent. The fluctuation may have been due to changes in subsurface caused by precipitation events.

TABLE 1 - VAPOR DISCHARGE RATES AT THE OAK BROOK SITE

Well No.	Range of Rates liter / sec	Average Rate liter / sec	Fraction discharged from 1.68 to 1.98 m bgs	Fraction discharged from 2.90 to 3.20 m bgs	Fraction discharged from 4.42 to 4.72 m bgs
RW2	0.047 - 2.2	0.52	0.47	0.27	0.24
RW3	1.0 - 10.4	6.7	0.61	0.09	0.30
RW4*	13.2 - 20.1	16.1	0.34	0.36	0.23
RW4**	8.1 - 14.0	10.7	Not Applicable	Not Available	Not Available

* The 1.8 m fracture at Well No. RW4 vented to the surface. Data for this line include discharge when suction was applied simultaneously to all three fractures.
** This line shows data from when suction was applied to the 3 m and 4.6 m fracture only; hence, well discharge was less than when suction was applied to all three fractures.

Mass recoveries for ten targeted compounds were computed for each well from concentration and discharge measurements (Table 2). Mass recoveries from hydraulically fractured wells were approximately one order of magnitude greater than that from the unfractured well. Mass recovery rate from all wells decreased through time.

TABLE 2 - RECOVERY OF CONTAMINANTS FROM OAK BROOK SITE

Well No.	Time (days)	Mass of VOCs Recovered (kilograms)	Time (days)	Mass of VOCs Recovered (kilograms)	Time (days)	Mass of VOCs Recovered (kilograms)
RW2	60	2.3	110	2.7	160	2.7
RW3	60	10.4	110	16	160	19
RW4	60	3.6	110	7.3	160	8.6

Suction head measurements provide insight into the extent of influence of a well. Suction head decreased abruptly with distance from the unfractured well, from 670 cm of water suction in Well No RW2 to a few millimeters (mm) of water at a piezometer 1.5 m away. On the other hand, suction head decreased gradually with distance from the fractured wells, ranging through pressures of 40, 33, 1, and 0.5 cm of water at distances of 1.5, 3, 4.6, and 7.6 m from the well, respectively.

Dayton Site

At the Dayton Site, six underground storage tanks (UST's) were removed prior to fracturing work. Soil contaminants included benzene, toluene, ethylbenzene, xylene (BETX), and other petroleum hydrocarbons. The site is underlain by stiff sandy to silty clay with traces of gravel. Hydraulic fractures were place at depths of 2.1, 2.4, 3, and 3.7 m bgs. Water containing hydrogen peroxide and biological nutrients was introduced into a fractured well and an unfractured well.

Soil samples were collected at distances of 1.5, 3, and 4.6 m from the wells using a split spoon sampler before and during remediation. The sample from each spoon was analyzed for moisture content, BETX, total petroleum hydrocarbons (TPH), number of hydrocarbon degraders (colony forming units [CFU]), and microbial metabolic activity.

Flow rates into the fractured well were 25 to 40 times greater than into the unfractured well, and this difference clearly affected the moisture in the soil. After 1 month, soil moisture content 1.5 m from the fractured well was 1.4 to 4 times greater than the unfractured well. Moisture content generally were greater near the fracture, with the largest increase near the uppermost fracture. The same trends in moisture content were also observed 3 and 4.6 m from the wells.

TABLE 3 - CONTAMINANT DEGRADATION AT THE DAYTON SITE

	Percent Degradation After 1 month				Percent Degradation After 6 months			
	Benzene	Ethyl benzene	Toluene	TPH	Benzene	Ethyl benzene	Toluene	TPH
At 5 feet from								
Fractured Well	NI*	97	NI	77	80	60	NI	71
Unfractured Well	NI	8	NI	0	NI	37	NI	55
At 10 feet from								
Fractured Well	47	79	NI	58	12	NI	NI	54
Unfractured Well	NI	72	NI	27	NI	90	NI	67
At 15 feet from								
Fractured Well	64	73	NI	51	38	56	NI	68
Unfractured Well	NI	NI	NI	NI	NI	NI	NI	25

* No Impact

Effectiveness of bioremediation was gauged by reduction in BETX and TPH concentrations in soil samples. Percentages of contaminant degradation, compared to baseline measurements, are reported in Table 3. Generally, reduction was greater around the fractured well than the conventional well. Considerable variation among the degradation data is evident and may be due to local variations in contaminant concentration that was unresolved by sampling, or other factors.

CONCLUSIONS

Hydraulic fractures can substantially improve performance of *in situ* remediation projects such as vapor extraction, bioremediation, and free product recovery. Using a well intersecting a hydraulic fracture, these improvements are realized as increased rate of removal or addition of fluids through the well and more wide-spread influence of the well. The rate of discharge or injection appears to be more than 10 times greater than for a conventional well. Wells intersecting hydraulic fractures appear to affect the pressure distribution 10 times further distant (and 100 times the area) than their conventional counterparts. These improvements in physical performance are matched by similar improvements in remediation, according to available data.

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X-RAY TREATMENT OF ORGANICALLY CONTAMINATED AQUEOUS SOLUTIONS

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INTRODUCTION

Ionizing radiation is highly effective in decomposing or modifying organic compounds. This paper discusses the use of ionizing radiation, namely x-rays, to decompose toxic organic substances. X-ray treatment of organically contaminated aqueous solutions is based on the in-depth deposition of ionizing radiation. Collisions of energetic photons (x-rays) with matter generate a shower of lower energy secondary electrons within the contaminated waste material. The secondary electrons cause ionization and excitation of the atomic electrons, break up the complex molecules of the contaminants, and form the oxidizing hydroxyl radical (OH·) and the reducing aqueous electron (e^-_{aq}) and hydrogen radical (H·) that react with the contaminant materials to form nontoxic by-products such as water, carbon dioxide, and oxygen. Since high energy x-rays and electrons transfer their energy to the background media by similar interactions, x-ray processing should be similar to direct electron beam processing which has also been shown to be a highly effective means of destroying organic contaminants in aqueous solutions (1).

The effective penetration depth of an x-ray in a material is much larger than that of a electron of the same energy. For example, a 1 MeV x-ray has an effective penetration depth of 27 cm in water while a 1 MeV electron deposits its energy within 4 mm. At 10 MeV the effective range of an x-ray in water is 66 cm while that of the same energy electron is 5 cm. While x-rays have a larger effective penetration depth than electrons, the efficiency of producing x-rays is much less than that for electrons. X-rays for radiation processing are obtained by first producing a high energy electron beam which is directed into a high atomic number material (called a converter) thereby producing bremsstrahlung radiation as the electrons slow down. The conversion efficiency from energy of the incident electrons to energy in the escaping x-rays is a strong function of the energy of the incident electrons. The useful conversion efficiency of 1, 5, and 10 MeV electrons in a tantalum converter are 1.6%, 8.4%, and 16.6% respectively. The maximum energy of either x-rays or electrons used in radiation processing is generally limited to < 10 MeV to avoid nuclear activation (photo-disintegration reaction) of the working media.

Even though x-ray treatment is inherently less efficient than direct electron beam treatment, x-ray treatment is either the preferred method or the only option available when the depth of penetration is important such as treatment of thick waste streams (> 2 inches), soils, and solids. Since electrons do not penetrate deeply, contaminated material must be presented to the beam in thin sections and handling can be a problem especially if the contaminated liquid is stored in a barrel or tank. The deeper penetration of similar energy x-rays offers the potential for in-situ treatment of contaminants in a barrel or a tank. Because of the much larger efficiency, direct electron beam treatment is preferred when the depth of penetration of the electrons is not a problem such as treatment of thin streams of liquids.

A high power, high energy electron accelerator plus x-ray converter generate the x-rays used in the treatment process. The accelerator energy which must be small enough to avoid activation and as large as possible in order to improve the bremsstrahlung conversion efficiency will most likely be ≈ 8-10 MeV. A pulse of electrons 50 to 100 nanoseconds long is directed onto a cooled high atomic number converter to efficiently generate x-rays.

The viability of x-ray treatment of organic wastes depends on the existence or development of an efficient high power, high energy electron accelerator. RF linacs can easily obtain the energies of interest but are limited to power levels of approximately 50 kW and electrical conversion efficiencies of less than 20%. New developments in RF sources will most likely increase the power levels to ≈ 100 kW but the efficiency is expected to remain low. Electron accelerators such as the insulated core transformer or Cockcroft-Walton (Dynamitron) are very large accelerators and are limited to energies ≤ 5 MeV. The linear induction accelerator (LIA) in which the beam passes through a large number of acceleration gaps thereby summing the energy of the gaps, can be efficient electrically (≈ 50%), easily produce the energies of interest (50 MeV ATA accelerator) and high power (> 175 kW based on existing sources). A compact, transportable induction accelerator called the Spiral Line Induction Accelerator (SLIA) is being developed by Titan/Pulse Sciences, Inc. (PSI). The estimated size, weight, and cost of a transportable 400 kW (8 MeV, 1.8 kA, 25 nsec, 1.1 kHz) SLIA are 12 m^3 for the size, 4.5 tons for the weight, and $3 M for the cost of the accelerator.

METHODOLOGY

The U.S. Environmental Protection Agency (EPA) and the Department of Energy (DOE) under the SITE Emerging Technology Program have entered into a cooperative agreement with Titan/PSI to evaluate the x-ray treatment process for the remediation of liquid wastes contaminated with volatile (VOCs) and semi-volatile (SVOCs) organic compounds. The objective of the program was to demonstrate in small scale experiments the efficacy of x-ray treatment for liquid wastes contaminated with VOCs and SVOCs, and to determine the x-ray doses required to reduce the organic contamination to acceptable levels.

A linear induction accelerator at PSI was used to generate a 1.2-1.4 MeV, 800-1000 A, 55 nsec electron beam at the rate of 1-2 pulses per second. The energy of the electron beam was converted to x-rays in a high atomic number bremsstrahlung converter. The converter consisted of an electron beam vacuum window (2 mil titanium foil), a high "Z" material (5 mil tantalum foil) and a beam stop (0.2 inch graphite). The converter was water cooled to allow continuous operation. At a 10 cm distance from the converter an x-ray dose of 5-8 rads per pulse was applied to the samples under test. To accumulate a large x-ray dose in the sample, multiple radiation pulses were applied to the sample at the repetition rate of one pulse per second. The samples were continuously rotated during irradiation thereby allowing a more uniform dose of x-rays to be applied to the samples. A closed irradiation chamber allowed the samples to be irradiated in a nitrogen atmosphere to prevent ozone formation.

Radiation dosimeters were placed directly on each of the samples being irradiated. Below 20 krads lithium fluoride TLDs (thermoluminescence detectors) were used to measure the dose and above 20

krads the x-ray dose was measured with radiochromic film. Both dosimetry techniques have been calibrated against NIST standards.

The samples which were irradiated were either prepared by certified laboratories from neat (no solvents) solutions of VOCs or SVOCs in reagent grade water or were from contaminated wells. There were two sources of contaminated well water. Florida International University (FIU) provided well water primarily contaminated with carbon tetrachloride. A certified laboratory then added a known amount of additional contaminant to these samples before they were irradiated. Contaminated well water samples from a Superfund site (Lawrence Livermore National Laboratory, LLNL) were also included in the investigation. The samples were generally prepared in 40 mℓ VOA vials.

Samples with the identical contaminant concentration levels were irradiated at increasing dose levels to determine the rate (concentration versus dose) at which the contaminants were being destroyed and the x-ray dose required to reduce the organic contamination to acceptable levels. After irradiation the samples were analyzed by a certified analytical laboratory.

RESULTS

The results of the x-ray irradiation of the samples prepared with a neat solution of the contaminant in reagent grade water are shown in Table 1. Twelve different contaminants in 15 aqueous matrices were investigated. The compounds such as chloroform, methylene chloride, 1,1,1 trichloroethane and carbon tetrachloride which do not contain a double bond and do not react as strongly with the hydroxyl radical required a much large dose to destroy than the VOCs which do react with the hydroxyl radical.

TABLE 1. SUMMARY OF X-RAY RADIOLYSIS EXPERIMENTS ON NEAT SOLUTIONS OF CONTAMINANTS IN REAGENT GRADE WATER.

Compound	Matrix	Initial Concentration (ppb)	Final Concentration (ppb)	X-ray Dose (kR)	Test Method
TCE	Deionized Water	64,000	< .5	180	8010
TCE		2100	< .5	20	8010
TCE		1000	< .5	10	8010
TCE		490	< .5	10	8010
PCE		230	3.6	4.2	8010
Chloroform		2000	4.4	178	8010
Methylene Chloride		270	3.1	145.9	8010
Trans 1,2 Dichloroethene		260	.78	10.6	8010
Cis 1,2 Dichloroethene		13	< .5	10.6	8010
1,1,1 Trichloroethane		590	54	207.1	8010
Carbon Tetrachloride		180	14	224	8010
Benzene		240	< .5	8.8	8020
Toluene		150	< .5	4.83	8020
Ethylbenzene		890	3.6	20.4	8020
Xylene		240	1.2	5.6	8020

Table 2 summarizes the results for the well water samples from FIU and the Superfund site at LLNL. The doses required to destroy the VOCs which react strongly with the OH· radical increased for the well water sample. For example, benzene concentrations of 240 ppb and 262 ppb were irradiated in deionized water and well water. In deionized water, 8.8 krads mineralized the benzene while 30.9 krads were required for the mineralization of a similar initial concentration of benzene in well water. Both the spiked FIU well water samples and the two sets of samples from the Superfund site had high concen-

trations of carbonate and bicarbonate ions which have large reaction rates with the OH· radical. The carbonate and bicarbonate ions appear to act as OH· scavengers thus impeding the destruction of the VOCs which react strongly with the OH· radicals.

TABLE 2. SUMMARY OF X-RAY RADIOLYSIS EXPERIMENTS ON CONTAMINATED WELL WATER.

Compound	Matrix	Initial Concentration (ppb)	Final Concentration (ppb)	X-ray Dose (kR)	Test Method
Benzene/carbon tetrachloride	FIU Well Water	262/400	< .5/196	39.9/93.8	FIU
Ethylbenzene/carbon tetrachloride	FIU Well Water	1000/430	< .5/70.9	33.2/185	FIU
D-xylene/carbon tetrachloride	FIU Well Water	221/430	< .5/85	20.5/171	FIU
Superfund Well Water Sample #1:					
TCE	SFWW1	3400	< .5	99.0	8240
PCE	SFWW1	500	< .5	99.0	8240
1,1 Dichloroethane	SFWW1	< 10	1	145.4	8240
1,1 Dichloroethene	SFWW1	25	< 1	49.9	8240
1,1,1 Trichloroethane	SFWW1	13	2.0	145.4	8240
Cis 1,2 Dichloroethene	SFWW1	44	< .5	49.9	8240
Superfund Well Water Sample #2:					
TCE	SFWW2	5000	< 1.0	291	8240
PCE	SFWW2	490	1.6	291	8240
Chloroform	SFWW2	250	81	291	8240
Carbon tetrachloride	SFWW2	14	4	291	8240
1,2 Dichloroethane	SFWW2	38	17	291	8240
1,1 Dichloroethane	SFWW2	11	6.8	291	8240
Freon	SFWW2	71	32	291	8240

An x-ray dose of 150 krads was sufficient to reduce all the contaminants in the first (sample #1) Superfund water samples to values which were below those established by the California Primary Drinking Water Standards. For the second more highly contaminated sample #2, a maximum dose of 291 krads was applied to the sample. This dose reduced three out of the seven contaminants to below the drinking water standards. It is estimated that a maximum dose of 500 krads would be required to reduce all of the contaminants to concentrations below the drinking water standards.

High contaminant levels of TCE and PCE in aqueous solutions were treated with x-rays to investigate the potential for hazardous by-product formation. Preliminary analysis of five out of six sets of experimental samples showed concentrations of chlorinated hydrocarbons which were below the detection limit (< .5 ppb). In one set of experiments in which chlorinated hydrocarbons were found a problem with the analytical analysis is suspected. Analysis of the final set of samples for evidence of the aldehydes or organic acids is in progress.

CONCLUSION

A large number of VOC and SVOC contaminants found in Superfund sites were successfully decomposed (destroyed) by x-ray treatment (radiolysis) of the contaminated aqueous solutions. The

concentrations of all of the VOC and SVOC contaminants which were investigated were significantly reduced during x-ray irradiation. When no OH· scavengers were present, contamination levels of a few 1000's ppb were destroyed by doses of a few 10's of kilorads for the contaminants which react strongly with the hydroxyl radical. Much larger doses were required to remediate the contaminants which contained a double bond and did not react as strongly with the hydroxyl radical. For these contaminants, a few 100's of kilorads were required to destroy initial concentrations of a few 100's ppb.

The five sets of experiments carried out with contaminated well water demonstrated the effects of having OH· scavengers present in solutions with an OH· active contaminant. Approximately a factor of five higher x-ray doses were required for the OH· active contaminants when the OH· scavenger carbonate and bicarbonate ions were present. As would be expected the rate of remediation for carbon tetrachloride, which is not OH· active, was not effected by the carbonate and bicarbonate ion in the contaminated FIU well water. The addition of an OH· active contaminant to the well water did not effect the rate of decomposition of the carbon tetrachloride.

The contamination levels of the moderately contaminated sample of well water from LLNL, a Superfund site, were reduced to less than those set by the California Primary Drinking Water Standards by an x-ray dose of 150 krads. For the more highly contaminated LLNL well water sample, the dose to reduce the contamination levels to drinking water standards was estimated to be 500 krads based on the experimental data. The amount of x-ray radiation required to decompose the organic contaminants in an aqueous solution is a strong function of the contaminants present and the exact chemical composition of the solution. In principle, the rate coefficients which were determined from the data can be used to predict the dose level required to destroy mixtures of multiple VOC contaminants and OH· scavengers.

Experiments with high concentrations of TCE and PCE are being completed to determine reaction by-products. Preliminary analysis of the results showed no evidence of chlorinated hydrocarbons when the TCE or PCE concentrations had been reduced to below detectable levels. As with high energy electron beam destruction of TCE and PCE, low level concentrations of the aldehydes and organic acids are expected.

X-ray treatment of organically contaminated aqueous solutions is a viable method for reducing the contamination to acceptable levels when a large depth of treatment is desired or required, such as for contaminants in thick streams of liquids (> 2 inches), barrels, or tanks. When a large depth of penetration into the contaminated material is not required (e.g. thin streams of liquids), the bremsstrahlung x-ray converter can be removed from the accelerator and the contaminated material treated directly with the high energy electron beam.

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THERMAL DESORPTION OF SVOC, VOC, AND PESTICIDE CONTAMINATED SOIL AT THE PRISTINE FACILITY TRUST SUPERFUND SITE, READING, OHIO

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In September 1993, SoilTech ATP Systems, Inc. (SoilTech) mobilized their 10 tph Transportable Anaerobic Thermal Processor (ATP) System to the Pristine Facility Trust Superfund Site (Pristine) in Reading, Ohio to treat approximately 13,500 tons of SVOC, VOC, and Pesticide contaminated soil and sediment. The SoilTech ATP System anaerobically desorbs organic contaminants from a solid matrix at temperatures in excess of 900 degrees Farenheight (°F). The principle products of this process are clean treated soil and vapor condensate containing the organic constituents. SoilTech is operating a 25 gpm Waste Water Treatment System at the Pristine Site to remove organic contaminants from the vapor condensate. The treated condensate is added as quench water to the processed soils while the organic phase will be sent for off-site disposal.

Site specific conditions that are presenting new challenges to SoilTech include limited site access, adverse feed soil characteristics, and strict delisting criteria for the processed soil. Mobilization logistics were extensive because the site had no road frontage and limited access was available only through neighboring industrial facilities. The feed material is a wet clay containing a high percentage of fines which poses significant material handling difficulties. Samples of the feed soil indicate elemental sulfur in the range of 1 to 6 percent which significantly increases the potential for high sulfur dioxide emissions and corrosion of process internals. SoilTech successfully met the performance criteria of 99.99% destruction and removal efficiency (DRE) for organic contaminants in stack emissions required by the U.S. Environmental Protection Agency. The low concentrations of individual organic contaminants meant that addition of surrogate compounds to the feed was necessary to demonstrate that the ATP System could meet the performance criteria. The soil delisting criteria includes maximum total concentrations for 51 organic compounds and TCLP limits for 9 inorganic compounds.

The ATP System, under normal operating conditions, concentrates organic contaminants to the extent that compounds below detection limits in the feed soils can sometimes be detected in the organic concentrate. During waste profiling activities, PCBs were unexpectedly detected in the organic concentrate resulting in potential increased cost for off-site disposal. SoilTech instituted a significant operational change that greatly reduced the volume of organic waste generated for off-site disposal.

To date, SoilTech has processed and met the delisting criteria, without failure, for over 11,600 tons of site feed soils. The completion of processing, equipment decontamination, and demobilization is expected to be March 1994. A technical paper will be available subsequent to that time.

Thermal Desorption/Base Catalyzed Decomposition (BCD) A Non-oxidative Method For Chemical Dechlorination Of Organic Compounds

Introduction

Thermal desorption has become an acceptable and effective alternative for the non-oxidative treatment of organic contaminated soils, sediments and sludges. Physical separation of the contaminants from the media through indirect heated thermal desorption results in lower volume off-gas which allows for contaminant recovery through condensation of the organic compounds from the off-gas. The Base Catalyzed Decomposition (BCD) Technology detoxifies and chemically decomposes contaminants by removing chlorine atoms. The BCD process can be combined with medium temperature thermal desorption (MTTD) to dechlorinate high-hazard organics including polychlorinated dibenzo-p-dioxins (PCDD), polychlorinated dibenzofurans (PCDF), pentachlorophenol (PCP), polychlorinated biphenyls (PCB) and pesticides/herbicides. The combination of MTTD with BCD allows for meeting the objectives of minimizing/ concentrating the organics requiring BCD, treating the contaminated media for recycling as backfill, minimizing air and water discharges, and recovering the dechlorinated organic compounds for utilization as a fuel supplement in an industrial boiler.

EPA's Risk Reduction Engineering Laboratory (RREL) in Cincinnati, Ohio developed and patented the BCD technology. RREL initiated research to develop innovative alternatives for treatment of chlorinated organic compounds in 1980. The challenge was to modify catalytic transfer hydrogenation process extensively utilized in the chemical process industry to result in a cost effective commercial process which would meet applicable regulatory standards. In January, 1989 experimental results confirmed that a process for chemical dechlorination had indeed been developed on a laboratory scale [1]. The Federal Technology Transfer Act (FTTA) allows private sector firms like ETG Environmental, Inc. ("ETG") and Separation and Recovery Systems ("SRS") to conduct BCD and other technology commercialization in conjunction with the USEPA.

ETG/SRS has worked with RREL/USEPA since 1991 to develop the SAREX® Therm-O-Detox® system to be used with the BCD process on a commercial level. Through a cooperative effort between the EPA SITE Program, EPA Region 4, and the NC-DEHNR, a BCD technology demonstration was conducted by ETG and SRS at the Koppers Superfund site in Morrisville, North Carolina in September, 1993.

Methodology

The principle of the BCD process is the utilization of hydrogen radicals (Acceptor-H) generated from a hydrogen donor to completely replace the chlorine ions in the chlorinated hydrocarbons[2]. The key operating vairables for the reactions are temperature, base catalyst and hydrogen donor concentrations.

Indirect heated thermal desorption of organics from contaminated soils and sludges is well studied and documented[3]. Indirect heated systems transfer heat from steam, hot oil, molten salt or electricity through metal surfaces to the waste materials. A sweep gas with low oxygen content is used to physically separate the organic contaminants from the media (e.g. soil) through thermal desorption. Desorbed organic compounds are condensed and recovered. Carbon adsorption may be used to polish the off-gas prior to discharge into the atmosphere. Particulate carryover is minimized due to the decreased volume of exhaust gas. Condensed water is recycled to the treated media for cooling, dust suppression, and to provide a moisture content suitable for backfill compaction.

ETG/SRS have observed through their own field experience, as well as published information, that heat transfer to the waste and degree of waste mixing are two of the most critical factors for effective thermal desorption. Increased mixing will lead to the reduction of material residence times. A thermal desorption system that processes a material quickly and thoroughly also has less chance for thermal decomposition of organic compounds or forming coke in the system caused by higher hydrocarbon concentration from the feed material. A continuing trend is to increase the process temperature of the thermal desorption system to a higher range (750°F to 950°F) defined by ETG/SRS as medium temperature thermal desorption (MTTD), for the removal of heavy organic and chlorinated organic compounds.

The SAREX® Therm-O-Detox® system as shown in Figure 1 includes an indirect heated MTTD unit to physically separate moisture and organics from the media, an extensive vapor recovery system including condensing unit(s) and carbon adsorption, and a BCD liquid tank reactor (LTR) unit. The contaminated/screened materials are fed to a feed hopper and conveyed through an enclosed hopper to the solids reactor (MTTD). Dechlorination agents are added in the feed conveyor to allow premixing with the contaminated media.

The indirect heated MTTD can be controlled to a desirable temperature and residence time as required by the BCD process. Vapors are discharged to the scrubbing and condensing system and a carbon polishing system prior to atmospheric discharge. Clean media is discharged to an enclosed cooling conveyor where condensed, polished water from the vapor recovery system is recycled and utilized to cool the media, as well as to control dust and produce a material with proper moisture content for compaction as on-site backfill.

The organic contaminants recovered from the vapor recovery system are sent to the BCD LTR. The LTR is prepared to treat contaminants by adding base (i.e., sodium hydorxide), a catalyst, and a hydrocarbon which serves as the reaction medium and the hydrogen donor. The LTR contents are heated to a temperature of 320° - 340°C (610° - 650°F) to effect dechlorination of contaminants. After dechlorination reactions are completed, the LTR contents can be reused to treat other contaminants with chemical additions or used as a fuel supplement in an industrial boiler such as a cement kiln.

The BCD chemistry[4] in the LTR is illustrated as follows:

$$R\text{-}(Cl)_x + R' \xrightarrow[620^\circ F - 650^\circ F]{Na^+} R\text{-}H + NaCl + R''$$

Catalyst

R-$(Cl)_x$ as shown can be any halogenated compound such as PCDDs, PCDFs, PCBs, 2,4-D or 2,4,5-T. In principal R' is a hydrogen donor whose oxidation potential is sufficiently low to generate nucleophilic hydrogen in the presence of base Na^+ (sodium hydroxide) and at temperatures between 250° - 350°C. Under these conditions, chlorine on R-Cl is replaced by H to produce R-H with loss of hydrogen from R' to R" and the formation of sodium chloride. This reaction achieves complete dechlorination of chlorinated compounds.

The MTTD/BCD system has the following advantages:

- The unit has a high heat transfer surface area resulting in <u>high heat transfer efficiency</u>.
- The MTTD unit provides <u>complete local mixing action</u> exposing most of the particles of the process mass to the heat transfer surface. This reduces the dependency of heat movement on the thermal conductivity of the process.
- System equipment components are proven effective and commercially available. No new or experimental equipment is required.
- The MTTD system can be modified to incorporate stabilization/fixation additives if heavy metals are present.
- The uniform bed conditions will promote direct surface thermal desorption comparing to the ineffective diffusion phenomena when the particles are stuck together in lump or cake. The homogenous bed will result in the <u>reduction of the retention time</u> required to meet the treatment standards.
- The MTTD unit can process sludge, sediment and clayey soils directly to meet treatment requirements. No pre-drying is required.
- There is no large volume of sweep gas flow through the MTTD indirect heat unit, resulting in true, non-oxidative physical separation. The off-gas can be condensed without the requirement of an afterburner (incinerator). The MTTD/BCD system will have <u>less environmental impact</u> and <u>permitting requirements</u>.

- BCD reagents are inexpensive and do not require reuse, in contrast to other dechlorination processes (APEG/KPEG).

- Lower cost than incineration and other higher temperature thermal desorption systems.

- The higher material temperature and uniform material bed will assure the higher removal rate for high boiling point contaminants.

SITE Demonstration

In late 1992, ETG/SRS was contacted by the USEPA Office of Research and Development (ORD) to demonstrate the MTTD/BCD technology using the SAREX® Therm-O-Detox® system at a Superfund site in Morrisville, North Carolina under the Superfund Innovative Technology Evaluation (SITE) program[5]. The objectives of this demonstration are listed below:

- Assess the effectiveness of the MTTD/BCD process in treating PCP, dioxins, and furans to levels below those stated in the ROD.

- Determine if treatment residuals (air, water, oil) also meet appropriate clean-up levels.

- Develop information to evaluate the cost-effectiveness of MTTD/BCD for future Superfund projects, RCRA corrective actions, or voluntary remediation projects.

The Koppers site in Morrisville was a former wood preserving operation utilizing the Cellon process, which involves pressure treating of wood with PCP and subsequent steaming for wood preservation. The rinsate was placed in unlined lagoons where leaching into the soil occurred. Contaminants included PCP in excess of 10,000 ppm, and lesser concentrations of dioxins and furans.

Following completion of bench-scale testing and approval of the Quality Assurance Project Plan, an MTTD/BCD system capable of handling 0.25 - .5 TPH throughput was mobilized. The equipment was placed into a portable containment pad with approximate dimensions of 60' x 80'. Soil was excavated from the documented "hot spots" on the site and hand screened to less than 0.5 inches and placed in 55 gallon drums for transport to the processing area.

Results

One test run was completed per day during the demonstration. The operating parameters were recorded (drum weight, reagent dosage, retention time, operating temperature, contaminant concentration, etc.) throughout the demonstration. Each of seven total test runs lasted between four and eight hours and processed 2,000 to 4,000 pounds of feed per run[7]. Samples of treated solids, air, water, and organics were collected during

each run. Preliminary results look encouraging and appear to be similar to the bench-scale treatability results. Final results will be reported in the USEPA's SITE Demonstration Summary Report expected to be released in 1994.

Bench scale analytical testing on the contaminated soils indicated that the MTTD/BCD process was very successful in dechlorinating the PCP, dioxins and furans. As indicated in Table 1, destruction and removal efficiencies of 99.99% or greater were achieved in most cases[6]. These results indicate that the treatment standards of 95 ppm for PCP and 7 ppb for dioxins specified in the Morrisville, North Carolina ROD will be easily met.

Table 1
Treatability Test Results For A Soil Sample From The Koppers Site, Morrisville, NC

Contaminant	Feed Soil	Soil Following 800°F Treatment	Percent Removal	Treatment Standard
Chlorophenol (CP), PPM				
Total Tri-CP	90	0.001	99.99	
Total Tetra-CP	750	0.0005	99.999	
Penta-CP	35,000	0.0006	99.9999	95
Dioxins, PPB				
Total TCDDs	1.46	0.121	29.489	7.0*
Total PeCDDs	11.40	0.129	90.373	
Total HxCDDs	726.00	0.173	99.349	
Total HpCDDs	4810.00	0.122	99.978	
OCDD	31.20	0.0945	99.997	
Furans, PPB				
Total TCDFs	3.5	ND (<0.0007)	>99.832	
Total PeCDFs	40.9	ND (<0.0012)	>99.975	
Total HxCDFs	529.0	ND (<0.0016)	>99.997	
Total HpCDFs	3020.0	ND (<0.0030)	>99.999	
OCDF	3540.0	ND (<0.0057)	>99.999	

* 2,3,7,8 TCDD equivalent

Based on the operating data and equipment efficiency monitored during the USEPA SITE Demonstration, ETG/SRS have developed preliminary cost estimates for the MTTD/BCD system of $150 - $250/feed ton for sites containing more than 10,000 yd^3 of contaminated soils. Systems capable of handling 5-15 TPH are currently under construction and are available immediately after a 2-3 month (typical) treatability study. Treatability bench and/or pilot-scale studies typically cost $20,000 - $200,000. System economics are determined by a number of factors including volume and concentrations of contaminated material, required clean-up standards, utility availability, physical nature of contaminated wastes (necessity of pre-treatment), and permitting requirements. Due to the varying nature of these factors, treatability studies are strongly recommended.

Conclusions

Medium Temperature Thermal Desorption (MTTD) is a proven commercial process to physically separate organic contaminants (VOCs, SVOCs, Coal Tar, etc.) from contaminated media (soil, process sludges) by indirect heating. The low volume of off-gas results in condensation and ultimate recycling of the organic contaminants. The technology has proven to be technically and economically effective at a number of oil refining and chemical industry sites for soil and process sludge treatment.

MTTD can be combined with Base Catalyzed Decomposition (BCD) to chemically dechlorinate high-hazard organics such as chlorinated dibenzodioxins and furans, polychlorinated biphenyls (PCBs), pentachlorophenol (PCP), and pesticides/herbicides (2,4-D 2,4,5-T, silvex, DDT, DDD, lindane, etc.). Bench-scale testing indicates destruction and removal efficiencies in excess of 99.9% can be achieved. For a site containing greater than 10,000 yd^3 of contaminated soils, the estimated remediation costs of $150 - $250/ton of feed are applicable for a 5-15 TPH system.

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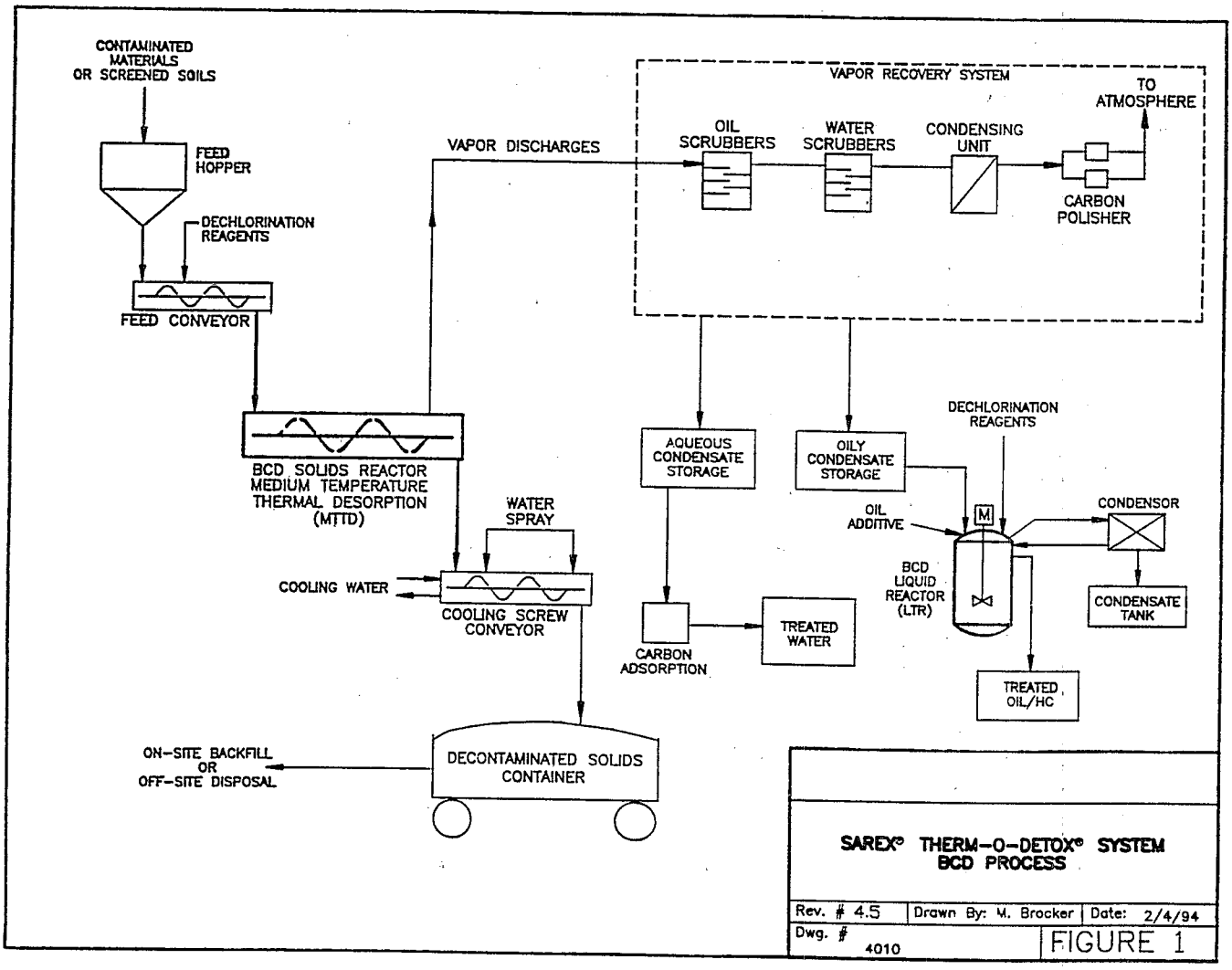

RADIATION PROCESSING OF GROUNDWATER FOR CHLORINATED SOLVENTS WITH AND WITHOUT COMBINATION OF OZONE

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INTRODUCTION

Of the various organic contaminants found in groundwater the widely used industrial solvents trichloroethylene (TCE) and perchloroethylene (PCE) are the most common. However, to a minor extent also 1,1,1-trichloroethane and its decomposition product 1,1-dichloroethylene (DCE) have been detected. The conventional methods for the treatment of such polluted water, i.e. adsorption onto activated carbon do remove the contaminants from the water but they do not destroy them. This might often result in a mere displacement of the problem from the water to the carbon.

An attractive solution of this problem offers the mineralization of the contaminants by oxidation directly in water because such a process remediates the water and disposes of the contaminants in a single step. At present on a technical scale the only oxidant for trace amounts of these chlorinated compounds in water is the hydroxy free radical (OH).

Hydroxy free radicals are generated in water by the so-called Advanced Oxidation Processes (AOPs). Application on a technical scale has been reported for the combinations ozone/UV, ozone/hydrogen peroxide and hydrogen peroxide/UV. All these AOPs have in common that the OH originates from **one** single source only (ozone or hydrogen peroxide). An AOP based on the combination of ozone with ionizing radiation generates the hydroxy free radicals from **two** sources:

- directly from the water to be remediated by water radiolysis and
- from ozone decomposition promoted by the reducing species formed during water radiolysis.

The resulting OH concentration is significantly higher than those of the above mentioned AOPs. The combination ozone/electron beam irradiation, therefore, is especially apt for the remediation of groundwater containing pollutants in trace amounts only - a situation which often occurs with chlorinated solvents.

METHODOLOGY

The ionisation and excitation of water molecules by high-energy radiation are known to result in the formation of free radical and molecular species. For low level contamination of groundwater (< 1 mg.dm^{-3}) just the highly reactive free radical species OH, e^- and H are of interest for pollutant decomposition. The pollutants compete for the free radical species with the natural solutes and the oxygen contained in the water.

In air-saturated groundwater containing the chlorinated compounds as micropollutants most of the solvated electrons e^- and the hydrogen radicals H are scavenged by the oxygen present forming superoxide radical anion and hydroperoxy radical HO_2, respectively. The latter is in an acid-base equilibrium with the superoxide anion ($p_K = 4.7$). At the usual pH-values of groundwater the equilibrium is shifted towards the superoxide anion i.e. most of the reducing species are converted into the superoxide anion which is a rather inert radical. It certainly does not react with PCE, TCE, DCE and 1,1,1-trichloroethane. Its probable fate is its disproportionation into H_2O_2 and O_2. Roughly speaking only OH remains as active species for pollutant decomposition in irradiated groundwater. In other words more than 50 % of the radiation energy is wasted.

Under the conditions given and as long as the nitrate concentration is low only bicarbonate ions are serious competitors for OH according to their high concentration. For nitrate concentrations higher than about a few ppm scavenging of solvated electrons and subsequent formation of nitrite ions cannot be longer ignored. Nitrite scavenges OH radicals very effectively and considerably worsens the conditions of pollutant decomposition. Moreover, nitrite itself belongs to hazardous substances in drinking water. Consequently a process for groundwater clean-up based on irradiation alone can never be applied for drinking water production because of exceeding the limit values of nitrite as well as hydrogen peroxide in drinking water.

The situation is completely changed when the water irradiation is performed in the presence of ozone: On the one hand, ozone is known to oxidize nitrite to nitrate very fast; on the other hand, ozone also reacts with hydrogen peroxide. Therefore, a residual ozone concentration present after the irradiation indicates that inadmissible amounts of nitrite as well as hydrogen peroxide do not exist.

Moreover, ozone acts as additional OH source as it decomposes into OH; the decomposition is promoted by the reducing species formed during water radiolysis. In this way almost the whole radiation energy is used for OH generation.

Ozone is added as aqueous solution (figure 1): the O_2/O_3 mixture from the ozone-generator is mixed with purified water at elevated pressure. In the gas seperator the excess O_2 is removed. The ozonewater is then mixed with the polluted groundwater and irradiated with fast electrons.

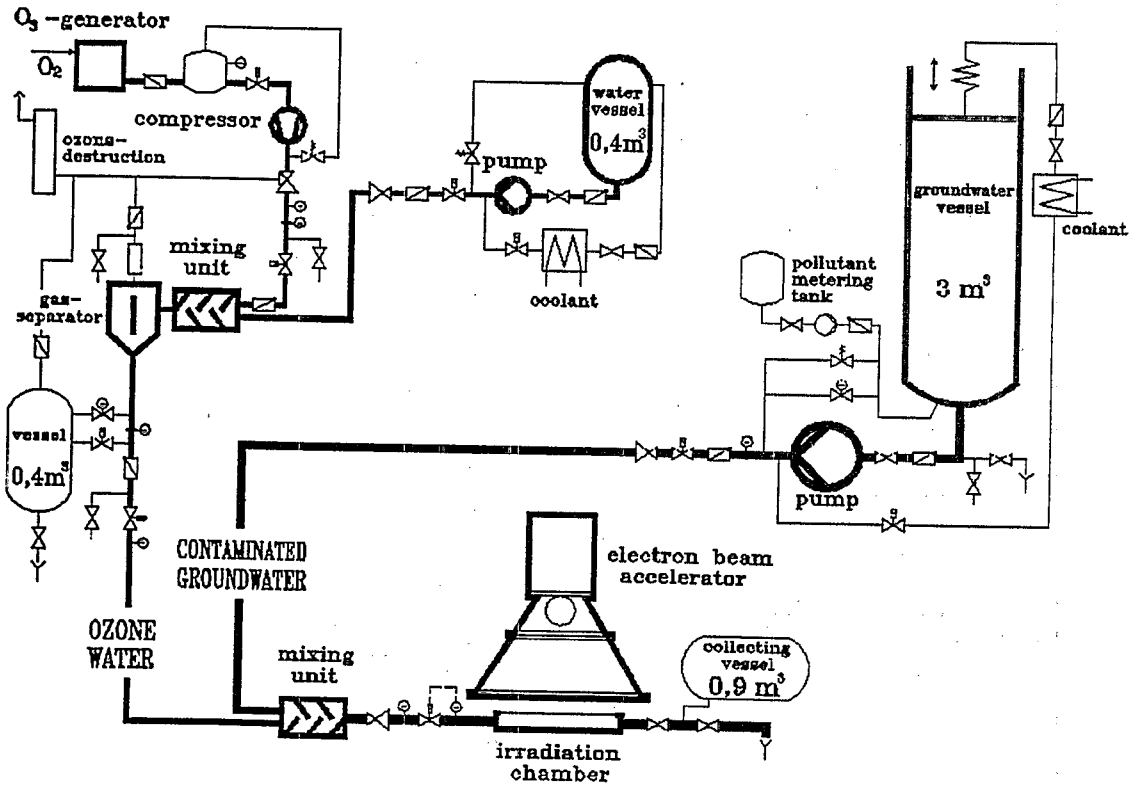

Figure 1. Prototype for continuous ozone/electron beam irradiation treatment of water.

RESULTS

In a water work south of Vienna groundwater contaminated with about 50 ppb PCE and about 5 ppb TCE is purified by activated carbon filtration. The plant flow is 300 dm^3/s (about 6.9 million gallons a day), the total capital cost amounted to 2.5 million US dollar, the operating cost are expected to be around 4-5 cents per m^3 treated water.

Experiments applied with this groundwater have demonstrated that 250 Gy in combination with 3 ppm initial ozone concentration reduce the PCE below 10 ppb (see figure 2) and TCE below 1 ppb. Based on these results an appropriate ozone/electron beam facility would amount to about 2.35 million US dollar with operating cost of about 8 cents per m^3 treated water.

Among the chlorinated ethylenes PCE is most resistent against OH attack, its decomposition need relatively high radiation doses together with relatively high ozone demand, therefore. On the other hand adsorption onto activated carbon is best for PCE. That means worst conditions of oxidation have to compete with best conditions of adsorption - and this is reflected in the cost. However, the advantages in improved water quality and reduced environmental pollution may outweigh purely economic considerations in some areas.

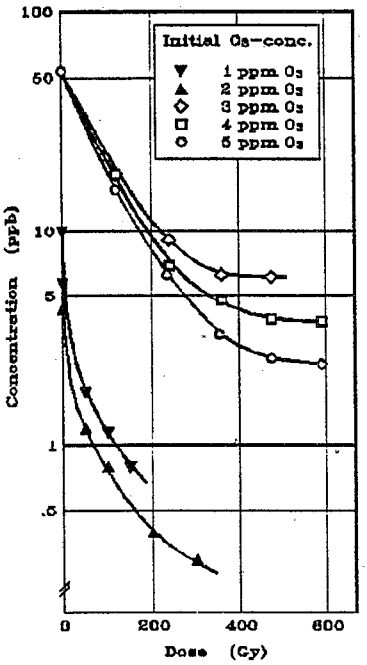

Figure 2.
Decomposition of PCE (◇,□,○) and DCE (▼,▲), respectively in groundwater (297 ppm bicarbonate, 18 ppm nitrate, 1 ppm DOC) by ozone/electron beam irradiation treatment.

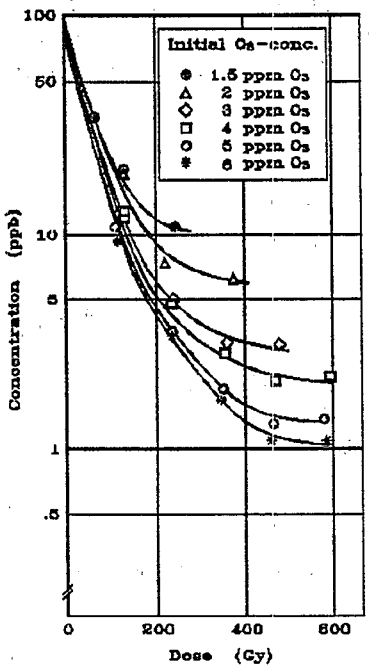

Figure 3.
Decomposition of TCE in groundwater (402 ppm bicarbonate, 30 ppm nitrate, 0.5 ppm DOC) by ozone/electron beam irradiation treatment.

The unit of the radiation dose is Gray (Gy). 1Gy = 1 $J.kg^{-1}$

Also contained in figure 2 is the decomposition of 10 ppb DCE in relation to radiation dose and initial ozone concentration. DCE is the most toxic compound among the chlorinated ethylenes mentioned; its limit concentration in potable water is restricted to 0.3 ppb, therefore. Regarding the competion conditions between activated carbon and oxidation the inverse situation to PCE is valid for DCE: easy to oxidize, very bad to adsorb. Together with the required low limit concentration the oxidation should be also economically the better alternative.

In the drinking water works of Niederrohrdorf near Zürich, Switzerland an ozone/UV-combination system for groundwater remediation contaminated with about 100 ppb TCE was installed by WEDECO, Germany. The groundwater contains about 402 ppm bicarbonate, 30 ppm nitrate and about 0.5 ppm DOC. The plant flow is 180 m^3/h, for a TCE reduction just below 10 ppb TCE 1.3 kg ozone and 7.8 kW UVC are needed.

TABLE 1. COST EVALUATION OZONE/UV VERSUS OZONE/ELECTRON BEAM (FOR GROUNDWATER REMEDIATION)

Process and Cost Parameter for 810 m^3/h = 500 million gallons/day	O_3/UV radiation	O_3/electrons
Radiation source	UV-medium pressure 35 kW UVC	800 kV-accelerator 67.5 kW
Energy consumption	234 kWh	135 kWh
O_3-demand	5.85 kg/h	2.25 kg/h
O_2-consumption	50 m^3/h	20 m^3/h
Energy consumption	50 kWh	20 kWh
Energy (total)	284 kWh	155 kWh
Capital requirement		
Radiation source	675 000 $	1 700 000 $
Ozone generator	420 000 $	186 000 $
Capital cost (9.5 % interest ave., 10 years)	175 000 $/yr	302 000 $/yr
Hourly charge (8500 h/yr)	21 $/h	36 $/h
Variable cost		
Electric power (15 ¢/kWh)	42.6 $/h	23.1 $/h
Oxygen (45 ¢/m^3)	22.5 $/h	9.0 $/h
Total cost	**86 $/h**	**68 $/h**

Figure 3 shows the decomposition of about 100 ppb TCE in simulated Niederrohrdorf water by ozone/electron beam irradiation treatment as a function of the radiation dose and the initial ozone concentration. In contrary to the ozone/UV-combination which needs about 6-7 ppm initial ozone concentration for a TCE reduction just below 10 ppb the ozone/electron beam treatment meets this goal already with about 2 ppm initial ozone concentration. Using 5-6 ppm initial ozone concentration

in the ozone/electron beam combination would result in a residual TCE concentration near 1 ppb, almost one order of magnitude better than the ozone/UV-combination. Both results are clear indications for the higher OH free radical concentrations yielded by the ozone/electron beam combination.

The cost comparison of the two processes is shown in table 1 and is based on the following considerations. Both processes use ozone and radiation, both processes produce ozone water with a high ozone concentration and add it to the polluted groundwater before irradiation. Maintaining that in both processes the ozone water production can be performed exactly in the same way reduces the cost comparison of the two processes to a cost comparison of the radiation sources and the ozone production. According to the capital cost of an electron beam accelerator the ozone/electron beam process should be preferably applied to high throughput capacities. Therefore, a throughput of about 5 million gallons a day was chosen for the evaluation.

As the capital cost for an electron beam accelerator are rather high - in the present case 3 times more than the UV-lamps - the hourly charges are $ 36 to $ 21 only. However, the operating cost show the opposite situation according to the lower ozone demand and the lower energy consumption of the accelerator. As a consequence the resulting total cost are in favour of the ozone/electron beam process!

CONCLUSIONS

The combination ozone/electron beam irradiation is unique among the AOPs because of two outstanding features: (1) the energy absorption proceeds via the water to be remediated initiating (2) two different OH generation processes simultaneously. Compared to the other AOPs a higher OH concentration results which causes a lower residual pollutant concentration (when the same ozone concentration is considered) or less ozone consumption (when the same residual pollutant level is considered). Moreover, a high efficacy at low pollutant levels exists bringing about throughput capacities of 5-6 million gallons a day and more at competitive cost. Accordingly the ozone/electron beam irradiation process is especially apt for the remediation of low level contaminated groundwater.

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THE OXYJET TECHNOLOGY: AN INNOVATIVE APPROACH FOR THE WET OXIDATION OF HAZARDOUS WASTES

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INTRODUCTION

The potentially harmful effects of organic substances present in many hazardous wastes have generated interested in establishing effective treatment technologies for these wastes. Technologies used for the treatment of such wastes should preferably accomplish transformation of the hazardous components to innocuous end products.

Wet Oxidation is an attractive alternative for the treatment of hazardous wastes with relatively high nonbiodegradable organic material content (COD ranging from 10 to 200 g/l). This treatment consists of oxidizing organic and inorganic compounds in an aqueous solution by means of molecular oxygen at elevated pressures and temperatures. The temperature in the reactor depends on the nature of the organic compounds to be destroyed and the degree of oxidation required, and it ranges from 175 to 325 °C. The total pressure to be applied (2 to 20 MPa) is the sum of the steam pressure and the necessary oxygen pressure to reach a sufficient concentration of oxygen in the aqueous phase (2,7). The oxidation end products may be inorganic salts, simpler forms of biodegradable compounds (mainly consist of low molecular carboxylic acids) or may lead to complete oxidation to carbon dioxide and water (5,8,14,15).

Wet oxidation is an established technology which has been demonstrated to be effective in treating a wide variety of hazardous organics contained wastes (6). It has been used extensively for the treatment of: hazardous waste (chemical and pharma-chemical industry), landfill leachate, paper-mill black liquor, petrochemical, activated carbon regeneration, cyanide wastewaters, herbicide and pesticide wastes, etc. (1,4,10,13).

In the conventional wet oxidation technologies, like ZIMPRO (16, 17) or WETOX (12) processes, the mass transfer is often the controlling step (depending on the relative mass transfer and intrinsic kinetic rates). This fact besides the relatively moderate temperatures of wet oxidation results in long reaction times (from 30 to 60 minutes).

Oxyjet technology is an innovative wet oxidation system based on jet-mixers that was initially developed by Chornet (3). The Oxyjet process consists of a high interfacial area contactor placed at the entrance of a tubular reactor, followed by a secondary spray chamber where additional oxidant (i.e. O_3 or H_2O_2) can complete the oxidation when needed. One of the special features of the Jet-Mixer placed in Oxyjet is contacting gas and liquid in such a way that the kinetic energy of the gas is used to disperse the liquid into fine droplets. With this configuration the gas-liquid interfacial area is enhanced, the mass transfer resistance is minimized and the oxidation process is fully governed by the kinetics of chemical reactions. The net effect is that the residence times required in the Oxyjet system are smaller than in conventional bubbling or stirring technologies (8).

This new approach was tested in a pilot-scale plant. The treatment capacity of this experimental unit ranged from 0.1 to 0.3 l/min ($1.7 \cdot 10^{-6}$ - $5 \cdot 10^{-6}$ m^3/s) of aqueous wastes. The experiments performed in the pilot plant proved that wet oxidation process using compact jet-mixers reactors is a promising technology for the treatment of organic industrial wastes. It should be noted that in these experiments,

the same reaction extent was attained with retention times about ten times lower than those required in conventional wet oxidation technologies (9).

An Oxyjet Demonstration Unit has been designed and constructed. Due to the special characteristics of the Oxyjet technology, this demonstration unit is a necessary previous step to a full scale development of this process in order to establish the most favourable conditions, select the most suitable equipment and materials and assess the reliability of this new approach.

The purpose of this paper is to illustrate the application of the Oxyjet technology to treatment of a high strength industrial waste. This is done through the review of the main engineering feature and economic evaluation of the ODP, currently in operation, for the treatment of a problem waste stream produced in an existing chemical facility.

METHODOLOGY

The ODP has been installed in Sant Celoni's site (Barcelona, Spain) and has a treatment capacity of 3 l/min of waste ($50 \cdot 10^{-6}$ m^3/s), with organic loads ranging from 20,000 to 200,000 mg/l of COD. It is a compact industrial plant with a modular and versatile structure. This implies that the ODP has been designed for wide working conditions depending on the specific characteristics of the organic aqueous waste to be treated. The Oxyjet process consists of four zones: 1) feeding an organic waste and oxygen to the reaction system, 2) mixing of both streams, 3) reaction in an aqueous phase between oxygen and organic compounds, and 4) separation of gas and liquid phases. The principles of operation can be best understood by referring to the Oxyjet process diagram. Figure 1 shows this process flowsheet.

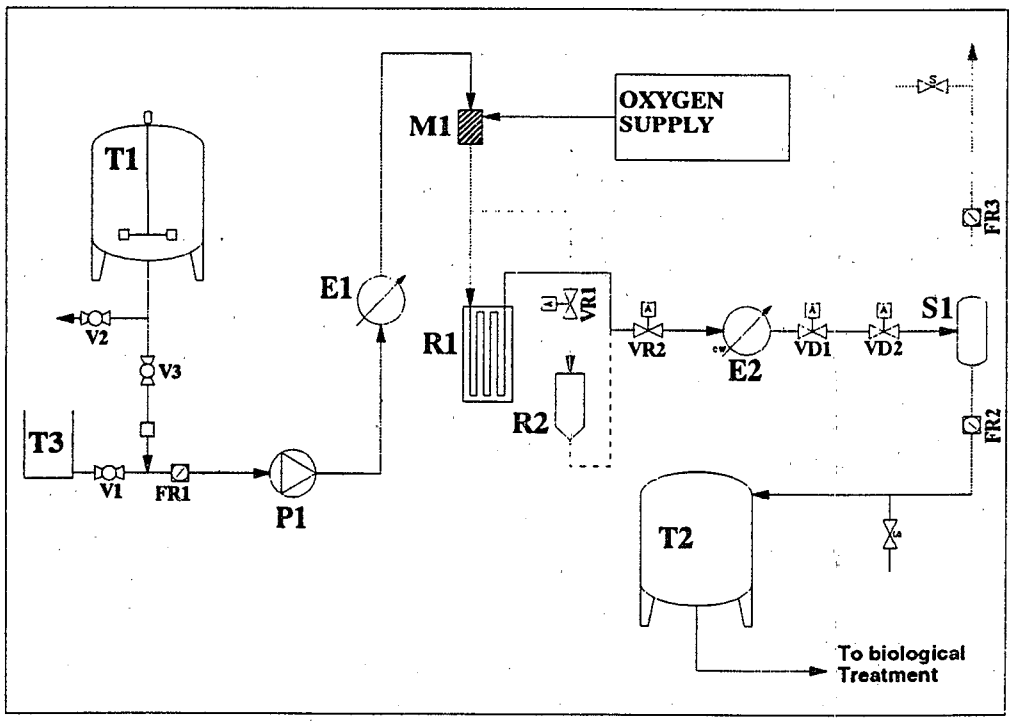

Fig. 1 Diagram process of the Oxyjet Demonstration Plant

Hazardous waste, as an aqueous solution, is fed to the Oxyjet process from an agitated storage tank (T1) through a high pressure diaphragm pump (P1). The pump has a nominal capacity of 180 l/h ($5 \cdot 10^{-5}$ m^3/s), and a maximum discharge pressure of 20 MPa. The pressurized liquid passes through a heat exchanger (E1) which preheats it to a maximum of 260 °C using a hot organic heat-transfer

fluid. The heat exchanger is designed with one pass on the shell and four passes on the tube side. The heat-transfer fluid flows through the shell side and waste in the tube side.

At the entrance of the Jet-Mixer (M1), the incoming preheated liquid encounters the injected oxygen. One special feature of the Jet-Mixer is that the kinetic energy of the gas is used to disperse the liquid into fine droplets. The technological aspects of jet-mixers devices were initially described in previous publications (11,3). The Jet-Mixer used in this work is an advanced version of the same principle.

The two-phase mist formed at the jet mixers device enters a tubular reactor (R1). In the reactor, temperatures are increased to needed levels (between 200 °C and 350 °C) through both indirect heat exchange with organic heat-transfer fluid and the heat released exothermically by the oxidation reactions. For aqueous wastes having COD values greater than 10 to 15 g/l, additional external energy is only required during start-up. The tubular reactor consist of a shell, 0.8 m in width and 1.6 m high. Three concentric coils are placed inside the shell. The three coils have a total length of 174 m. The heat-transfer fluid flows through the shell side and the two-phase mist moves inside coils. This configuration gives operational flexibility to the reactor system, since coils can be easily added or removed. The tubular reactor had to a back-pressure regulating valve (VR1). The pressure drop through this valve ranges from 3.2 to 15.2 MPa.

The hot oxidized liquid waste is cooled, after valve (VR1), in a heat exchanger (E3). The pressure is dropped to atmospheric by two control valves (VD1 and VD2) and the liquid and non-condensible gases are disengaged in the separator drum (S1) and discharged separately. The treated aqueous waste is collected in a storage tank (T2). The residual gas, mainly composed of oxygen added in excess, carbon dioxide and water, is released, in the ODP, to the atmosphere.

Besides the equipment described above, the Oxyjet system has as auxiliary facilities the oxygen supply plant and the heat transfer circuit.

Oxygen Supply Plant. Liquid oxygen is received and stored in a low pressure (0,8 MPa) cryogenic tank with a capacity of 3000 l. From this tank, oxygen is pumped with a positive-displacement pump through a vaporizer (atmospheric heat is used to vaporize the oxygen) and introduced into a high pressure (20 MPa) receiver with a capacity of 840 Nm^3/h. Oxygen is injected in the Jet-Mixer at specific flowrates and pressures, which are controlled by a control loop composed of: a PID controller, a mass-flow meter, and a control valve.

Heat Transfer Circuit. The heat needed to preheat the feed and trigger the oxidation is transferred via a synthetic, organic heat-transfer fluid which, is moved by forced circulation with a centrifugal pump, to the heat exchanger (E1) and reactor (R1). The fluid is heated by seven electrical resistances of 20 kW (total electric power of 140 kW). During operation, when excess of heat derived from the reaction, must be removed the thermal fluid is cooled by a water-cooler heat exchanger. All pipes and devices that compose the heat transfer circuit are adequately insulated against heat losses.

Instrumentation and Control. The temperatures are measured eleven points of the oxidation process by temperature transmitters inserted into thermowells immersed in the aqueous phase. Eight gauge pressure transmitters have been installed to measure and control the pressure in several zones of the ODP. Flow rates for feed and treated aqueous waste are measured using magnetic flowmeters. All these parameters are measured on-line and recorded in a data acquisition system.

Laboratory Support. During operation, direct control is provided by the system instrumentation. COD of feed and effluent are determined in-situ. Other waste analysis such as TOC and pH are also performed periodically. Additional state-of-the-art analyses include: gas chromatography using a mass selective detector (GC/MS), gas chromatography using with a flame ionization detector (GC/FID), gas chromatography using with a thermic conductivity detector (GC/TCD) and high performance liquid chromatography using with a UV detector.

RESULTS

The ODP was designed and constructed in 1992. It was located in Sant Celoni (Catalonia, Spain) at an industrial site in January 1993 and started-up in February 1993. Until September 1993, the ODP has been operated for 250 hours with a high-load phenolic waste generated in a phenolic resin polymerization unit. The characteristics of the phenolic waste stream are:

- COD ranging from 120,000 to 170,000 mg/l
- Temperature about 20 °C
- pH= 9
- Average waste stream generation rate 10 m^3/week (2 m^3/hour)

This hazardous waste was chosen because its treatment by means of existing biological processes is not possible due to its high organic material concentration and toxicity. Moreover, its incineration is not cost-effective due to its high water content. Wet oxidation is a suitable option because the biological inhibition is reduced and energy recovery from the relatively high COD waste is feasible. Experimental work ODP conditions and results are presented in Table 1. A significant amount (>90%) of the initial COD can be eliminated at the most severe operating conditions (i.e. temperatures higher than 305°C and pressures greater than 16 MPa). At lower severities (i.e. temperatures lower than 300 °C and pressures of 15 MPa), the COD reduction ranges from 35 to 70%. A very significant reduction (more than 99%) of the initial organic compounds (expressed as phenol) is achieved during the wet oxidation process at the severities studied.

The carbon conversion results observed during aqueous oxidation are in agreement with the mechanisms of oxidation in liquid phase proposed in the literature (5,14,15). Basically, the wet oxidation has been found to convert large molecules (initial phenols) to carbon dioxide (which was confirmed by GC/TCD analysis of the gas samples) and smaller oxygenated organic molecules (which were detected by HPLC/UV analysis of the liquid phase). These smaller organic species remaining in solution consist of low molecular carboxylic acids (such as formic, acetic, oxalic, etc.) which are slowly oxidized. Therefore the biodegradability of the feed waste is significantly increased during the wet oxidation process.

It should be noted that in the experiments carried out using the ODP, the residence time is comprised between 1 and 10 minutes, which is far below that of conventional wet oxydation systems.

TABLE 1 EXPERIMENTAL DATA OF THE OXYJET DEMONSTRATION UNIT

F_{liquid} (l/h)	F_{gas} (l/min)	$P_{reactor}$ (MPa)	$T_{reactor}$ (ºC)	COD_i (mg/l)	COD_f (mg/l)	COD_r (%)	$C_6H_5OH_i$ (mg/l)	$C_6H_5OH_f$ (mg/l)	rC_6H_5OH (%)
124	354	15.1	298	145000	67500	53.4	5000	0.8	100.0
124	445	15.9	307	120000	78000	35.0	4800	0.6	100.0
124	426	16.0	308	120000	59000	50.8	4800	0.6	100.0
128	438	16.0	317	168700	13900	91.8	12500	12.0	99.9
128	434	16.0	318	168700	14300	91.5	12500	14.5	99.9
129	434	17.0	320	168700	15000	91.1	12500	4.0	100.0
124	455	15.9	299	168700	110000	34.8	12500	2.0	100.0
124	445	16.0	319	168700	14000	91.7	14000	9.0	99.9
124	450	16.0	317	168700	11500	93.2	14000	8	100.0
124	450	16.0	321	168700	15600	90.8	14000	10	100.0
124	430	16.0	323	168700	12600	92.5	14000	8	100.0
125	435	16.5	308	168700	45000	73.3	6000	2	100.0
125	435	16.5	318	168700	70000	58.5	6000	2	100.0
124	435	16.5	323	168700	15750	90.7	6000	8	100.0
124	435	16.5	312	168700	13000	92.3	6000	3	100.0
126	450	15.0	317	168700	13400	92.1	6000	60	99.0
127	450	15.0	304	168700	12000	92.9	6000	40	99.3

The total purchased equipment cost (PEC) of the demonstration plant installed in Sant Celoni was of 214,600 USD. It should be noted that the oxygen supply plant and heat transfer system, taken together, account for almost 70% of the total PEC of $214,600. Cost of jet mixer and tubular reactor represent only 10% of the PEC. The total capital investment for the ODP is 347,000 USD. Capital investment was divided in direct costs, indirect costs and working capital both were estimated based on real data of the Oxyjet plant.

Operation costs of the demonstration unit are function of the combination of temperature, residance time and oxygen needed for the oxidation, which is related to the organics present in the aqueous waste. In our case the treatment cost of the waste has range from 6.5 to 19.5 PTA/l (0,05 to 0,15 USD/l). It should be pointed out that the cost to incinerate these wastes ranges from 40 to 60 PTA/l (0.31-0.46 USD/l). In a commercial unit, based on the experience ganed during the demonstration step, costs lower than those mentioned would be achieved.

Investment and operating costs are given on the basis of December 1992 costs, at the exchange rate of 1 USD equal to 130 PTA.

CONCLUSIONS

A demonstration unit based on the Oxyjet technology has been designed and constructed. It is currently in operation and has a capacity to treat a wastewater rate comprised between 1 to 3 l/min ($17 \cdot 10^{-6}$ to $50 \cdot 10^{-6}$ m^3/s). In the design of the ODP, the Jet-Mixer and the tubular reactor present the greatest degree of uncertainty, particularly because they involves a two-phase reaction where diffusion and mixing can have a major role in the determining overall reaction rate. Therefore, it has been necessary to install operational flexibility into the reactor system (i.e. the tubular reactor has been designed so that reactors coils can be easily added or removed).

Moreover, the auxiliary systems, i.e the preheater and the thermal fluid circuits have been designed with sufficient spare capacity in order to explore a wide range of oxidation conditions.

In addition to the need for flexibility and integrated design, it must be remembered that a demonstration plant is a data gathering device. Therefore, the ODP has been equipped with adequate instrumentation, laboratory support, and sample gathering devices so that all aspects of the process can be confirmed.

The results obtained with nonbiodegradable phenolic wastewater have shown that under the ODP configuration at the most severe conditions (temperatures around 310 °C, pressures about 16 MPa and with about 5 minutes as reaction times), it is possible to achieve 90% reduction of COD and 99% reduction of initial compounds (expressed as total phenols).

In summary, this paper shows that for those wastes which are too diluted to be incinerated economically and are not biotreatable, Oxyjet process is a feasible and economically attractive method to reduce oxygen demand and to increase the biodegradability of hazardous wastes.

ACKNOWLEDGEMENT

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FULL-SCALE APPLICATION OF ADVANCED PHOTOCHEMICAL OXIDATION TO GROUNDWATER TREATMENT

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INTRODUCTION

Photochemical oxidation of organic contaminants in water has been studied since the early 1900s. However, commercial photochemical oxidation systems became available as recently as the early 1980s. The technology has been advancing rapidly since that time due to aggressive research by several independent companies. To date, well over one hundred treatment processes have incorporated photochemical oxidation equipment into the final treatment design. Full-scale applications range from groundwater remediation at Superfund sites to treatment of wastewater for reuse, and include organic contaminant destruction in landfill leachates, tank bottoms, drinking water, stream condensate and chemical process streams. A wide variety of organic contaminants have been destroyed including volatile organic compounds (VOCs), semi-VOCs, aromatics, alcohols, ketones, aldehydes, phenols, ethers, phthalates, glycols, pesticides, ordnance compounds, dioxins, PCBs, PAHs, COD, BOD, TOC and most other forms of organic carbon. Photochemical oxidation is most effective for contaminant concentrations below 500 mg/l, and is capable of destruction to below the lowest detection limit.

A common application of photochemical oxidation is groundwater remediation. While the type of contaminants varies between sites, the organic matrix often includes halogenated VOCs. Therefore, enhanced destruction of these compounds has been the primary driving force behind the advances in the leading commercial photochemical oxidation system, the **perox-pure™** Process developed by Vulcan Peroxidation Systems, Inc. Improvements in equipment and process implementation during the last ten years have resulted in as much as a 20 fold increase in the full-scale destruction rates for some contaminants.

The latest generation of the **perox-pure™** full-scale equipment was evaluated by the EPA during a SITE demonstration in September 1992. Although more than eighty full-scale **perox-pure™** systems have been installed in the United States, Canada, Europe and the Caribbean, the SITE demonstration afforded the opportunity for the EPA to verify treatment results and evaluate all aspects of the **perox-pure™** Process. The results of the SITE demonstration are provided below along with treatment cost projections.

METHODOLOGY

The **perox-pure™** photochemical oxidation process utilizes high intensity broad-band ultraviolet (UV) radiation and hydrogen peroxide (H_2O_2) to photolyze and oxidize organic compounds present in aqueous media. Hydroxyl radicals, the active oxidant, are produced by the direct photolysis of H_2O_2. The **perox-pure™** UV lamps are designed to produce a high intensity peak at 254 nm, the wavelength which results in the highest quantum yield of hydroxyl radicals. The hydroxyl radicals attack organic molecules resulting in dissociation. The reaction is aided by the direct photolysis of the organic molecule by the UV light which breaks or weakens certain atomic bonds making the molecule more susceptible to oxidation. With sufficient oxidation and exposure to UV energy, the reaction by-products are carbon dioxide and water. There are no air emissions or solid by-products formed by the **perox-pure™** Process. Neither are there toxic or hazardous reaction products formed by the recombination of molecules as can occur in high temperature/high pressure or air-phase oxidation systems.

A **perox-pure™** Model SSB-30R full-scale system was used during the SITE demonstration. This unit was chosen because it was small in size (5-feet long by 3-feet wide by 7-feet high), provided an extended oxidation time at the planned flow rate of 10 gpm, yet had a hydraulic capacity of several hundred gpm so that higher flows could be evaluated if desired. Ancillary equipment provided for the demonstration included a H_2O_2 storage and feed unit, and acid/caustic feed systems for in-line pH adjustment and monitoring.

The full-scale **perox-pure™** equipment is a single skid mounted unit consisting of an oxidation chamber, an electrical enclosure and a control panel. In the case of the SSB-30R, the oxidation chamber is made up of six horizontal sub-chambers, each housing one UV lamp inside a high-purity quartz tube. The water to be treated enters the lowest sub-chamber and flows through the annular space between the chamber wall and the quartz tube where it is exposed to the UV light. The water passes through each of the identical sub-chamber in series. H_2O_2 is added at the influent to the first sub-chamber, and can be added between each sub-chamber to provide a constant oxidant supply throughout the oxidation chamber.

In photochemical oxidation reactors, the UV density, surface area to volume ratio and turbulent mixing are of paramount importance. The oxidation chamber of the latest generation **perox-pure™** equipment, which was used during the SITE demonstration, has been designed to optimize the parameters listed above. Various UV lamp types and sub-chamber configurations are available to address the needs of the different contaminant and water quality matrices. The SSB-30R chosen for the SITE demonstration has six sub-chambers with one 5-kilowatt UV lamp inside. The chamber configuration is ideal for treatment of low level VOCs in groundwater and produces effective turbulent mixing at a minimum flow rate of 5 gpm. The design also allows for flexibility in power turn-down capability and multi-point sampling while maintaining consistent UV density.

Oxidation reactions can be affected by factors other than the UV source and reactor design. Process variables include contaminant type and concentration, water quality, pH of the water, oxidant dosage and fouling of the quartz tubes. In most cases, bench or pilot-scale testing is required to evaluate these parameters and provide a reliable full-scale system design. The majority of these variables were evaluated during the SITE demonstration.

RESULTS

The SITE demonstration with the full-scale **perox-pure™** System was conducted at the Lawrence Livermore National Laboratories (LLNL) Site 300 Testing Facilities. The groundwater selected for the study was contaminated with approximately 1000 μg/l of trichloroethene (TCE) and 100 μg/l of tetrachloroethene (PCE). A detailed description of the demonstration can be found elsewhere[1].

Fourteen tests were conducted with the **perox-pure™** equipment to evaluate the effects of pH adjustment, H_2O_2 dosage, and quartz tube fouling. The best treatment results were achieved without pH adjustment (pH 8.0) using a H_2O_2 dosage of 40 mg/l. Higher H_2O_2 dosages reduced the treatment efficiency of the TCE and PCE. The lower pH values did not effect treatment. The results from the best test (Test 8) are shown in Table 1 below. As shown, the contaminants were destroyed to below the analytical detection limit by fist sample time. It is likely that similar or improved contaminant destruction rates could be achieved using a H_2O_2 dosage lower than 40 mg/l.

Testing was also conducted on the groundwater after spiking with approximately 150 μg/l each of chloroform, 1,1-dichloroethane (DCA) and 1,1,1-trichloroethane (TCA). The pH and H_2O_2 dosages were not optimized for the spiked water, but were selected based on field data available during the demonstration from the earlier tests on the unspiked groundwater. Accordingly, pH adjustment to 5 was used along with a total H_2O_2 dosage of approximately 85 mg/l. The treatment results for the contaminants spiked into the groundwater are shown in Table 1 below. As shown, the contaminant destruction proceeds rapidly towards the detection limit. Destruction of the contaminants to below the detection limit can be achieved with additional oxidation time.

Other findings from the SITE demonstration were: (1) the **perox-pure™** System met California drinking water action levels (CADWAL) and federal drinking water maximum contaminant levels for all of the contaminants tested at the 95% confidence level, and (2) the automatic quartz tube wiper employed by the **perox-pure™** System was effective in keeping the tubes clean for consistently high performance.

TABLE 1. **perox-pure™** TREATMENT RESULTS FROM SITE DEMONSTRATION

	Oxidation Time (min.)				
Contaminant (μg/l)	0	0.063	0.25	0.75	1.5
Unspiked Groundwater					
Trichloroethene	1300	<1			
Tetrachloroethene	150	<1			
Spiked Groundwater					
Chloroform	150	---	89	36	14
1,1-Dichloroethane	160	---	23	<5	
1,1,1-Trichloroethane	110	---	84	47	7.8

The treatment costs associated with the **perox-pure™** Process for both the spiked and unspiked contaminant concentrations from Table 1 are shown in Table 2 below. In each case, the projections are for contaminant destruction to the CADWALs at a flow rate of 50 gpm. The power rate was assumed to be $0.06 per kWh and the H_2O_2 cost was assumed to be $0.50 per pound on a 50% basis. Acid for pH adjustment is not considered since it was not demonstrated to improve treatment performance. Maintenance costs are estimated at 8% of the capital investment per year. Labor for repair and maintenance is estimated at 2% of the capital investment per year. Other operator attention is not normally required.

TABLE 2. DIRECT COSTS FOR **perox-pure™**
TREATMENT OF SITE DEMONSTRATION GROUNDWATER

	Unspiked	Spiked
Capital Investment ($)	$55,000	$125,000
Power ($/1000 gallons)	0.10	0.90
50% H_2O_2 ($/1000 gallons)	0.34+	0.71+
Maintenance Parts ($/1000 gallons)	0.17	0.38
Maintenance Labor ($/1000 gallons)	0.04	0.10
Total Operating Cost ($/1000 gallons)	0.65	2.09

+ Based on non-optimized H_2O_2 dosage.

CONCLUSIONS

The results of the SITE demonstration with the full-scale **perox-pure™** equipment show that unsaturated VOCs can be rapidly destroyed by more than three orders of magnitude in a few seconds. With the latest generation oxidation chamber design, saturated VOCs are also rapidly destroyed. The total treatment cost associated with the **perox-pure™** System can be lower that $1 per 1000 gallons and is economically competitive with conventional treatment processes which produce solid or vapor-phase emissions.

The **perox-pure™** technology is ideal for those applications where carbon adsorption and air stripping are not economical or viable. For example, some priority pollutants such as methyl-tert-butyl ether, vinyl chloride and methylene chloride are not readily adsorbed by carbon. Other organics, such as alcohols, phthalates and certain PAHs, are resistant to air stripping. Further, multi-contaminant matrices present difficulties for consistent performance because of competitive adsorption effects. The **perox-pure™** Process provides reliable, consistent destruction in each of these cases. In certain instances, it is advisable to combine the **perox-pure™** System with a conventional treatment method to provide the most economical treatment scheme.

FOR MORE INFORMATION

Additional information on the **perox-pure™** photochemical oxidation process can be obtained by contacting Christopher Giggy of Vulcan Peroxidation Systems, Inc. at (800) 552-8064. This contact can also be used to determine if the **perox-pure™** Process is applicable to a specific contamination problem or obtain a written estimate of treatment considerations and economics.

REFERENCE

1 "**perox-pure™**" Chemical Oxidation Technology", EPA Applications Analysis Report, EPA/540/AR-93/501, July 1993.

THE CAV-OX* PROCESS

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INTRODUCTION

The CAV-OX* Process is a synergistic combination of hydrodynamic cavitation and ultraviolet radiation which oxidizes contaminants in water. It is a cost effective method of removing organic contaminants from waste streams and/or ground water without releasing VOC's. The Process can achieve reduction levels necessary for meeting discharge specifications in most aqueous contaminant situations. The total CAV-OX* Process consists of either the CAV-OX*I Low Energy UV Module and/or the CAV-OX*II High Energy UV Module. "Easy" contaminants such as gasoline or TCE require only a CAV-OX*I system, while more difficult contaminant streams such as PCP require a CAV-OX*II system. The CAV-OX* process generally reduces contaminants by 95% to 99.99%.

The CAV-OX* technology is covered by three issued U.S. Patents and one pending Patent Applications. CAV-OX* is a Registered Trademark.

HYDRODYNAMIC CAVITATION

When a body of liquid is heated under constant pressure, or when its pressure is reduced at constant temperature by static or dynamic means, a state is ultimately reached at which vapor or gas and vapor-filled micro bubbles, or cavities, become visible and grow. The bubble growth will be explosive if it is primarily the result of vaporization into the cavity.

The condition is known as "boiling" if it is caused by temperature rise and **"cavitation"** if it is caused by dynamic pressure reduction at essentially constant temperature. Cavitation involves the entire sequence of physical events beginning with bubble formation and extending through cavity collapse.

Cavitation is very useful in the breakdown of organic chemicals and living organisms. (Figure 1). Quoting Scientific American Feb. 1959, in cavitating water: "The heat from cavity implosion decomposes water into extremely reactive hydrogen atoms and hydroxyl radicals. During the quick cooling phase, hydrogen atoms and hydroxyl radicals recombine to form hydrogen peroxide and molecular hydrogen. If other compounds are added to the water, a wide range of secondary reactions can occur. Organic compounds can be oxidized or reduced".

"The heat from cavity implosions decomposes water into extremely reactive hydrogen atoms and hydroxyl radicals - - - Organic compounds can be oxidized or reduced."

Scientific-American 1959

FIGURE 1

In recent cavitation experiments, quoted in Science Sept. 1991, "the temperature of collapsing bubbles have been determined experimentally to be 5075 degrees K +/- 156 degrees K." (Figure 2). This high temperature provides insight into the efficacy of the cavitation process to break down complex organic compounds." When the micro bubble collapse occurs, in addition to instantaneous temperatures of up to 5000 degrees K, pressures of over 1000 atmospheres are produced.

....the temperature of the collapsing bubbles has been determined experimentally to be

5075 K +/- 156 K

Science 1991

FIGURE 2

CAV-OX* APPLICATION

In the CAV-OX* system organic wastes are oxidized into carbon dioxide by a free radical mechanism. Free radicals are generated and maintained by the combination of cavitation, seeding with hydrogen peroxide, metal catalysts and UV excitation. If required, reaction initiators are first added to the waste water entering the cavitation chamber. The oxidation process begins in the cavitation chamber, then in the UV reactor and continues after the stream leaves. Recycling back through the entire process can be controlled either after cavitation, after UV oxidation, or with a combination of the two. During the oxidation, organic carbon is converted to carbon dioxide and the sulfides to sulfates. No solids are generated. The effluent from the system is low in organics and is disinfected by the high intensity UV and carbon transition.

RESULTS: CAV-OX* CHAMBER ONLY Test Data

As stated above the CAV-OX* Process is a synergistic combination of three chemical processes in treating contaminated waste water:

(1) hydrodynamic cavitation (from the CAV-OX* Chamber)
(2) ultra-violet radiation (from the UV reactors)
(3) hydrogen peroxide injection (as necessary)

The best results are always attained in using the above combination in the process. However, occasionally it is desirable to use the CAV-OX* CHAMBER ONLY applications, that is NO hydrogen peroxide, NO ultraviolet. Table 1 shows test results with BETX and TCE. Test Analyses were by SHIMADZU GC-14A Gas Chromatograph using EPA Method 8021.

EXAMPLE 1: EDWARDS AIR FORCE BASE TESTS

TABLE I

CAV-OX* CHAMBER ONLY TEST DATA

PERCENT REDUCTION

Benzene	Ethyl Benzene	Toluene	Xylene	TCE
PROTOCOL A				
57%	11%	37%	+	65%
54%	39.6%	52%	51%	60%
41%	71%	49%	59%	45%
32%	20%	43%	ND	41%
PROTOCOL B				
37%	44%	38%	38%	38%
37%	43%	37%	37%	37%
40%	ND	55%	ND	33%
PROTOCOL C				
23%	54%	31%	38%	24%
17%	60%	26%	42%	22%
19%	53%	26%	35%	19%
16%	24%	20%	23%	18%

NOTE: **NO** UV; **NO** H_2O_2.

EXAMPLE 2: SOUTHERN CALIFORNIA EDISON COMPANY

CAV-OX* CHAMBER ONLY tests were done for Southern California Edison Company. A tank with 3 million gallons of contaminated salt water was to be cleaned to discharge levels using only CAV-OX*. (**No** H_2O_2, **NO** UV.) The contaminants were oils, surfactants, dyes & ferric oxide. The contaminated salt water did not meet discharge criteria. The following test data is from the SCE Laboratory. In the opinion of SCE, if CAV-OX* ONLY was used, no PERMITS were required since the CAV-OX* pump moved the salt water from a tank to a discharge line that met discharge criteria. Economic cost data for this proposed installation was $0.13 per 1,000 gallons.

Results: **86% reduction in BOD**

RESULTS FROM THE SITE DEMONSTRATION, EDWARDS AIR FORCE BASE

The preferred operating conditions for the CAV-OX*I Low Energy configuration was an influent hydrogen peroxide concentration of 23.4 mg/L and a flow rate of 0.6 gallon per minute (gpm). At these conditions the effluent TCE and benzene levels were generally below target levels (5 ug/L and 1 ug/L, respectively). The average removal efficiencies for TCE and BTEX were about 99.9 percent.

The preferred operating conditions for the 5-kW CAV-OX*II High Energy configuraton was an influent hydrogen peroxide concentration of 48.3 mg/L and an flow rate of 1.4 gpm. At these conditions, the effluent TCE and benzene levels were generally below target levels (5 ug/L and 1 ug/L, respectively). Average removal efficiencies for TCE and benzene were about 99.8 percent.

The preferred operating conditions for the 10-kW CAV-OX*II High Energy configuraton was an influent hydrogen peroxide concentration of 48.3 mg/L and an flow rate of 1.4 gpm. At these conditions, the effluent TCE and benzene levels were generally below target levels (5 ug/L and 1 ug/L, respectively). Average removal efficiencies for TCE and benzene were about 99.7 and 99.8 percent, respectively.

RESULTS FROM SELECTED CASE STUDIES

Superfund Site, Pensacola, Florida

Pentachlorophenol reduced by 96%.

CHEVRON Service Station, Long Beach, California

TPH reduced by 99.94%.

US Army - Presidio, San Francisco, Califonia

TPH, ethylbenzene reduced to Non-Detectable

Steel Mill, South Korea

Cyanide, phenol reduced by 99.9%.

Chicken Farm, Virginia

2,000,000 cfu/mL Salmonella reduced to .01 cfu/mL.

Chemical Plant, Baltimore, Maryland

BOD reduced by 94.1%.

DEVELOPMENT STATUS

Tables II and III give a list of CAV-OX* installations and CAV-OX* demonstrations sites.

TABLE II

CAV-OX* Systems have been installed at:

Chevron Environmental Services	10 gpm CAV-OX*I
Southern California Edison Co.	1 gpm CAV-OX*I
Advanced Micro Devices Corp.	10 gpm CAV-OX*I
International Technology Corp.	10 gpm CAV-OX*I
U.S. Army Presidio	20 gpm CAV-OX*I
Private Ranch-Well water for drinking purposes	5 gpm CAV-OX*I

TABLE III

CAV-OX* Systems have been demonstrated at:

EPA Superfund Site - Pensacola, Florida
Edwards Air Force Base - SITE Demonstration
EPA Superfund Site Bog Creek Farm Site - New Jersey
San Bernardino Water Department
Orange County Water District
Geological Research Inc.
CMIMSA S.A. de C.V., Saltillo, Mexico
Resources of the Pacific Ltd., Fiji Islands

MEDIA AND POLLUTANTS TREATED

CAV-OX* is only applicable to aqueous streams with low contaminant levels: for example, BETX below approximately 100 ppm. Grease, oil and turbidity decrease the efficiency of the UV reactors. However, the cavitation chamber is unaffected by such factors. Tables IV, V, and VI give specific chemicals treated by the CAV-OX* Process.

TABLE IV

Contaminants Treated by the CAV-OX* Process

- Atrazine
- Chlorinated organics
- Halogenated organics
- Petroleum hydrocarbons
- Polychlorinated biphenyls (PCB)
- Polynuclear aromatic hydrocarbons (PAH)
- Benzene, toluene, ethylbenzene, and xylenes (BTEX)
- Cyanides
- Phenol
- Bacteria
- Viruses

TABLE V

The CAV-OX* process can treat the following contaminants in industrial wastewater:

- Amines
- Chlorinated solvents
- Complex cyanides
- Hydrazine compounds
- Methyl ethyl ketone (MEK)
- Methyl isobutyl ketone (MIBK)
- PCP
- Polynitrophenols
- 2,4,6-Trinitrotoluene
- Xylene
- Aniline
- Chlorobenzene
- Creosote
- Isopropanol
- Methylene chloride
- PCB
- Pesticides
- Cyclonite
- Toluene

TABLE VI

The CAV-OX* process can treat the following contaminants in groundwater:

- Bis(2-chloroethyl) ether
- 1,2-Dichloroethane
- Dioxins
- Freon 113
- MIBK
- PCBs
- Pesticides
- Tetrachloroethene
- Trichlorothene
- Triglycol dichloride ether
- Creosote
- Dichloroethene
- Dioxanes
- MEK
- Methylene chloride
- PCP
- PAHs
- 1,1,1-Trichloroethane
- Tetrahydrofuran
- Vinyl chloride

INITIAL AND FINAL POLLUTANT CONCENTRATION

The cavitation chamber ONLY process reduces contaminant concentrations by about 20 to 50 percent. The synergistic combination of cavitation and UV radiation can reduce contaminant concentrations from 95 to 99.99 percent.

The CAV-OX* process produces no air emissions and generates no residue, sludge, or spent media that require further processing, handling, or disposal. If contaminants are reduced to non detectable levels, the effluent consists of water with some dissolved carbon dioxide gas, halides (for example, chloride), and in some cases organic acids. No VOCs are released to the atmosphere. Any remaining contaminants remain in the effluent.

RATED THROUGHPUT

Theoretically any size CAV-OX* System can be built. The largest built to date is a 50 gallon per minute unit. A 20 gpm unit is used at a U.S. Army site and several 10 gpm units are employed cleaning up ground water from gasoline stations.

ECONOMIC ANALYSIS

Table VII give economic cost data for the CAV-OX* Systems.

TABLE VII

Typical operating costs for the CAV-OX* process are:

- CAV-OX* cavitation chamber only - about $0.50 PER 1,000 gallons of treated water
- CAV-OX* cavitation chamber with low-energy UV radiation and hydrogen peroxide - about $2.00 per 1,000 gallons of treated water to $4.00 per 1,000 gallons.
- CAV-OX* cavitation chamber with high-energy UV radiation and hydrogen peroxide - about $4.00 per 1000 gallons of treated water to $10.00 per 1,000 gallons.

Table VIII presents cost data for the CAV-OX*I Low Energy System process with UV radiation plus hydrogen peroxide. The contaminant of concern was benzene, and the treatment goal was to reduce concentration from 50,000 micrograms per liter (ug/L) to 50 ug/L.

TABLE VIII

ECONOMIC ANALYSIS FOR GROUNDWATER TREATMENT

Process rate: 25 gpm	CAV-OX*I LOW-ENERGY PROCESS
CAPITAL COST	
Equipment	58,000
Installation	3,000
Total	61,000
ANNUAL OPERATING COSTS	
Power ($0.08/kWh)	3,592
Carbon	0
Chemicals	1,741
Maintenance	5,114
Amortization (20% per yr.)	11,600
Labor (air monitoring)	0
TOTAL	22,047
Treatment Cost/1,000 gal	$1.67

CONCLUSION

The CAV-OX* Process has been proven in various installations and demonstrated in a variety of contaminant situations. The EPA SITE Demonstration at Edwards Air Force Base has produced an Applications Analysis Report giving precise technical details of the CAV-OX* Process. Also, a technical video is available on the CAV-OX* SITE tests available from the EPA.

The CAV-OX* Process is economically cost effective and is less expensive than other Advanced Oxidation Systems.

A NEW AIR STRIPPING METHOD TO ECONOMICALLY REMOVE VOCS FROM GROUNDWATER

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INTRODUCTION

The use of air for stripping volatile organic contaminants (VOCs) from water is well established and is an accepted treatment process in the environmental field. By choosing the proper stripper dimensions, number of stripping stages, and air-to-water ratio, a wide range of water flows and VOC concentrations can be treated, in many instances, to meet non-detectable levels.

Frequently, the regulations limit the amount of VOCs that can be emitted into the air. This in turn requires the use of offgas treatment such as carbon adsorption or catalytic incineration. Both of these processes add significant capital and operating costs to the cleanup operation.

The development of triplan's vacuum stripper extends the range where a stripper is a viable technology. Since the air-to-water ratio, for the same removal, is significantly reduced, the concentration of the VOCs in the offgas is proportionately higher. Because triplan manufactures both atmospheric and vacuum strippers, an unbiased evaluation can be made as to which technology is appropriate.

METHODOLOGY

The design of the stripping tower is based on the theoretical height and number of transfer units concept. This means that the packing height is the result of the product of the height of a transfer unit (HTU) and the number of transfer units (NTU's). The height of a transfer unit is directly proportional to the liquid flow per unit cross sectional area and inversely proportional to the initial VOC concentrations, the overall liquid mass transfer coefficient, and specific interfacial area of the packing.

The number of transfer units is a function of the desired concentration change, the air-to-water ratio, Henry's constant and the system pressure. The latter three factors relate, as shown below, to quantify the stripping factor:

$$R = (H/Ps)(G/L)$$

where:

R = stripping factor
Ps = system pressure
H = Henry's constant
G = air rate
L = water rate

The larger the stripping factor the better the VOC removal. Usually the stripping factor should be greater than two.

An inspection of the aforementioned equation shows that in a conventional air stripper, operating at atmospheric pressure and a given temperature, the only variable is the air-to-water ratio. However, it's also obvious that, if the pressure is reduced, the stripping factor is increased. This leads to two advantages which the engineer can evaluate. First, the same performance can be achieved by reducing the air-to-water ratio in direct proportion to the reduction in pressure. Secondly, when compounds such as naphthalene and ammonia, which have low Henry's constants, must be removed, the stripping

factor, and thus the performance at the same or lower air-to-water ratio, can be increased by reducing the pressure.

Typically, the vacuum stripper is designed with an air-to-water ratio one-tenth that of an atmospheric stripper. As a result the same VOC removal is obtained at a similar consumption of energy. This reduction in air volume results in a proportionate reduction in the size of the offgas treatment equipment. In addition, the resultant increase in the concentration of contaminants can result in a 30-100% increase in the capacity of activated carbon. Likewise, catalytic oxidation efficiency is improved. Furthermore, with favorable Henry constants, the vacuum technique can remove contaminants to stringent effluent water specifications without additional treatment such as liquid phase carbon being required.

Figure 1 shows the flow scheme of a vacuum stripper system which typically includes: stripping tower(s), fluid pump(s); vacuum pump(s); a dehumidifier; and an offgas treatment system. The pumps are especially selected for removing treated water from the stripper. The offgas treatment system is somewhat independent, but normally consists of activated carbon adsorption or catalytic oxidizer components. Atmospheric strippers have similar components except for the vacuum pump.

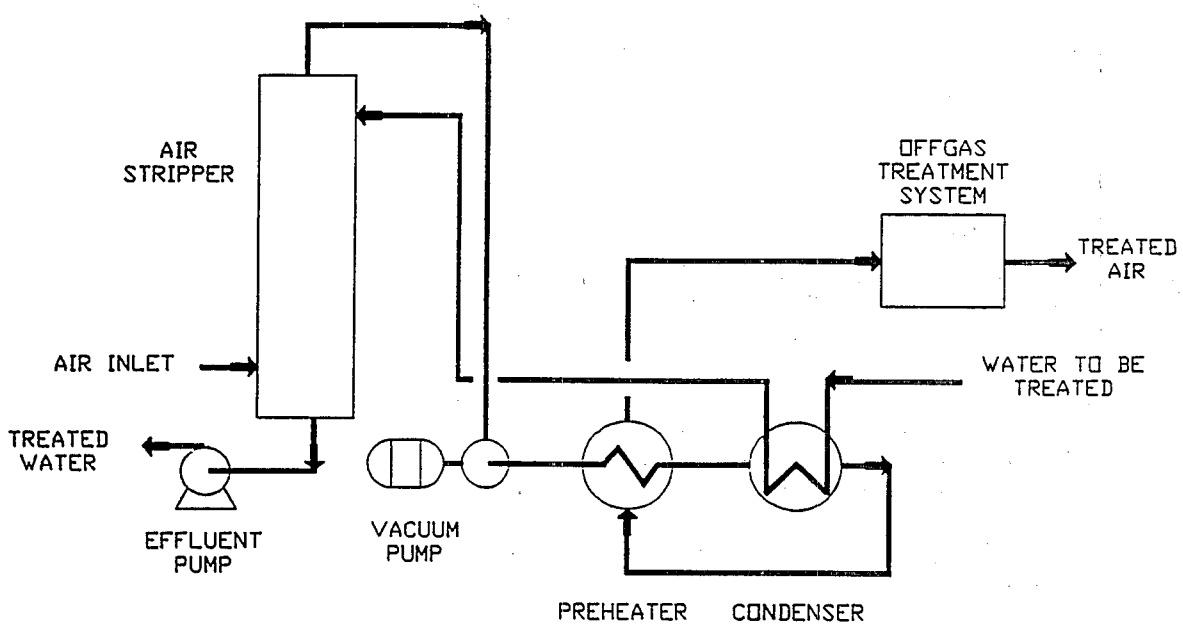

Figure 1. Schematic of a typical system

As with other contactors, proper packing and good air and liquid distribution are important so that the vacuum effect will not be impaired and its theoretical advantages achieved. Another requirement is that the liquid to be stripped should not contain appreciable amounts of foaming constituents or oils.

RESULTS

To date there are five operating systems that have operated a total of 20,000 hours. Thus, the technology is not a laboratory curiosity but is field proven. Most liquids which contain strippable compounds can be treated via this technology. At the present time it does not appear that there

are any limitations to the degree of removal that can be obtained, especially with the use of two towers in series.

Table 1 summarizes the operating conditions for three vacuum air stripper systems utilizing two stripping towers in series. An inspection of the data in this table reveals the effectiveness of this technology.

TABLE 1. SUMMARY OF PERFORMANCE OF THREE SYSTEMS

CASE	WATER	AIR	CONTAMINANTS	INFLUENT	EFFLUENT	REMOVAL
NO.	GPM (m3/h)	SCFM (m3/h)		ppm	ppb	%
1*	4.5 (1)	3 (5)	Xylene, Methylene chloride	27	<20	99.93
2**	119 (27)	30 (50)	BTX, chlorinated hydrocarbons	47	250	99.47
3	35 (8)	12 (20)	Trichloroethylene	125	7	99.99

* In this case the iron level was 11 mg/l. Hardness was >300 mg/l.
** In this case the iron level was 3 mg/l.

A beneficial feature of the vacuum technique, which is not part of the theory, is the ability to minimize microbiological growth and fouling of the packing due to chemical precipitation. In a vacuum stripper the growth of the microorganisms is suppressed because of the low pressure and low air-to-water rates. As a result, downtime for cleaning and replacing packing is significantly reduced. These effects were observed in Cases 1 and 2. In Case 1 the stripper column did not require the initial cleaning until 4000 operating hours. This compares to an expected 400-500 hours for conventional strippers. It's obvious that this will result in lowered operating costs and greater convenience.

As would be expected, the capital cost of a vacuum stripper is higher than capital for traditional atmospheric stripping. The column(s) must be built for the vacuum duty, and instrumentation is more elaborate. This extra capital is in the range of 30-40%. However, this is somewhat offset by the lower capital cost of the offgas treatment section.

The electrical operating costs for the vacuum system are about 10% above those for the atmospheric systems. The major operating cost savings occur in the offgas treatment system. Because of the typical 10:1 reduction in air flow the treatment systems are smaller and more efficient. Operating costs for these systems can be on the order of one half that of traditional systems. Further savings are experienced in those instances where there would be less frequent cleaning due to minimization of biological fouling and chemical precipitates.

CONCLUSIONS

Vacuum stripping is becoming an established treatment method in Germany. In a series of full scale applications, this technology has demonstrated highly efficient water purification performance at low air-to-water ratios which resulted in reduced offgas production. It is compatible with all standard offgas treatment schemes such as adsorption, solvent recovery, and catalytic incineration.

Advantages are found in the insensitivity of the technique to fouling due to bacterial and chemical precipitation with lower attendant maintenance; high stripping efficiency; smaller, higher efficiency offgas treatment equipment; and in many cases, the elimination of the need for liquid phase carbon following the stripper. Because of these inherent technical and practical advantages, vacuum stripping is very versatile and can be adapted to numerous field variables and challenges.

PILOT SCALE INVESTIGATIONS OF THE IN SITU IMMOBILIZATION OF HIGHLY ARSENIC CONTAMINATED SOIL

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INTRODUCTION

The site of about 100 000 m² (25 acres) is located in an industrialized area within the boundaries of Berlin. At the beginning of this century it was owned by a chemical company which produced sulfuric acid by roasting sulfide minerals such as arsenopyrites. The solid residues of the roasting process were probably deposited on the company site.

Since 1926 the site is owned by an Oil Company. Various buildings and storage tanks were erected. Later, roads and railroad tracks were added. The site is still commercially used by the Oil Company. First reports on groundwater pollution became known in the 1980th, when an approximately 2 km distant waterwork observed arsenic in some of its production wells. An extensive investigation was initiated which indicated that the contamination source is on the site in question, and covers an area of approximately 10 000 m^2 (2,5 acres).

The main contamination sources are in the eastern part of the area with arsenic concentrations of > 1 g/ kg. Peak values of up to 78 g As/kg were measured. The contamination has penetrated to depths of > 7 m. The waterwork is located about 2 km east of the site, therefore the groundwater flow direction is toward east.

The goal of this project is to protect the waterwork wells from As-contamination with as little as possible disturbances of the commercial operations at the site.

CHARACTERIZATION OF THE AS-CONTAMINATION

Roasting sulfides for instance FeAsS results in the formation of SO_2 (gas) and oxidic iron and arsenic compounds. Of specific interest here are the oxidic arsenic compounds. All of them have an appreciable solubility in water, which is of the order of >10 g/Liter and which explains the contamination of the waterwork wells. To reduce the solubility substantially, for instance by reforming the sulfides in situ, using H_2S, $(NH_4)_2S$ or similar compounds bears the danger of large scale secondary contamination. Besides, the formed sufides show either an appreciable carbonic acid or NH_4^+ solubility . Therefore a literature search was initiated.It showed that from the point of view of stability and insolubility ferric arsenates are promissing candidates for an immobilization process.

LABORATORY STUDIES

The laboratory experiments were aimed to obtain information on the
- selection of suitable compounds for the As-immobilization in the soil
- conditions for the immobilization of As
- process parameters (concentration, volume of required solutions, P_H, and reaction time) for the fixation.

The geological and chemical site analyses revealed the following facts:
- The As-contamination reached peak values of up to 80 g As/kg Soil
- As-concentrations of >1 g As/kg soil were found in depths of up to 7 m
- The water and carbonate solubility of Arsenic-compounds is considerable.

The arsenic compounds contain predominately As(V). As long as the soil is acidic(P_H<6), arsenates and arsenites will go into solution. With increasing P_H-values ferric-hydroxide gels and ferric-arsenates are precipitated.

METHODOLOGY

A total of 6 glas-columns were filled with 1,25 kg of contaminated soil containing 800-7700 mg As/kg soil. Two sets of experiments were conceived to immobilize the arsenic.

Ferric chloride ($FeCl_3$) was used in set 1 while ferric acetate was injected in set 2. All experiments were carried out over a time period of 264 h.

An appreciable mobilization of As occurs, when Fe Cl_3 (Set 1) is injected. This mobilization is accompanied by a rapid drop of the P_H-value to 1.4, The P_H-value recovered only very slowly with time.

The injection of ferric acetate also causes a reduction of the P_H-value, however, only to a $P_H = 5$, with a rapid recovery to neutral.

After a short mobilization phase no further arsenic was detectable in the leachate.

The P_H-stability has been ascertained between 6,0 and 7,8. However, it can be assumed that the stability range of the formed ferric arsenate is wider than that.

RESULTS

Before conceiving and planning a field experiment it was decided to verify the results on a larger scale. In addition we wanted to obtain information on

- horizontal flow conditions
- on site preparation of ferric-salt solutions
- methods to externally precipitate the mobilized As.

The experiments were carried out using a containment with the dimensions
length: 2,0 m; width: 1,0 m; height: 1,5 m
The containment was filled with contaminated soil from the site with known As-content and compacted. A typical sequence of operations shows an oxidation period of approximately 12 days, and an immobilzation time of about 30 days.
The As leachability during this time period shows that the mobilization phase starts at about day 28 (during the injection of ferric acetate) and ends at about day 65 with continuously dropping As-values in the leachate. After about 80 days 0,07 mg As/Liter were found in the leachate with steadily decreasing values.

REMEDIATION COSTS

As mentioned earlier, no field tests have been performed which would permit a more accurate cost comparison with other suitable methods. Regardless, we have attempted to calculate the remediation cost for a defined area and compare them with a possible alternative, the soil washing, a technology also practised in Europe.

The cost calculations for the in situ immobilization of arsenic in soil are based on the following site parameter

<u>Site parameter:</u>

Total area :	100 000 m^2 ~ 25 acres
Contaminated area:	10 000 m^2 ~ 2,5 acres
Contamination depth (average) :	4,5 m
total contaminated volume density ~ 2,0:	45 000 m^3 ~ 90 000 t
Average As-contamination:	>100 mg As/kg soil
Total As-content in soil:	9 t
Soil permeability:	$>10^{-7}$ m/s

Depending upon the distribution of the contaminants in horizontal and vertical direction, hydraulically closed circuits will be established consisting of several remediation islands.
Each island consists of an arrangement of injection and discharge wells.
As a rough estimate we assume about 2500 Injection probes and approximately 100 discharge wells .
The probes are in average about 2 m apart from each other.

INVESTMENTS (in 10^3 DM)

- 2500 injection probes	2.500,– DM
- 100 discharge wells, 15 m deep	500,– DM
- pipes, connectors, pumps	1.500,– DM
- Equipment: chemical tanks storage tanks, precipitators	1.700,– DM
~	6.200,– DM

ANNUAL OPERATING COSTS (in 10^3 DM)

- chemicals, other materials	300,– DM
- personnel costs	350,– DM
- energy, disposal, others	250,– DM
	900,– DM

Add up to a total of **DM 7.100.000,–**

Considering the uncertainties involved in this rough estimate one can figure the total remediations costs for the 45 000 m^3 to be of the order of

~ 12 000 000,– DM

or ~ 7 000 000,– US $

Specifically the costs can be expressed to

DM 270,– /m^3 ~ US $ 157 /m^3

or on a weight basis

DM 135,–/ton ~ US $ 80,–/ton

for the in situ immobilization.

Currency exchange rate: 1 US $ = 1,7 DM.

A comparison of remediation costs per ton for the in situ immobilization of heavy metals and the soil cleaning methods (from organic contaminants) is finally shown below:

In situ immobilization :	80 US $ / ton
Soil washing (Harbauer) (1)	125-200 US $/ton
Soil Cleaning (MTB Umwelttechnik AG) (2)	250 US $/ton

Because these Figures are encouraging, we are looking for a suitable site to field test the described method.

CONCLUSIONS

An in situ immobilization of arsenic contaminated soil is possible, using state of the art technologies. A precondition for the described process is a certain permeability of the soil for water.

Due to the high carbonic acid solubility of arsenic sulfides the conversion to ferric arsenates is favored. Using on-site preparation methods of ferric acetate, secondary pollution is minimized. The $P_H$stability-range of ferric arsenites lies between 6 and 8.

During the injection phase, mobilization of As has been observed.

By properly placing discharge and monitoring wells around the in situ-treatment zone, further spreading of the contamination can be avoided.

The As-leachability dropped to below 0,07 mg As/liter. No field test has yet been carried out. This was mainly due to a change of the anticipated utilization of the site in question.

However, we believe that the described method is suited as a remediation of heavy metal contaminated soil, in particular arsenic, where excavation is uneconomical and where possible commercial operations must continue during remediation. The cost comparision to soil washing methods is favorable.

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Colloid Polishing Filter Removal of Heavy Metals, Uranium and Transuranic Pollutants from Groundwater at The DOE Rocky Flats Plant

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INTRODUCTION

DOE Rocky Flats Plant and ITPH

The U.S.D.O.E.(DOE) Rocky Flats Plant is located in northern Jefferson County, Colorado about 16 mile NNW of downtown Denver. The RFP consists of a 400 acre plant site situated inside a 6,550 acre restricted zone. Agricultural land and mountains are situated just North of the plant, with residential and commercial industrial development to the East and West. A lake is located immediately South of the site. Five Solar Ponds were placed into service between August, 1956 and June, 1960 and used until 1986 as illustrated in figure 1. The solar ponds were used for storage of nuclear weapons production liquid wastes, contaminated groundwater, sewer sludge, sanitary treatment plant effluent and treated acidic wastewater. Examples of pollutants known to have been introduced into the Solar Ponds are listed below.

Low-level radionuclides(tritium, & long-lived alpha emitters
Nitrates/nitrites
Solvents
Acids (HCl, H_2SO_4, HNO_3)
Aluminum hydroxide
Hexavalent chromium
Ammonium persulfates
Bicarbonate
Cyanide solutions
Ferric chloride
Lithium chloride
Lithium metals

The integrity of the Solar Pond liners was breached by physical and chemical action by the late 1970's and early 1980's, thereby contaminating the groundwater. The ground water flow from the five solar ponds is North initially, were an interceptor trench pump house (ITPH) collects the contaminated groundwater, while an interceptor trench system (ITS) on the hill side just North of the Solar Ponds.collects surface water. In 1992 three (3) 500,000 gallon, plastic lined, metal storage tanks (OU4 IM/IRA tamls) were installed on the hillside at a higher elevation, West of the ITPH (see figure 1).

Colloid Polishing Filter Method (CPFM)

The *Colloid Polishing Filter* was developed as an economical, yet high performance sorption filter for removing trace heavy metal and non-tritium radionuclide pollutants from water. By using efficient, insoluble, inorganic sorption bed material (i.e. **Fitler Flow-1000)** , together

with specially designed and engineered equipment to control fluidics and then optimizing the influent water chemistry and flux rate, it is feasible to efficiently remove a side spectum of inorganic metallic pollutants from water that exist not only as soluble ions, but colloids, and complexed and chelated forms. The sorption filter functions predominantly via efficient surface sorption and charge dependent chemical complexing phenomena and to a lesser extent (appx. 5%) by physical particle filtration. This report describes the U.S.E.P.A. (EPA) SITE Demonstration experimental testing and results obtained for the *Colloid Sorption Filter* treatment of the DOE Rocky Flats Plant ITPH groundwater removal of representative heavy metal pollutants and Uranium, Plutonium-239 and Americium-241 radionulcides[1].

METHODS OF PROCEDURE

The EPA SITE Demonstration at the DOE Rocky Flats Plant was carried out jointly with the EPA. Regon VIII office, Denver, CO.and DOE under a Memorandum of Understanding between the EPA and DOE Headquarters. The purpose of the demonstration was to evaluate the *Colloid Polishing Filter* as an alternative methodology for treating and remediatiing Total Uranium, Uranium-238, Uranium-234, Plutonium-239 and Americium-241 pollutants in the ITPH groundwater.

ITPH groundwater bench testing was carried out at the Rocky Flats Plant during1992 and 1993 and the SITE Demonstrattion was conducted in September, 1994, using ITPH groundwater that had been pumped to the OU4 IM/IRA storage tanks West of the ITPH. The groundwater had been pumped into the tanks in June, 1993 in preparation for evaporator tests, but due to delays the water was stored in the tanks during late June, July and August prior to the demonstration and a heavy algae bloom was evident as fine green, cloudy particles in the 25 to 28°C, stored in the tanks by early September. The *Colloid Polishing Filter* equipment, together with mixing tanks, an incline plate clarifier, pre-filter assembly, pumps, pipes and electrical and electronic control panels was transported from Houston, TX to the Rocky Flats Plant. Following radiologically survey and inspection of the trailer and equipment, the trailer was moved to a pre-staging area for final checkout, then moved to the demonstration staging area at the OU4 IM/IRA tanks as illustrated in figure 1.

Figure 2 shows a CAD drawing of the *Colloid Polishing Filter* and equipment treatment train used for the demonstration. The tank stored ITPH groundwater was pumped at 5 gpm from the middle tank to a mixing tank and second reaction tank (for optional chemical conditioning), the bulk solids removed in an incline clarifier and overflow water positive pressure pumped through a pre-filter(10 micron, polypropylene, bag filter) and into the manifold assembly for distibuting the water in serial or parallel mode to two, vertically mounted, *Colloid Polishing Filters*. Effluent water from the polishing filters was collected in a third tank for final pH adjustment, then the water pumped to a different OU4 IM/IRA storage tank. A series of tests were conducted at 5 gpm, continuous flow using 4 hr test periods plus a 15 hr run, where samples of the influent groundwater (untreated, Control), intermediate (post clarifier, but pre-polishing filters) and effluent water (treated, downstream from the polishing filters). PRC Environmental Management, Inc. (Denver, CO) prepared the demonstration

Figure 1. Drawing of the DOE Rocky Flats Plant showing the loction of the Interceptor Trench Pump House (ITPH) relative to the Solar Ponds (i.e., 207C, 207A, 207B North, 207B Center and 207B South) contamination source. The SITE Demonstration staging area is shown (upper left) at the OU4 IM/IRA tanks.

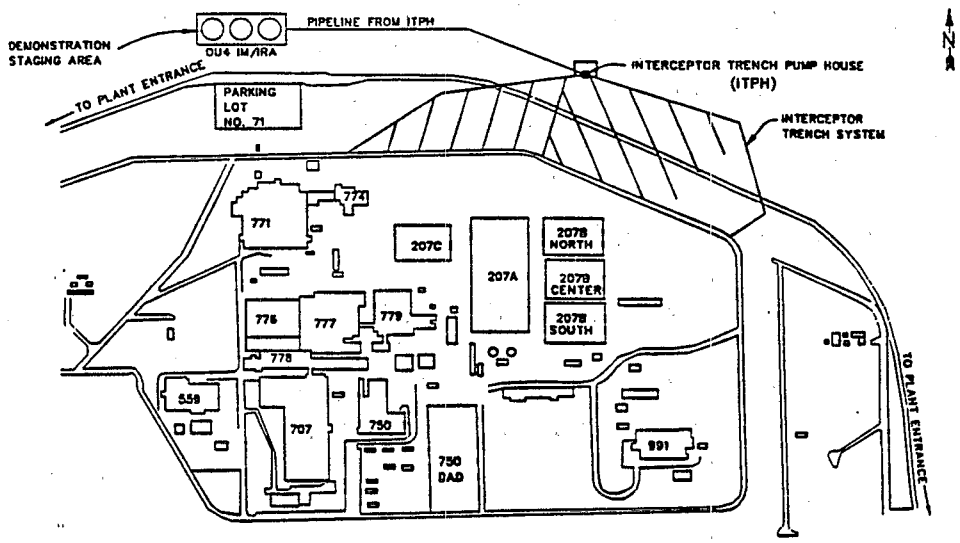
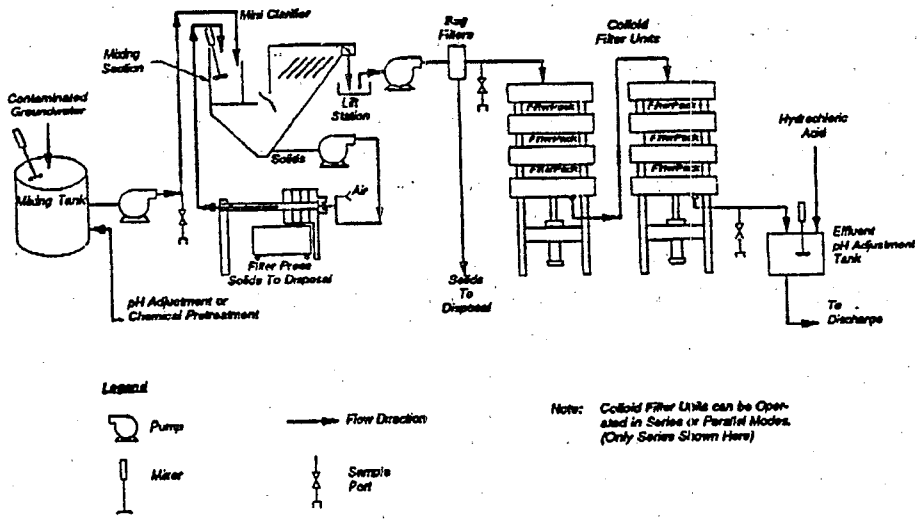


Figure 2. Compter CAD drawing showing the treatment train used for the SITE Demonstration Project at the DOE Rocky Flats Plant. The equipment was mounted on a 30 ft trailer.



plan[1], provided the demonstration test staging, health safety, QC/QA and support and was responsible for all sampling and laboratory analysis procedures. An EPA Program Fact Sheet[2] and Demonstration Bulletin[3] were prepared by the EPA. The sampling procedures followed the GA/QC outlined in the SITE Demonstration Plan based on EPA guidelines[2-4]. An independent, EPA certified commercial laboratory was responsible for the analytical chemistry, heavy metals and radiochemistry, which was carried out following standard EPA procedures. This report describes results obtained for treating the ITPH groundwater at the DOE Rocky Flats Plant heavy metals, uranium, Plutonium-239 and Americium-241.

RESULTS AND CONCLUSIONS

Table I shows representative analytical data obtained for the influent (Control) versus *Colloid Polishing Filter* treated (effluent) ITPH groundwater at the DOE Rocky Flats Plant. based on the bench and pilot testing. With the exception of mercury (concentrations to low to evaluate) and Silicon (influent conentration low), which was 98% the Percent Removal Efficiency for 18 seventeen heavy metals was 99.4% to >99.9%. Considereing the complex water chemistry for the ITPH groundwater, it was concluded that the *Colloid Polishing Filter Method* performance for removing metals from the goundwater was competitive with conventional microfiltration, ultrafiltration, ion exchange and reverse osmosis (RO) techniquies. The advantages of the methodology for treating groundwater metal pollutants, would be expected to be higher removal efficiencies for colloidal and complexed/chelated forms not readily removed by ion exchange and RO and lower capital equipment and operational costs. In addition, the *Colloid Polishing Filter Method* has application for removing colloidal and soluble ions at moderate to higher flux rates not achievable with the micromembrane filtration methods.

Figure 3A shows the histogram plots for the bench tests The radiochemical data are plotted as isotope activity (pico Curies per liter, pCi/l) representing the influent (Control) versus effluent (treated)) groundwater samples. For the bench tests (figure 3A) the influent mean (and two sigma) Total Uranium was 98 12 pCi/l compared to 0.15 0.12 pCi/l for the *Colloid Sorption Filter* treated samples or an estimated >99 % Removal Efficiency. Influent Uranium-234 (56 10 pCi/l) and Uranium-238 (35 6 pCi/l) were observed to be reduced down to <0.03 pCi/l each based on alpha spectrometry. Control (Influent) Plutonium-239 (7 1 pCi/l) and Americium-241 (22 4 pCi/l) were removed by the "polishing" filter down to the alpha spectroscopy, radiochemical lower limit of detection ranges of <0.01 pCi/L. These results indicate that the *Colloid Sorption Filter* efficiently removed the Plutonium-239, and Americium-241 transuranic pollutants from the groundwater at a >99 % Removal Efficiency.

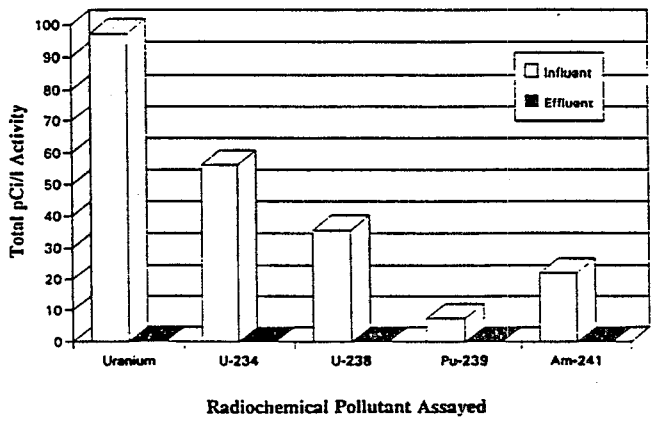
Represenative radiochemical data obtained for the continuous demonstration at the Rocky Flats Plant, Golden, CO. are plotted in figure 3B. The ITPH groundwater (containing algae) was treated at 5 gpm with the *Colloid Sorption Filter Method* using trailer-mounted equipment in September of 1993. The concentrations of influent Uranium, Plutonium-239 and Americium-241 were very similar to the bench test data, despite a one year period between the tests. The influent (Control) groundwater contained 98 12 pCi/l Total Uranium that was reduced to 0.15 0.12 pCi/l after *Colloid Sorption Filter* treatment (>99 % Removal Efficiency). Isotopic alpha spectroscopy data obtained for Uranium-234 and Uranium-238

Table 1. Exmples of bench and demonstration data obtained for heavy metals. Data (statistical means) are shown for the Influent (Control) versus Effluent (Treated) using the *Colloid Sorption Filter Method* in tests at the DOE Rocky Flats Plant, Golden, CO.

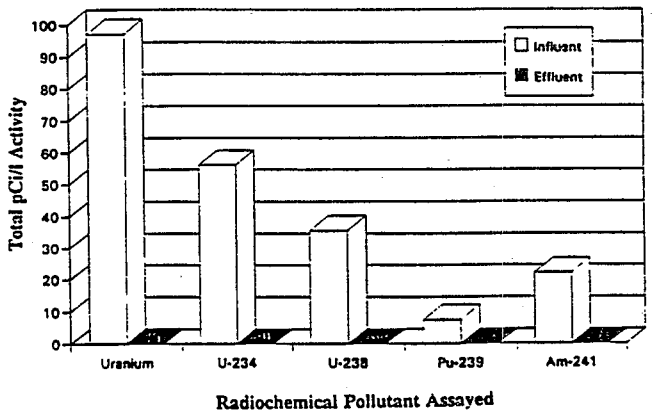
Heavy Metal	Control (Influent) mg/l (mean)	Test (Effluent) mg/L (mean)
Boron	0.660	0.006
Cadmium	0.033	<0.001
Chromium $^{+3}$	2.971	0.006
Cobalt	0.046	<0.002
Copper	35.290	0.003
Iron	0.230	<0.001
Lead	4.461	0.008
Mercury	<0.0002	<0.0002
Molybdenum	47.565	0.018
Nickel	1.540	0.009
Selenium $^{+4}$	1.715	0.004
Selenium $^{+6}$	0.750	0.003
Silicon	0.021	<0.003
Silver	0.055	<0.005
Strontium	0.751	0.007
Tellurium	0.103	0.004
Thallium	0.032	<0.001
Vanadium	6.740	0.006
Zinc	58.357	0.005

Figure 3. Examples of performance achieved by the *Colloid Polishing Filter* for the removal of Uranium, Plutonium-239 and Amnericium-241 pollutants from the ITPH groundwater. (A) Bench test experiments and (B) pilot demonstration tests.

A



B



indicated that the influent activities were 56 10 and 35 6 pCi/l respectively and the "polished" effluent reduced to the 0.02 to <0.01 pCi/l range (>99 % Removal Efficiency). Similarly, >99% Removal Efficiency was observed for the transuranics. The influent Plutonium-239 7 1 pCi/l and Americium-241 22 4 pCi/l activities were lowered to <0.01 pCi/l by the *Colloid Politshing Filter Method* consistent with high performance "polishing" of these transuranic pollutants.

Uranium, Plutonium and Americium isotopes are Actinides and characterized by long-lived, alpha emitting decay products which are major environmental and health hazards, due to high biological toxicity. For both the bench and pilot tests Uranium, Plutonium-239 and Americium-241 was experimentally tested for removal by the *Colloid Sorption Filter* in the +6 and +4 oxidation-reduction states and no significatnt difference was observed in the % Removal Efficiency for these radionuclides for removal as +6 or +4. Under these testing conditions for the ITPH groundwater (pH 7 to 9), the Actinides, would be expected to form comnplexes with anions in aqueous mileau.that produce polyhydroxyl colloidal species.

Based on the bench and demonstration tests conducted at the DOE Rocky Flats Plant, Goldent, CO described in this report, it was concluded that the *Colloid Polishing Filter Method* performed efficiently (>99% Removal Efficiency) as a "polishing" filter for heavy metal, Uranium, Plutonium-239 and Americium-241 pollutants in the ITPH groundwater. The methodology has application as an inorganic metallics "polishing" filter for a wide range of soluble ionic as well as colloidal, complexed and chelated forms. An operational requirement of the methodology is for low suspended solids influent water, optimized water chemistry and carefully designed bed volume and configuration for site specific applicaitions. The equipment tested performed adequately. The methodolgy evaluated in the EPA and DOE bench and demonstration tests[1,5-9] should provide an alternative treatment and remediation strategy for inorganic metallaic polluted groundwater at Superfund and weapons sites.

The *Colloid Polishing Filter Method* can be used as trailer or skid mounted equipment; as a "polishing" filter for in-line systems; as an efficient treatment system for removing heavy metals and non-tritium radionulcides from sludge or soil washing wastewater; and for remediation of secondary wastewater generated from Decontamination and Decommissioning projects with mixed-waste, LLRW or Uranium and transuranic pollutant contaminated concrete and scrap metals. A detailed review and evaluation of the capital equipment costs and operational costs is in progress.and will be reported.

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APPLICATION OF MINERAL BENEFICIATION PROCESSES FOR LEAD REMOVAL AT A CAMP PENDLETON, CA, SMALL ARMS FIRING RANGE

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INTRODUCTION

The U.S. Bureau of Mines, Salt Lake City Research Center (SLRC), and the Naval Facilities Engineering Service Center (NFESC) assembled and operated a 1,500 lb/hr pilot plant designed for the removal of heavy-metal contamination at active and abandoned small-arms firing ranges. The plant, designed to be mobile for on-site treatment of contaminated soil, was transported to Marine Corps Base (MCB) Camp Pendleton, Oceanside, CA. The pilot plant operated for a 2-week period processing over 15 tons of lead-contaminated soil. This paper describes the field testing of the mobile plant, evaluation of its performance, and the future of the process.

To identify the extent of environmental problems associated with small arms ranges, an extensive characterization of several ranges was conducted by the NFESC. The study revealed that the build-up of bullets in the target and impact berms creates source areas for metals contamination. Lead concentrations have been found to be as high as 33,000 ppm. Left unattended, contamination may be dispersed into the environment along various pathways,including surface-water runoff and airborne dust migration. Thus, these berms and their surrounding areas, if not properly managed and remediated, are potential sources of groundwater and non point-source pollution. Furthermore, the presence of high levels of toxic metals in the soil may be a threat to humans, wildlife, and plants.

Traditional berm maintenance consisted of excavation and landfilling of the soil. Not only is disposal of the soil as a hazardous waste costly and environmentally unfriendly, it does not solve the problem of possible future contamination. This process solves the problem by removing the heavy metals from the soil.

Vegetation samples obtained from small arms ranges indicate that lead levels for plants growing in contaminated soil may be 100 times that of background samples. Copper levels are slightly elevated.

The majority of lead and copper in the berm exist as large fragments, but significant amounts of fine particles, smeared lead, and weathered products were also found during mineralogical examination. Heavy-metal contamination in surface soil samples increases parallel to the direction of fire for the small arms range. Similar profiles extend to a depth of more than three feet in the impact berms. Elevated lead levels have been observed in the area behind the berm due to stray rounds and runoff.

The remediation study consisted of applying techniques used in mineral beneficiation of ores produced by mining to firing range soils. Metallurgical testing generally begins with a liberation/gravity amenability study. The procedure consists of screening the sample into a series of particle size intervals and processing each interval by some gravity technique such as tabling.

The case of the firing range soils is similar to gold placer ores where the heavy metals are not locked in the matrix of the particles and do not need to be liberated by grinding. However, the liberation/gravity amenability study was very useful in evaluating the distribution of the metals through the particle size range. The liberation/gravity amenability tests identified four major characteristics of the soil which determined the process selection, (1) a size was identified where bullets and large fragments

could be efficiently collected simply by screening, (2) gravity beneficiation was very effective in recovering the free heavy metal,(3) residual lead not recovered by gravity concentration was smeared or attached to the soil grains, and (4) the lead contamination was elevated in the ultra-fine grain fraction (particle diameters less than 10×10^{-6} m) of the soil.

Gravity separation techniques were therefore selected as the first step to remove the free heavy metals from the soil. Leaching was the method selected to remove the lead smeared or attached to the soil grains and the fine lead particles, described in characteristics 3 and 4. The residual lead in the gravity tails was present as well-exposed smears and should be amenable to leaching. Selection of a lixivant involved a literature search which identified nitric acid and acetic acid as reagents that efficiently dissolve lead. Acetic acid was selected over nitric acid because it is more selective and less harsh to the environment. Laboratory tests showed that an acid concentration of 2.5 volume percent was of sufficient strength to dissolve the lead.

The volume of soil (gravity plant tailings) with smeared lead produced from a full size plant could be considerable. A method used in the mineral industry to easily leach large volumes is the heap leach. A heap leach comprises piling the soil on some kind of impervious liner, pumping the leach solutions onto the heap, and collecting the solution after it has percolated down through the heap. This method allows for construction of the heap as fast as the tailings are produced. The soil can then be leached upon completion of the heap without throughput constraints.

The fines cannot be placed in the heap because they will inhibit percolation of the leach liquor. Therefore, the fines are leached in agitated tanks as they are produced. Since the duration of this leach could run for days, the rate the fines could be processed would be limited to a rate slow enough to fill reasonably sized and quantity of mixing tanks. The controlling step in the digestion of lead by acetic acid is the oxidation of elemental lead. This required the addition of an oxidizer to the leach liquor; bleach (NaOCl) was found to be an effective oxidant.

METHODOLOGY

The pilot-scale study at MCB Camp Pendleton demonstrated methods to remove three forms of metal contamination: large fragments, fines and smears. The plant was divided into three main circuits, the gravity plant, fines leach, and heap leach circuits. Each circuit is briefly described below.

The <u>gravity plant</u> removed the large bullet fragments.

1. First the soil was screened into three size fractions;

   a. The coarsest size fraction contained particles larger than 0.25 inch.

   b. The middle size fraction (minus 0.25 plus 0.05 inch) was processed by a mineral jig.

   c. The undersize (minus 0.05 inch) from the second screen was fed to a classifier.

2. The mineral jig used a pulsed upward flow of water to collect the metal fragments which settle into the concentrate hutch. The lower density soil particles spilled over the top and were used to construct the heap pile.

3. The classifier removed the fine particles or fines (<0.003 in.) from the minus 0.05 inch fraction. With the fines removed, the classifier sand fraction was then fed to a spiral concentrator.

4. The densest fraction of the classifier sand was collected by the spiral concentrator (the concentrate) and fed to a shaking table where the lead concentration was upgraded and the rest of the classifier sand joined the jig tailings to construct the heap pile.

5. The fines from the classifier were first fed to the Mozley Multi-Gravity Separator (MGS) which removed lead particles larger than 5×10^{-6} m. The tailings from the MGS were fed to the fines leach circuit.

The fines leach circuit was run concurrently with the gravity plant and leached the MGS tailings to extract the fine lead. The leach solution was then washed from the residue in a three-stage wash. The lead-bearing water was recycled after the lead level was reduced using beads containing a metal-sorbing biomass. This lead-bearing water was batch fed into tanks containing the beads. This was continued until the beads reached the break through point and could not remove any more metals. The metals were then stripped from the beads using a nitric acid solution. The beads were then reconditioned with a sodium hydroxide solution before being reused to clean more water. Leach solutions were kept separate from the gravity circuit water to reduce the volume of water requiring extensive cleaning prior to disposal.

The heap leach pile was constructed using the tailings produced while the gravity plant was in operation. Following the week-long test of the gravity plant, the heap was leached using a dilute acetic acid and bleach solution.

RESULTS

The overall on-site plant performance showed good results and full potential to perform as designed. The gravity circuit removed 96% of the total lead and produced four lead-bearing byproducts. The coarsest soil fraction contained 78% of the total lead, the mineral jig collected 13%, the spiral/table collected 4%, and the MGS collected 1%. The gravity circuit lowered the lead contamination from 1.2% to 0.05%. The heap residue, after the 4-day run, had 2 out of 20 soil samples pass the TCLP limit (5 Mg/l Pb) with values about 3 Mg/l Pb. About 10% of the soil had a TCLP lead value of 6.5 Mg/l Pb. The overall average was 10 Mg/l Pb, showing that the leach was terminated prematurely and has the potential to clean the soil. The fines leach circuit tested three leach conditions with one of five samples approaching the TCLP value of 15 Mg/l Pb. With the fines leach residue at 15 Mg/l Pb, they could be recombined with heap leach residue (3 Mg/l Pb) producing overall clean soil (5 Mg/l Pb). There were some difficulties experienced at MCB Camp Pendleton and they are discussed below for each circuit.

The gravity circuit efficiency could be improved by preventing the following conditions. The soil was processed wet to reduce airborne lead-bearing dust. The feed pile was kept damp to reduce air emission, but resulted in the soil sticking to the feed conveyor. A second problem was low screen efficiency with 10 to 20 weight percent of the undersize from each screen short circuiting to the oversize fraction. This resulted in lower efficiencies for the concentrating equipment, the mineral jig, and spiral/table. This drop in efficiency can be easily seen in table 1 which gives the analysis of screen fractions of the jig feed and tailings. The short circuit fraction contained 9.8% of the lead in the feed, but 70% of the lead in the tails. The jig very effectively removed the lead from the - 0.25 + 0.05 inch size fraction, dropping the grade from 0.32% to 0.009% lead. Even with the short circuited undersize, the jig efficiency was 95%.

TABLE 1. COMPARISON OF JIG CONCENTRATION EFFICIENCY ON DESIRED FEED SIZE AND SHORT CIRCUITED UNDERSIZE

	Jig feed			Jig tailings		
		Lead, %			Lead, %	
Size interval, inch	Weight percent	Grade	Dist	Weight percent	Grade	Dist
- 0.25 + 0.05	85.8	0.32	90.2	83.0	0.009	29.9
- 0.05	14.2	0.21	9.8	17.0	0.103	70.1

The fines leach circuit experienced difficulty in keeping the fines suspended. This was largely due to improper size and shape of the rented tanks, tanks of the desired specifications were not available.

The heap leach circuit could be improved by two changes; first, improved screening will raise the concentration efficiency by processing each particle size interval in the proper apparatus. Second, a longer heap time will allow the acetic acid to pass completely through the heap pile coming into contact with more of the lead.

Initially, the water treatment plant effectively removed the lead from the fines wash water, allowing it to be recycled with very low recirculating lead loads. During the first two load-strip-recondition cycles, the beads removed over 95% of the lead in the liquor. However, after the third cycle, the beads lost their loading capacity, see table 2. The system does not appear to be over loaded with lead as can be seen by the similar cycle feed concentrations; the problem appears to be in the stripping. The nitric acid solution was recycled for the first five cycles without any regeneration. After cycle number 5, the lead from the stripping acid was precipitated with sodium sulfate and more nitric acid was added (but not to the strength of the original strip). This regeneration step appeared to restore only part of the loading capacity. Attempts to clean the water prior to final disposal were marginally successful due to this lowered loading capacity of the beads. Further studies are being conducted to solve this problem.

TABLE 2. LOADING EFFICIENCY OF THE IMMOBILIZED BIO-MASS BEADS IN REMOVING LEAD FROM LEAD BEARING FINE WASH WATER

		Percent of lead removed, 1 period = 400 liters					
Cycle	Cycle feed, Mg/l Pb	Period 1	Period 2	Period 3	Period 4	Period 5	Period 6
3	131	87	81	70	74	75	66
4	150	87	30	26	9	NR	NR
5	146	44	8	0	0	0	0
7	222	74	61	49	44	38	31

NR Not run.

Recycling heavy metal byproducts for their metal content was another goal of this research. There were five lead-bearing byproducts resulting from cleaning the soil in the on-site plant, the pounds of product per ton of soil processed is provided in the {}:

1. The plus 0.25 inch fraction was upgraded from about 5% metal to 82% metal by using a water elutriator, {82}.

2. Mineral jig concentrate (can be upgraded to 82% metal by elutriation), {2.8}.

3. Non-magnetic fraction of the shaking table concentrate (50% lead), {1.6}.

4. MGS concentrate. From processing the minus 0.003 inch fraction of the soil and includes metal fragments down to 3×10^{-6} m (1.3% lead), {13}.

5. A sulfate precipitate is produced from the water treatment which is mainly calcium, 20% with 2.5% lead, {not determined}.

Two secondary lead smelters were sent samples of these products, plus one sample made of weighted portions of samples 1 through 4. They felt samples 1, 2, 3, and the weighted combination, could technically be recycled but there were significant problems.

The copper content is very high and unless the smelter has a copper bleed from their circuit, there would be a recirculating load problem if significant quantities were recycled. However, they felt there are applications where these byproducts could be used. The other contaminates (soil) would reduce the metal value and increase the amounts of waste to be disposed. Both of these problems reduce the value of these byproducts. The price that would be paid for these materials is very low because of the abundance of lower-contaminated scrap. One smelter concluded that limited quantities could be accepted but they would have treatment charge beyond the value of their metal contents.

Samples 4 and 5 are too low in metal content and neither smelter felt they could, by themselves, be recycled.

CONCLUSIONS

This on-site test was very beneficial toward commercialization of this technology. First, it was established that a plant of this nature could be transported to a contaminated site, reconstructed, and operated. Second, the importance of efficient screening and classifying was learned. Third, the immobilized bio-mass beads appear to be a viable method of treating lead-bearing liquors produced from the leach circuits if the stripping stage is improved. Fourth, the heap leach residue approached the TCLP limit for lead. This, coupled with the bench scale work and in-house pilot plant work, seems to show the technology will work. Finally, though the fines leach residue failed the TCLP, the lead contamination was lowered. With more efficient leach conditions, the TCLP value might be lowered to allow a single cleaned soil product when combined with the heap residue.

The SLRC and NFESC are in the planning stages to perform a second on-site demonstration plant. This second plant will be used to evaluate engineering changes made after the MCB Camp Pendleton project, capable of removing lead contaminates from all Navy small arms range impact berms, and to finalize the engineering data needed to construct a full size mobile plant.

FOR MORE INFORMATION

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ACOUSTIC BARRIER PARTICULATE SEPARATOR

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The acoustic barrier particulate separator is a new technology for separation of particulates in a gas flow. The purpose of this study is to design, construct, and test a pilot scale device. The technology, previously demonstrated at the lab scale, is applicable to removal of particulates from the off-gas stream of incinerators and thermal treatment processes. The pilot scale system is a 300 cfm prototype module suitable for parallel arrangement to treat larger gas flows.

The test gas is generated by heating an air stream, then injecting a measured dust feed into it to produce a synthetic flue gas. The test gas flows through a muffler into an acoustic agglomerator section, then vertically against an acoustic wave of a specific waveform propagating opposite the gas flow. The acoustic wave exerts a nonlinear force on the particulates such that they are stagnated and drift to the wall of the separator chamber. There the particulates form cake that falls into a solids collection hopper that also serves as an acoustic absorber. The clean test gas flows around the acoustic horn and out through another muffler.

The sound is generated using a gas siren. The waveform is tailored by the pattern of apertures in the siren rotor and stator. The spent siren air is diverted by an isolator to minimize dilution of the test gas. The siren air is generated by a blower and flows through mufflers both before and after the siren.

The pilot scale test will integrate two separate acoustic effects to provide for removal of the entire spectrum of particulate sizes. Acoustic agglomeration will be used to convert fines to larger aggregates, and the acoustic barrier effect will be used to remove those aggregates.

Subscale testing is scheduled to begin in May 1993. This will be followed by up to full scale operation in unheated gas, then prototype testing in heated gas.

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Terra Vac has designed, installed and operated over 300 in-situ remediation systems based on air-driven techniques. Air-driven techniques rely on the mass transfer of contaminants from the dissolved, adsorbed, vapor and free phase to the vapor phase. These techniques are typically orders of magnitude faster when compared to pump and treat. The air-driven techniques will generally include the process of vacuum extraction for the recovery of the contaminant. Several enhancements have been developed to increase the effectiveness of vacuum extraction (VE) in different hydrogeologic settings, address different contaminant types, and allow VE to be combined synergistically with other techniques to address not only the unsaturated soils, but contamination in the saturated zone also.

One major development has been the Dual Vacuum Extraction technology. This technique combines VE with groundwater recovery, thus remediating both the source and contaminated groundwater. In some situations, Groundwater Sparging (the injection of air into the aquifer) can be combined with VE to also address the source and contaminated groundwater, especially when disposal of groundwater is a problem. In low permeability settings, Terra Vac has successfully used VE combined with Pneumatic Soil Fracturing (injection of high pressure air into the clays to create subsurface flow paths) to achieve site closure. Other, less aggressive techniques, BioVac and Biosparging, rely on enhancing the natural rates of biodegradation of petroleum contaminants by increasing the subsurface oxygen levels with VE.

Each of these techniques has been developed to further improve the effectiveness of the basis vacuum extraction technology. These enhancement techniques now provide a toolbox of technologies, all based on vacuum extraction, which can remediate soils and groundwater, address low permeability soils, or use natural biodegradation to remediate soils and groundwater.

For More Information Contact: Robert Piniewski, Terra Vac, Midwest Division (800) 825-0013 or Rolf Laukant, Terra Vac, One Oak Hill Center, Westmont, IL (708) 850-9358

Applications of Chemical Oxidation and Electrochemical Iron Generation for Removing Arsenic and Heavy Metals from Water

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As a result of many power generation operations, groundwater and/or surface water has been contaminated with arsenic and heavy metals. Simultaneous extraction is complicated due to the various chemical properties that metals exhibit. A comprehensive understanding of solubilities, oxidation states, and adsorptive mechanisms is needed to accomplish treatment objectives. This paper uses data from treatability and pilot studies to discuss the electrochemical iron addition process developed by Andco Environmental Processes, Inc. Sacrificial steel electrodes were used to put ferrous ions into solution. Adjustment to an optimum pH resulted in excellent adsorption and coprecipitation with a ferrous hydroxide floc. When extremely low residual arsenic concentrations were needed, an oxidizing environment improved treatment. Hydrogen peroxide was used to convert Fe^{+2} to Fe^{+3} and arsenite to arsenate. By rapidly and efficiently shifting the existing equilibrium state, having all of the aqueous arsenic as arsenate, and adjusting pH to create conditions for 100% anion adsorption, arsenic concentrations below 5 μg/l were achieved. The formation of ferric solids (hydroxide, arsenate) and improved adsorption on the hydrous ferric oxide floc accounted for increased removal efficiencies. When the necessary treatment conditions were created and maintained, removal by three major mechanisms resulted in an iron sludge that was able to pass the regulatory levels listed in conjunction with the Toxicity Characteristic Leaching Procedure (TCLP). Presented data confirms that arsenic, mercury, cadmium, chromium, lead, selenium, and copper can be removed simultaneously using this treatment process.

"APPLICATION OF FULL-SCALE SOIL/SEDIMENT WASHING FOR THE U.S. CORPS OF ENGINEERS & TORONTO HARBOUR COMMISSIONERS"

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During 1991 and 1992, **Bergmann USA** provided a 5-10 TPH Soil/Sediment Washing System to the U.S. Army Corps of Engineers for the full-scale demonstration of volumetric reduction and waste minimization of PCB contaminated dredge spoil from the Saginaw River in Michigan. The demonstration project was conducted under the ARCS (Assessment and Remediation of Contaminated Sediments) Program.

This plant was placed into operation in October 1991 a mile and a half off shore aboard a 120'x33' Army Corps of Engineers dredge support barge. Results indicated a reduction of 88% of the initial PCB concentration with only .2 mg/kg of PCBs remaining in the "clean" coarse +45 micron (325 mesh) fraction. The -45 micron fines were enriched to a maximum level of 14 mg/kg PCBs, and the humic fraction (leaves, twigs, roots, grasses, etc.) contained up to 24 mg/kg of PCBs. These materials were scheduled for a biodegradation during the Summer of 1992. Working with the EPA Hazardous Waste Engineering Research Laboratory in Cincinnati, this **Bergmann USA** system was evaluated by the Superfund Innovative Technology Evaluation (SITE) Program in May/June 1992.

Bergmann USA was contracted with the Toronto Harbor Commission in the operation of a 5-10 TPH Soils Washing system for the demonstration of volumetric remedial operations coupled with an innovative metal extraction and biodegradation technologies for the treatment of the -63 micron fines fractions. With the receipt of permits from the Ontario Ministry on the Environment, the demonstration commenced the first week of January 1992 (-10°F) concluding the initial Phase I operations in September 1992. Five varying contaminated soil feeds were processed by the **Bergmann** plant. In addition, the Wastewater Treatment Centre of Environment Canada contracted to have the **Bergmann** plant process 500 tons of contaminated Toronto harbor sediment, and the Canadian Ministry of Defense had the **Bergmann** plant process 200 tons of lead contaminated material shipped in from Montreal from the Longue Pointe Garrison Site. Based upon the results of this demonstration project, it is anticipated that a full-scale plant would then be designed for installation for a three year, 85 TPH (300,000 tons per year) remedial project of the Toronto harbor front area. This project was conducted for the Toronto Harbour Commissioners and evaluated under the USEPA's SITE Program.

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APPLICATION OF SONOTECH'S CELLO BURNERS IN SUPERFUND SITES CLEANUP APPLICATIONS

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Sonotech has developed a novel, frequency tunable, Cello® burner that burns the fuel in an oscillatory combustion process. Typically, the Cello® burner is used to supply process energy and generate sound that is used to improve the incineration process performance. In a Superfund application, a Cello® burner of needed capacity is retrofitted to the incineration system and operated at a frequency that excites large amplitude sound waves within the incinerator. The gas oscillations that accompany the excitation of the sound increase the rates of mixing, heat and mass transfer within the incinerator, resulting in a drastically improved incineration process. The increase in the rates of transport processes improves the efficiency of the incineration process, resulting in lower emissions of soot, CO and unburned hydrocarbons, which are often responsible for puff formation. Furthermore, the improved mixing reduces the amount of air needed (by other burners) to completely burn the waste, which reduces operating and capital investment costs associated with the use of large air and gas handling systems. Also, the reduction in process air flow requirements, reduces stack losses, lowering the process fuel consumption. Also, the improved mixing eliminates hot spots within the incinerator, resulting in lower NO_x emissions. Finally, since the performance of the incineration system is controlled by the excited sound waves (and not by the gas velocity), it does not deteriorate when the incinerator is operated at part load, as is often the case when conventional burners are used.

The Cello® burner can improve the performance of existing and new incineration systems. When retrofitted to an existing incinerator, the Cello® burner improves the system's performance and it may increase its capacity. On the other hand, when it is retrofitted to a new incineration system, it reduces the size of the incineration system required (when conventional burners are used) to attain complete incineration, which reduces capital investment costs.

APPLICATIONS OF TRANSFERRED AND NON-TRANSFERRED PLASMA TORCHES IN HAZARDOUS WASTE TREATMENT

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Plasma technology for treatment of hazardous waste uses heat from a plasma torch to treat hazardous waste containing metals and/or organics. Retech's experience using transferred and non-transferred plasma torches will be presented. Relevant aspects of a treatment system design will also be presented. The merits of transferred and non-transferred plasma torches to melt metal-bearing solids and soils as well as thermally destroy organics will be compared and contrasted.

Retech has been developing plasma torches since 1970 when a license from Linde Division of Union Carbide was obtained. Over the years, Retech has produced more than 20 megawatts of plasma melting equipment for the vacuum metallurgical industry. To date, approximately 90% of the plasma equipment has been of the transferred arc type. Retech's attempt to develop equipment for treating hazardous waste is based on our vacuum metallurgical/controlled atmosphere background. So far our experience with contained treatment of hazardous waste has led to an awareness that a reliable, non-transferred plasma arc torch can offer definite advantages to the treatment system.

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BIOLOGICAL REMOVAL OF PERCHLOROETHYLENE FROM SATURATED SOILS

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ABB Environmental Services Inc. has conducted EPA sponsored research into the feasibility of using enhanced bioremediation for the restoration of Perchloroethylene (PCE) contaminated aquifers. The study was funded under the Emerging Technologies component of the SITE program.

PCE contaminated water was pumped through bench-scale saturated soil columns and the proposed in situ bioremediation process was simulated. Simultaneous microbiological studies were also carried out to help define the operating requirements. Two approaches to PCE degradation were evaluated; anaerobic dechlorination of PCE, yielding ethylene as the end product, and sequential anaerobic/aerobic degradation of PCE in which PCE is partially dechlorinated anaerobically and then further degraded by aerobic methane oxidizing bacteria, yielding carbon dioxide as the end product.

Results suggest that complete PCE dechlorination can be accomplished in situ at many sites by the engineered enhancement of indigenous anaerobic bacteria. Vinyl chloride is expected to be a significant intermediate product in this process. Therefore, under many circumstances sequential anaerobic/aerobic treatment may be desirable.

Data demonstrating both anaerobic and anaerobic/aerobic degradation of PCE in bench-scale will be presented, and the respective processes will be discussed. Data will also be presented which show that this process may be applied to dense nonaqueous phase liquid (DNAPL). Proposed field approaches will be presented and discussed.

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BIOREMEDIATION OF CYCLODIENE PESTICIDE-CONTAMINATED SOIL

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Cyclodiene insecticides, such as chlordane and heptachlor, have been applied for years in the preventative treatment of wood frame structures against termites. Cyclodiene pesticides have been determined to be one of the top 50 most frequently found contaminants at Superfund sites (52 FR 12866, 1987). The U.S. Environmental Protection Agency (EPA) has classified chlordane and heptachlor as priority pollutants and has mandated the restoration of impacted sites. Therefore, there is a great need for effective and cost-efficient remediation technologies.

Preliminary laboratory studies conducted by our laboratory and others have shown that bioremediation is a potentially viable method for treating soils contaminated with chlordane and heptachlor. However, its effectiveness as a treatment technology has not been demonstrated under field conditions. Additionally, some studies have indicated that these compounds can be persistent under natural soil conditions, and resistant to biodegradation by indigenous soil microbial populations.

Several species of lignin-degrading fungus have been shown to degrade recalcitrant organic contaminants, including chlorinated aromatic hydrocarbons, under select conditions. The efficacy appears to be due to the generation of enzymes which are used to metabolize naturally-occurring complex polymers such as lignin. The objective of the present study is to examine the ability of certain fungal strains to metabolize chlordane and heptachlor in a soil matrix. This is being done in laboratory microcosm studies examining degradation kinetics and the various factors influencing microbial activity. Following these tests, a pilot-scale soil reactor study will be conducted with the goal of demonstrating the effectiveness of fungal bioremediation under conditions simulating a field operation.

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BIOVENTING PAH CONTAMINATION AT THE REILLY TAR AND CHEMICAL CORPORATION SITE, THE FIRST YEAR RESULTS

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Bioventing is a proven technology for in situ remediation of various types of hydrocarbon contaminants. The technology has been successfully used to remediate sites contaminated with gasoline, aviation fuels (JP-4 and JP-5) and diesel fuel. This demonstration evaluates the potential of bioventing to remediate soils contaminated with polycyclic aromatic hydrocarbons (PAHs).

The Reilly Tar and Chemical Corporation Site is an abandoned wood-processing facility contaminated with creosote. The site has appropriate PAH concentrations, geologic characteristics, and responsible parties willing to establish a cooperative effort.

The pilot field study features active venting and monitoring of a "treatment area" and monitoring of a "no treatment control area." These two areas (50 feet x 50 feet) were chosen at the site after a soil gas survey. Composite soil samples (120 soil borings per area) used for PAH analysis, were prepared by homogenizing the soil obtained from the 4-8 foot depth of each boring. The resultant bore holes were filled immediately with bentonite. A single vent bioventing system was installed at the center of the "treatment area." The vent (injection) well was screened from 7-15 feet below the surface and packed with sand. T he vent well was then sealed with bentonite from the 7 foot depth to the surface. Twelve soil gas probes were installed along diagonals drawn from the corner of the square "treatment area," and four were installed in the corners of the "no treatment control area." The soil gas probes were constructed so that the soil gas withdrawal points and thermocouples were located at 4, 6 and 8 feet below the ground surface. Initial O_2 and CO_2 measurements were obtained as percetages of total soil gas using the gas probes in both areas. The blower was turned on for 24 hours, then turned off. An initial respiration test was conducted by withdrawing gas samples and measuring O_2 and CO_2 levels at measured intervals over a period of 48 hours. The blower was again turned on, and the air flow to the area was set at 10 cfm (3.5 inches of H_2O). Shut down-respiration tests are being conducted quarterly. The first two quarterly respiration tests lasted five days. Subsequent quarterly tests were conducted for two weeks.

Shut down-respiration tests have shown respiration rates ranging from below detection to 0.484 percent O_2 per hour. The highest respiration rates were found in the western half of the "treatment area" where PAH contamination was also shown to be the heaviest. Current measured respiration rates are consistent with a 14% reduction in PAH contamination per year.

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CAPABILITIES OF A TRAILER-MOUNTED DEBRIS WASHING SYSTEM DEVELOPED UNDER THE SITE PROGRAM

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IT Corporation has, under the EPA SITE Program, developed a full-scale, transportable, semi-automated debris-washing system (DWS) that can be used on site for the decontamination of debris. The debris-washing technology was recently utilized at the Summit Scrap Site in Akron, Ohio, by IT Corporation. During the 4-month period of this site remediation, 3000 tons of PCB-contaminated metallic debris were cleaned and the level of PCBs was reduced to $<7.7\ \mu g/100\ cm^2$. The decontaminated debris was subsequently sold to a scrap dealer.

In this poster presentation we describe IT's full-scale, trailer-mounted debris-washing system and present costs for on-site treatment of metallic debris.

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Combined Anaerobic In-Situ/Aerobic Ex-Situ Bioremediation of Chlorinated Ethenes Using an Immobilized Cell Bioreactor

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AlliedSignal Environmental Systems and Services has developed a fixed film bioreactor system that utilizes a high surface area polymer support that is coated with an active layer of powdered activated carbon. The biomass support matrix is a porous polyurethane foam with a surface area greater than 200 square feet per cubic foot. This support matrix is coated with a powdered activated carbon using a proprietary procedure that maintains the carbon in an activated state. The carbon coated foam support is mixed with a polypropylene HiFlow pall rings to provide good mass transfer and fluid dynamic characteristics.

This system is being evaluated for the co-metabolic oxidation of chlorinated ethenes using phenol as the co-substrate. Groundwater contaminated with a mixture of trichloroethylene, cis-dichloroethylene and vinyl chloride is pumped to the bioreactor system. Phenol and air are introduced to the bioreactor for co-metabolism of the chlorinated ethenes. The reactor utilizes both a submerged fixed film and a vapor phase biofilter to ensure that the chlorinated ethenes are biodegraded and not removed by air stripping. Biodegradation of TCE is greater than 99% in the bioreactor system.

The ex-situ bioreactor system can be utilized with an in-situ anaerobic reductive dechlorination step. Organic nutrients are introduced into the soil to promote reductive dechlorination of TCE to cis-dichloroethylene and vinyl chloride. These compounds are more readily desorbed from the soil matrix and can be recovered in the groundwater for biodegradation in the above ground bioreactor. This technology will be demonstrated under the EPA SITE program at the St. Joseph superfund site, St. Joseph, Michigan in the summer of 1994.

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Contaminated Soil Treatment Through Davy International IPDOCS Process

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ABSTRACT

Davy International has been developing a unique resin-in pulp and carbon-in pulp (RIP/CIP) for the treatment of contaminated soils through the EPA site emerging technology demonstration program. Davy has named this process the in-pulp decontamination of contaminated soils process (IPDOCS). The process is based on utilizing either resin or activated carbon in a pulp mode to recover metals or to remove heavy metal or organic content contaminants from contaminated soils, sludges, dredgings or sediments. These processes are based on unit operations utilized in the mining and mineral processing industries. The IPDOCS process is similar to soil washing or solvent extraction. Feed material is sized prior to entering an agitated tank where a leach reagent is added to extract the contaminants of concern. The leached solids are then passed through cyclones to separate coarse and fine materials. The coarse materials is washed and sent to disposal. The fine material in a wash solution pass to a RIP/CIP contactor where the contaminants are adsorbed on ion exchange resins and/or activated carbon. The resin of carbon pulp is separated from the fine fraction and is sent to a second contactor for elution and further concentration of the contaminants. The regenerated resin or carbon is then reused and the concentrated contaminants are further treated or recovered. The clean/fine fraction is dewatered and disposed or recycled.

Davy has been employing bench-scale proprietary RIP/CIP technology to develop criteria for a 2-ton per day demonstration plant capable of treating a wide range of contaminated soils, sediments and sludges. Davy has developed preliminary cost estimates for a full system for a number of different heavy metal contaminants of concern. This program is continuing with further defining of process strings for larger scale application.

CONTROLLED VAPOR CIRCULATION IN SUBSURFACE MATERIALS TO ENHANCE THE BIOREMEDIATION OF ORGANIC CONTAMINANTS

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The Subsurface Volatilization and Ventilation System® (SVVS®) is a bioenhancement process that promotes the removal and destruction of many xenobiotic organic compounds in subsurface materials. This technology is applied to promote the growth and activity of certain aerobic heterotrophs native to aquifer materials that are capable of metabolizing or cometabolizing these compounds. SVVS® delivers and circulates the terminal electron acceptors required for the microorganisms to complete oxidation/reduction reactions that result in the transformation or mineralization of the organic contaminants. Typically, this is accomplished through injection of oxygen-saturated air to the subsurface. Consequently, compounds possessing high vapor pressures and of low molecular weight may also be "stripped" from affected media by the circulating air. Stripped constituents captured within the vapor extraction component of the system are treated ex-situ with biofilters before discharge.

SVVS® currently is being studied under the Superfund Innovative Technology Evaluation program to evaluate its effectiveness for remediating petroleum and chlorinated aliphatic hydrocarbons in soil (alluvial sands), groundwater, and buried paint sludge. Prior to design and construction of the demonstration system, microbial enumerations and geochemical and contaminant profiles were developed for the site through extensive soil sampling and analyses. This information was used to estimate the volume of contaminated media and evaluate the potential for bioenhancement in the affected materials. In-situ respiration tests were also conducted. The results suggested that the soils originally possessed a viable population (10^5 cells/gram of dry soil) of microorganisms that were actively degrading the contaminants of concern. After initiation of the demonstration in March 1993, soil and offgas monitoring data were collected to evaluate the stimulation of the indigenous microflora by SVVS® and corresponding contaminant destruction by bioremediation, and to calculate mass removals promoted by the vapor extraction component of the system. These data suggest that, in seven months, at least 70% of the original contaminant mass has been remediated by SVVS®. Further, it appears that the indigenous microbial population has increased to approximately 10^8 cells/gram of dry soil, and that over 40% of the total contaminant mass remediated was destroyed in-situ through biologically-mediated chemical transformation reactions.

For more information contact Timothy J. Mayotte at the address and phone number listed above.

THE CROW™ PROCESS FOR IN SITU TREATMENT OF HAZARDOUS WASTE SITES

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The CROW™ process is an in situ remediation process for dense organic liquids such as coal tars, chlorinated hydrocarbons, and heavy petroleum products that have contaminated groundwater at numerous domestic and international industrial sites. Laboratory tests of the process using materials from MGP and wood treatment sites indicated that 60 to 70% of the MGP contaminant and 84 to 94% of the wood treatment contaminant can be recovered at the optimum water flushing temperature. Additionally, removals of 90% or greater can be achieved for MGP materials if surfactants, at 1% by volume, are incorporated into the flush water.

Plans for the full-scale remediation of a wood treatment and a MGP site are presently being implemented. The MGP site is a Superfund Site located in Stroudsburg, Pennsylvania. This remediation will involve the use of six injection and two recovery wells. The project is scheduled to begin operation in June 1994. The wood treatment project is located at the Bell Lumber and Pole facilities in New Brighton, Minnesota. The full-scale remediation is scheduled to being in the summer of 1994 and will be carried out as a staged remediation using three five spot patterns. Prior to implementing the full-scale project at Bell Lumber, a pilot test was operated to demonstrate the containment and organic removal features of the CROW process. The pilot test was a success in both areas.

If further remediation of a site is required, the use of bioremediation following the CROW process has been evaluated by Remediation Technologies Inc. (ReTeC). ReTeC has been successful in evaluating in situ bioremediation processes for treatment of CROW conditioned soils. In addition, biological treatment of CROW process product water was demonstrated. Biological treatment of the CROW product water is being incorporated into the Stroudsburg, Pennsylvania project.

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DEMONSTRATION OF AMBERSORB® 563 ADSORBENT TECHNOLOGY

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The overall objective of this SITE project is to demonstrate the technical feasibility and cost effectiveness of Ambersorb 563 carbonaceous adsorbent for the treatment of groundwater contaminated with volatile organic compounds (VOCs). Ambersorb carbonaceous adsorbents are a family of patented, synthetic, tailorable adsorbents that were developed by the Rohm and Haas Company, Philadelphia, PA in the 1970's for the remediation of contaminated water.

One of these adsorbents, Ambersorb 563, has been found to be extremely effective in the removal of low levels of VOCs and synthetic organic compounds (SOCs) from contaminated water. Previous applications using Ambersorb adsorbents have shown that they exhibit several key performance benefits over granular activated carbon (GAC). Ambersorb 563 adsorbent can be regenerated on-site using steam. Ambersorb 563 adsorbent has approximately five to ten times the capacity of GAC for VOC contaminants, such as chlorinated hydrocarbons, when the contaminants are present at low concentrations. Ambersorb 563 adsorbent can operate at higher flow rates than GAC, while maintaining effluent water quality below drinking water standards.

The Ambersorb technology demonstration will consist of a continuous pilot (1 gallon per minute) field study at Site 32/36 at Pease AFB, Newington, NH. The field testing program, scheduled to begin in April 1944, will consist of four service cycles and three steam regenerations over a period of approximately eight weeks. The pilot unit includes two adsorbent columns that will allow direct comparison of the performance of Ambersorb 563 adsorbent to GAC. The quality of raw contaminated groundwater (influent) and treated effluent will be monitored for VOCs during each service cycle in order to establish breakthrough curves. In addition to monitoring for VOCs, selected influent and effluent column samples will be measured for pH, conductivity, and alkalinity. After breakthrough, steam regeneration of the columns will be performed. Steam will be used to strip the VOCs from the Ambersorb adsorbent and the condensate will be collected. The organic phase which separates from the condensate will be disposed and the aqueous phase will be treated through the Ambersorb adsorbent column to demonstrate "superloading".

Analytical results and process data will be evaluated to determine the feasibility of using Ambersorb adsorption technology in groundwater remediation as an alternative to GAC. Cost and performance characteristics of this remediation system will be developed in order to compare full-scale uses for this emerging technology to other proven treatment systems.

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DEVELOPMENT OF FUNGAL COMPOSTING SYSTEMS FOR DEGRADATION OF POLYAROMATIC HYDROCARBONS ASSOCIATED WITH MANUFACTURED GAS PLANT SITES

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During the first half of this century, the production of manufactured gas from coal resulted in waste products containing a wide range of polyaromatic hydrocarbons. There are over 2000 contaminated manufactured gas plant (MGP) sites throughout the United States and the cost of remediation of these sites is estimated to range between $4-6 billion using conventional technology.

In two research and development programs sponsored by the Electric Power Research Institute (EPRI), over 15,000 fungal cultures were initially screened for their potential to degrade polyaromatic hydrocarbons (PAH). Over 500 cultures were screened in a laboratory robotics program that generated over 500,000 data points on how these fungal cultures responded to various environmental nutrient conditions and organic pollutants. From this screen, top cultures were identified for specific chemicals and environmental conditions. Control cultures such as *P. chrysosporium* and *C. versicolor* were used to calibrate how other fungal species responded in these tests in comparison to these well studied cultures. For most hazardous chemicals examined, many fungal cultures were identified that had enhanced potential in comparison to the two control fungal cultures described above.

In a related program at Michigan Biotechnology Institute which was also sponsored by EPRI, fungal composting systems were developed which would support these fungal cultures. Results in soil pan experiments with selected cultures showed that fungi could degrade the 2, 3 ,4, 5, and 6 ring PAH chemicals in soils.

Environmental Biotechnologies Inc, in a grant received from the EPA SITE Emerging Technology Program, will continue the development of fungal systems for PAH degradation and apply this process to soils contaminated with MGP wastes. This EPA sponsored program will examine 20 fungal cultures ranked high for PAH degradation as identified in the earlier screening program The focus of this program, which started in late 1993, is to optimize degradation conditions for the cultures which degrade PAH, scale up the process to small scale, and determine the effectiveness of this process for applications in the utility industry.

DEVELOPMENT OF THE UDRI PHOTOTHERMAL DETOXIFICATION UNIT

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There has long been interest in utilizing photochemical methods for the detoxification of hazardous organic materials. Unfortunately, classical, low temperature (i.e., ambient or near ambient temperature) photochemical processes are either too slow or fail to sufficiently mineralize the targeted wastes to be practical for wide spread use. Researchers at the University of Dayton Research Institute (UDRI) have recently developed a unique photothermal process that overcomes many of the problems previously encountered with photochemical detoxification techniques. It has been shown elevated temperatures (i.e., >200°C) significantly increase the rate of destructive photothermal reactions and that these reactions result in the complete mineralization of the organic components of the waste feed. Furthermore, it has been demonstrated that elevated temperatures that the spectral region of absorption broadens and shifts towards the visible portion of the electromagnetic spectrum thereby increasing the efficiency of the absorption of ultraviolet (UV) radiation with increasing temperature. These features (i.e., fast, efficient, and complete destruction of organic vapors) makes this process a promising technique for the on-site destruction of toxic organic effluents from many soil remediation technologies such as soil vapor extraction, steam extraction, and thermal desorption. In this poster the authors will present the theoretical foundation for the photothermal detoxification process along with a summary of the most recent test results from the Laboratory Scale-Photothermal Detoxification Unit (LS-PDU). The authors will also show how this data is being used to design a pilot-scale Photothermal Detoxification Unit (PDU).

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DU PONT/OBERLIN MICROFILTRATION TECHNOLOGY (SITE)

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The novel Du Pont/Oberlin Microfiltration Technology has recently been demonstrated in EPA's Superfund Innovative Technology Evaluation (SITE) program. Its key features are fine microfiltration at low cost using Du Pont's new Tyvek®* T-980 flashspun olefin filter media coupled with Oberlin's reliable automatic pressure filter (APF) and Enviroguard's PROFIX** filter aid for metals stabilization.

This new microfiltration technology is best suited for contaminated heavy metal wastewaters and groundwaters. The SITE demonstration (1990) actually removed Zn, Cu, Cd, Se and Pb from the Palmerton, PA Zinc smelting Superfund site. Basically, 99.95% removal of Zinc and Total Suspended Solids (TSS); and firm, dry (41% solids) cakes that passed both the "Paint Filter Test" and TCLP were demonstrated. Thus, this new technology provides low cost metals removal/stabilization all in one simple operation.

This poster will describe this new technology in detail, and will present some typical application results. It will also detail where it has been applied since the SITE demonstration.

For more information, please contact Mr. Mike Hughes, Oberlin Filter Co., 404 Pilot Court, Waukesha, WI, 53188, (414) 547-4900.

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* Du Pont's trademark for its flashspun HDPE nonwoven filtration media.

** Enviroguard's trademark for its patented filter aid/stabilization agent.

THE ECO LOGIC PROCESS

A GAS PHASE CHEMICAL REDUCTION PROCESS FOR PCB DESTRUCTION

Douglas J. Hallett, Ph.D.
Kelvin R. Campbell, P.Eng.

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The ECO LOGIC Process is a mobile and highly efficient destruction alternative to incineration. The process is based on a gas phase chemical reduction of hydrogen with organic and chlorinated organic compounds. At 850°C or higher, hydrogen combines with organic compounds to form smaller, lighter hydrocarbons, primarily methane. For chlorinated organic compounds, such as PCBs, the reduction products include methane and hydrogen chloride. This reaction is enhanced by the presence of water, acting as a reducing agent and a hydrogen source. Destruction removal efficiencies (DREs) of 99.9999% can be achieved.

A distinct advantage of the ECO LOGIC Process over incineration is that there is no possibility of dioxin or furan formation. In an actively reducing atmosphere with an abundance of free hydrogen and no free oxygen, the possibility of their formation is eliminated.

The use of hydrogen also creates a product gas of low molecular weight without the formation of heavier hydrocarbons common to pyrolysis processes. This product gas is continuously monitored by a very sophisticated on-line mass spectrometer measures organic compounds in the parts per billion range. Effective monitoring of destruction efficiency is accomplished by selectively analyzing for trace concentrations of known breakdown products of the hazardous waste.

This high efficiency has been demonstrated with PCBs, PAHs, chlorobenzenes, and organochlorine pesticides. The ECO LOGIC Process was demonstrated as part of the US EPA Superfund Innovative Technology Evaluation (SITE) Program at Middlegrounds Landfill, Bay City, Michigan. This site is contaminated by a dense oil containing approximately 40% PCBs. This oil, contaminated groundwater and contaminated soil were processed in separate streams. The evaluation was performed by the US EPA. A destruction removal efficiency for PCBs of 99.9999% was obtained for each of the test conditions.

The ECO LOGIC Process can be applied for the destruction of contaminated soils and sediments, and is also suitable for high-strength organic hazardous wastes such as obsolete pesticides, warfare agents, and industrial by-products.

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ELECTRON BEAM TREATMENT OF UNCONTROLLED HAZARDOUS WASTE LEACHATE

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The need for effective treatment technologies in destroying multi-source hazardous waste leachate is expanding as increasingly stringent regulations are being enacted to remedy past as well as prevent future environmental contamination. Multi-source hazardous waste leachates are of particular concern because these complex components are commonly found in groundwater and surface waters, and have the ability to persist in the environment for long periods of time. The contaminants discussed in this paper typically originate from industrial process wastewater, spills, contaminated landfill leachate and groundwater, or disposal operations associated with various governmental and/or civilian installations. The specific contaminants include halogenated solvents, aromatic hydrocarbons, polychlorinated biphenyls (PCBs), explosives, etc.

High energy electron beam (E-beam) treatment has proven to be an effective process for destroying hazardous organic compounds in aqueous solution. E-beam treatment is based on aqueous radiation chemistry where relatively high concentrations of hydroxyl radical (OH·), aqueous electron (e^-_{aq}), and hydrogen atom (H·) are generated when high energy electrons penetrate water. Because the resulting solution contains both oxidizing (OH·) and reducing (e^-_{aq}, H·) radicals, the process is effective in treating a myriad of individual organic compounds as well as complex mixtures commonly found in industrial wastewaters, landfill leachate, and contaminated surface and groundwater. High Voltage Environmental personnel have studied many of the regulated hazardous compounds at the Electron Beam Research Facility (EBRF) located in Miami, Florida. The EBRF houses a 1.5 MeV, 50 mA electron accelerator and water pumping systems capable of delivering 160 gallons per minute. The variable current allows for absorbed radiation doses between 0 and 800 kilorads. Removal efficiencies have been determined for various halogenated methanes, ethanes, ethenes, and propanes, phenols, aromatic hydrocarbons, and polynuclear aromatic hydrocarbons (PAHs). Bench scale ^{60}Co-γ irradiation studies have also shown the process to be effective at removing various explosives, chemical warfare agents, PCBs, and dense non-aqueous phase (DNAPL) and light non-aqueous phase (LNAPL) liquids.

This paper will present a brief overview of the technology, selected results from simulated groundwater experiments, and results from bench scale experiments on waters containing NAPL contamination. The economics of full scale treatment systems will also be discussed.

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EVALUATION OF SLURRY-PHASE BIOREACTORS FOR TREATING PAH-CONTAMINATED SOIL

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In slurry-phase biotreatment of contaminated soil, the excavated solids are typically treated in a continuously stirred reactor to which nutrients, microorganisms, and surfactants may be added to enhance the biodegradation of organic contaminants. Various versions of the bioslurry process have been implemented in the field; however, the effectiveness of key process parameters has not been systematically investigated.

A bench-scale bioreactor study was performed at the U.S. EPA Test and Evaluation (T&E) Facility in Cincinnati, Ohio, on a soil contaminated with polynuclear aromatic hydrocarbons (PAHs) obtained from a Superfund site in Minnesota. In this study, ten 6-liter glass bioreactors were employed and levels of soil- and liquid-bound PAH concentrations, nutrient levels, pH, dissolved oxygen, temperature, and microbial activity were monitored in an effort to identify and optimize key operating parameters. The operating parameters included solids concentration, agitation rate for the slurry, and pH. This poster presents the design of bench-scale equipment and results obtained during the bench-scale study of the slurry-phase bioreactors.

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HRUBOUT® THERMAL OXIDATION PROCESS

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The HRUBOUT® process (U.S. Patents 5,011,329; 5,251,750; 5,261,765) is a mobile thermal treatment process that removes volatile and semivolatile organic compounds from contaminated soils. In the process, heated air is injected into the soil below the zone of contamination, evaporating the soil moisture and removing the volatile organic compounds (VOC's) and semi-volatile organic compounds (SVOC's). Once the moisture is evaporated, the soil porosity and permeability is increased, allowing for increases in pressure and temperature. Low-volatility hydrocarbons can then be removed by slow oxidation at temperatures up to 800 degrees Fahrenheit.

The process is available in three embodiments: in-situ, ex-situ and a containerized version. In the in-situ method, injection wells are drilled in pre-determined distribution patterns to a depth below the contaminated zone. The wells are equipped with steel casing, perforated at the base, and cemented in the hole. Heated compressed air is introduced at temperatures up to 1200 degrees Fahrenheit. As the vapors reach the surface, which is covered with an impermeable cover, a vacuum directs the vent gases to an oxidizer, where they are destroyed at 1500 degrees Fahrenheit.

The ex-situ process involves a horizontal piping grid overlain with a mound of soil and remediates approximately 1,100 cubic yards per batch. The mound is covered with an impermeable membrane and is treated in the same manner with heated compressed air.

The containerized method remediates approximately 25 cubic yards per batch and is processed similarly, except that the soil is enclosed in an insulated container.

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IGT'S NOVEL TECHNOLOGIES FOR MGP SITE REMEDIATION

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IGT has developed and demonstrated two processes to efficiently remediate soils and sludges contaminated with hazardous compounds such as polynuclear aromatic hydrocarbons (PAHs), volatile hydrocarbons (e.g. BTEX), and polychlorinated biphenyls (PCBs). These processes combine biological treatment and physical/chemical treatment as follows: 1) the integrated Chemical/Biological Treatment (CBT) or MGP-REM Process and 2) the Fluid-Extraction/Biological Degradation (FEBD) process.

The MGP-REM process is version of the integrated chemical/biological process specifically designed for manufactured gas plant (MGP) sites wastes. Bench-scale studies as well as the field-scale tests show that the MGP-REM process is effective in significantly enhancing the rate as well as the extent of degradation of these contaminants. The field tests results show that the chemically enhanced bioremediation using the CBT process results in up to 90% improvement over conventional bioremediation for total PAHs (2-6 ring compounds) degradation and over 100% improvement over conventional bioremediation for carcinogenic PAHs (4-6 ring compounds) degradation.

The Fluid Extraction Biodegradation (FEBD) process has the potential to be an environmentally benign means of extracting organic contaminants from soil, delivering the contaminants to bioreactors, and biodegrading the contaminants to CO_2, water, and biomass at optimum conditions. PAHs with 2 to 6 rings were successfully extracted from contaminated soils using supercritical carbon dioxide and supercritical CO_2/methanol mixtures. The IGT mixed culture successfully degraded the PAHs in the FEBD extract in batch and continuous reactor systems. Extensive biodegradation up to 92 and 96% were obtained with 0.5 and 1% extract respectively. A minimum hydraulic retention time of 1.78 days was determined for the efficient removal of PAHs in the system. The volatile PAHs contributed an insignificant fraction to the total loss of PAHs.

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INNOVATIVE BIOSLURRY TREATMENT OF POLYNUCLEAR AROMATIC HYDROCARBONS

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IT Corporation (IT) will conduct a pilot-scale investigation using three, 60-liter (L) EIMCO Biolift™ Slurry Reactors (EIMCO Process Equipment Company, Salt Lake City, Utah) to biodegrade polynuclear aromatic hydrocarbons (PAH) in soil. The objective of the investigation is to increase the rate and extent of PAH biodegradation, thereby, making bioslurry treatment a more desirable remediation alternative.

IT will operate the Biolift™ reactors in series in semi-continuous, plug-flow mode. The first reactor will receive fresh feed daily with supplements of salicylate and succinate. These compounds have been shown to increase biological activity against naphthalene, phenanthrene and anthracene by inducing the naphthalene operon. Therefore, the first reactor in series will be utilized to remove easily degradable carbon and increase biological activity against more recalcitrant PAH (i.e., three-ring compounds and higher).

Effluent from the first reactor will gravity flow to the second reactor in series where Fenton's Reagent will be added to accelerate oxidation of contaminants. The third reactor in series will be used as a polishing reactor for the removal of any partially-oxidized contaminants remaining following addition of Fenton's reagent. Slurry will be removed from this reactor and clarified using gravity settling techniques. The clarified water will be recycled to slurry additional soils.

This technology is applicable to PAH-contaminated soils and sludges that can be readily excavated for bioslurry reactor treatment. Soils from coal gasification sites, wood treating facilities, petrochemical facilities, and coke plants are typically contaminated with PAH and may be remediated using this technology.

IT's bioslurry reactor system was accepted into the SITE Emerging Technology Program in 1993. The project was initiate in mid-January 1994.

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INTEGRATION OF PHOTOCATALYTIC OXIDATION WITH AIR STRIPPING

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In a collaborative demonstration program sponsored by the U.S. Environmental Protection Agency SITE program, ASU and IT Corporation are evaluating the integration of gas-solid ultraviolet (UV) photocatalytic oxidation (PCO) downstream of an air stripper unit as a technology for cost-effectively treating water pumped from a chlorinated volatile organic-contaminated aquifer. This work should also provide valuable information which could be applied to the evaluation of PCO for other environmental problems, including treatment of the off gases from soil vapor extraction, and contaminated air from manufacturing processes.

In photocatalytic oxidation, chlorinated VOCs are destroyed at ambient conditions over a UV-illuminated titanium dioxide thin film catalyst using the water vapor and oxygen in the air as oxidants. High conversion to carbon dioxide, water and HCl can be achieved for relatively short residence times. Based on experimental work performed at the bench scale in laboratories at ASU, engineers at IT Corporation have designed a demonstration scale PCO unit to be tested at a Superfund site in the Phoenix metropolitan area. The groundwater at this site is contaminated with trichloroethylene (TCE) as well as other chlorinated solvents, metals, and petroleum hydrocarbons.

The 150-300 cfm PCO demonstration unit is based on a "flow-through" design, which allows high destruction rates and uniform UV photon flux distribution at low pressure drop. A pH-controlled, low-profile, acid gas scrubber is integrated with the PCO reactor to remove HCl and other chlorine-containing byproducts from the PCO reactor exhaust. Process conditions and emissions are automatically monitored and logged. The entire unit, including controls and monitors, is skid mounted to allow rapid setup and decommissioning at demonstration sites.

This work should identify operability, reliability, control and safety issues associated with integration of PCO with air stripping, and will provide necessary engineering scale-up data for full-scale operation. This information can then be used by process development and design engineers to fully evaluate the economic viability of PCO for practical environmental remediation applications.

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IN SITU BIOREMEDIATION USING OXYGEN MICROBUBBLES

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Successful *in situ* biological treatment of groundwater and soils contaminated with hazardous wastes depends on accelerating the biodegradation rates of the indigenous microflora. A non-limiting supply of oxygen as the terminal electron acceptor is necessary to maintain these enhanced rates under aerobic conditions. Techniques for the subsurface delivery of oxygen include air sparging, hydrogen peroxide, and reinjection of aerated groundwater. An innovative method under development for *in situ* bioremediation is oxygen microbubbles. Oxygen microbubbles are generated continuously by mixing a concentrated surfactant stream with water under pressure. This solution is then mixed with a continuous supply of oxygen to produce a 65% dispersion of bubbles in the 45 ± 40 micron size range. The microbubble dispersion can be delivered into a saturated or unsaturated soil matrix under pressure through a well or trench delivery system.

One treatment scenario is to inject the microbubbles into a laminated coarse sand/clay layer treatment zone. Contaminated groundwater flows through the treatment zone and biodegradation occurs using the available oxygen. A second approach is to deliver the microbubble dispersion into the vadose zone. Injection rates would depend on specific matrix conditions.

A preliminary engineering technology comparison of *in situ* oxygen delivery methods indicated that microbubbles were a cost effective means to treat 10,000 cubic yards of soil contaminated with 1,000 mg/kg of petroleum hydrocarbons. Other oxygen delivery methods examined were air sparging, hydrogen peroxide, supersaturated water and aerated water.

A field scale demonstration of the oxygen microbubble technology for *in situ* bioremediation is in progress at a former fire fighting site contaminated with jet fuel at Tyndall Air Force Base in Panama City, Florida.

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IN SITU VITRIFICATION: SCOPE OF POTENTIAL APPLICATIONS

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In Situ Vitrification (ISV) is an innovative technology that has recently been initiated on a large-scale commercial operation basis. The ISV technology involves electric melting of contaminated earthen materials (e.g., soil, sediment, tailings, sludges) at high temperatures for purposes of destroying/ removing organics and volatile contaminants, and permanently immobilizing heavy metals. The product of ISV is a glass and crystalline vitrified residual that is monolithic in nature and has outstanding physical, chemical, biotoxicity, and weathering properties; and which has a geologic (permanent) life expectancy.

The ISV technology may be applied to contaminated materials "in situ" (where they presently exist), or where they have been "staged" for processing. Other application variations include "stacked" processing, where one melt is done atop another, and "layered" processing, where the contaminated material is vitrified and removed in progressively deeper layers. The technology may also be applied in "stationary-batch" and "stationary-continuous" modes wherein the processing equipment remains stationary and materials to be treated are brought to a stationary location for treatment, followed by intermittent or continuous removal.

The primary factors that must be considered in ISV application engineering include: 1) geochemistry of the material to be treated, 2) desired residual product properties, 3) contaminant types and concentration levels, 4) desired contaminant disposition(s), 5) media moisture content, and the possibility of groundwater recharge to the treatment zone, and 6) presence of debris, containers, and/or structures within the treatment zone. The technology may be adapted for a broad range of site-specific conditions.

ISV has been successfully tested, and is currently planned for use, on a large number of contaminant types, including organics, heavy metals, and radionuclides. The technology has a unique advantage in the ability to simultaneously process mixtures of contaminant types. Various media tested include most basic soil types, including limestone and dolomite-rich soils, uranium mill tailings, ocean harbor sediments, and process tailings containing glass forming oxide materials.

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LOW TEMPERATURE IN-SITU THERMAL DESORPTION OF ORGANICS FROM SOILS

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In-situ soils remediation has many advantages over ex-situ remediation because it remediates the soils without removal from the ground, does not transport soils to another location and, when applied with proper controls, does not impact on the local environment. Several approaches are commercially available for in-situ soils remediation, e.g. hot air, steam stripping (HASS), soil vapor extraction (SVE), stabilization, enhanced vapor extraction, and others. The report describes an in-situ soil treatment method which uses in-situ deep soils mixing combined with the injection of steam and hot air (HASS) to remove volatile organic compounds (VOC) and semi-volatile organic compounds (SVC). Hot air and steam are injected into the soil from mixing blades below the surface. VOC and SVC are heated by the steam and carried to the surface with air where they are collected in a shroud for treatment and subsequent disposal. A unique feature of this technology is that the below ground removal occurs not only by heating and vaporization, but also by the formation of organic compounds - steam azeotropes. These azeotropes facilitate the removal of the organic species. The limitation in using this technology is, therefore, the thermal desorption of VOC and SVC from soil. Examples of thermal desorption as a first order rate process are given from field studies. The results of a 30,000 yd^3 commercial project which received regulatory approval are also presented. This project was part of a 1990 USEPA Site Report.

This technology has application at sites where it is best suited. These are: 1). soils where both the vadose and saturated zones need remediation; 2). soils below the water table; 3). soils which have strata of varying permeability; and, 4). removal of hot spots in sites which can use more than one treatment approach. Use of this technology requires open areas and sites with manageable underground obstructions.

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PHOTOCATALYTIC REMEDIATION OF PCB-CONTAMINATED WATERS AND SEDIMENTS

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The degradation of polychlorinated biphenyls (PCBs) in aqueous solutions, clay and sediment suspensions was promoted by sunlight in the presence of TiO_2 as a catalyst. After 4 h irradiation, 83 and 81% of total PCBs were decomposed in the water solution and clay suspension, respectively. About 67% of the total PCBs was degraded in the sediment suspension after 6 h irradiation, while it took 4.5 h to decompose 98% of the total PCBs in the aqueous phase of the sediment suspension. It was observed that the lower chlorinated PCB congeners underwent the highest rate of decomposition in the aqueous systems. Study results indicate that photocatalytic processes have the potential to be an efficient and low cost technique to remediate PCB-contaminated water and sediment.

A bench-top photoreactor was built and currently is used to determine the variables for photocatalytic processes. Two pilot-scale photoreactors are under design and construction to remediate the PCB-contaminated soil from a casting site and sediments from a federal superfund site.

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PHOTOLYSIS/BIODEGRADATION TREATMENT OF PCB and PCDD/PCDF CONTAMINATED SOILS

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The primary project objective of this study was to perform a laboratory-scale evaluation and demonstration of two-stage detoxification process for the treatment of soils contaminated with polychlorinated biphenyls (PCBs), polychlorodibenzodioxins (PCDDs) and other chlorinated aromatics. Earlier work showed a practical rate of photolytic destruction of PCBs and 2,3,7,8-tetrachlorodibenzo-p-dioxins (TCDDs) on soil when the soil surface was treated with a surfactant solution and irradiated by ultraviolet (UV) light. It is expected that such a treatment would produce photolytic by-products that would be less resistant to further degradation by biological treatment.

The first stage of this process involved in situ photolytic degradation by periodic tilling, application of a surfactant, and irradiation of the soil surface for up to 30 hours. After photolysis, the second stage consisted of the soil being re-inoculated with indigenous microorganisms enriched from the original soil and supplied with nutrients to cause in situ biodegradation of less recalcitrant contaminants.

The results of the initial experiments indicate that the ability of surface irradiation to destroy PCBs or TCDDs depends on the soil type. Soils with higher content of humic materials or clay were less successful than on sandy soil. Natural sunlight was also found to be ineffective. Surface irradiation was found to remove chlorine from the highly substituted PCBs and form the bi and tri chlorinated PCBs. The initial biotreatment studies show that these compounds are more readily degraded.

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PNEUMATIC FRACTURING OF LOW PERMEABILITY FORMATIONS

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Pneumatic fracturing is an innovative technology which enhances the in situ removal and treatment of volatile organic compounds (VOC's) in low permeability soil and rock formations. The process may be generally described as injecting air into a contaminated geologic formation at a pressure which exceeds the natural in situ stresses, and at a flow rate which exceeds the permeability of the formation. This causes failure of the medium and creates a fracture network radiating from the injection point. Once established, the fractures enhance the permeability of the formation, thereby increasing the flow rate of vapors and liquids through the formation for more efficient contaminant removal or treatment.

During August 1992, the U.S. EPA sponsored a Superfund Innovative Technology Evaluation (SITE) field demonstration of the Pneumatic Fracturing Extraction (PFE) process at an industrial site in Hillsborough, N.J. For the demonstration, PFE was used to enhance a soil vapor extraction system installed in the low permeability siltstones and sandstones underlying the site. The test results showed that PFE significantly improved the ability to extract trichlorethylene (TCE) and other VOC's from the formation. Extracted air flow increased from 400% to 19,000%, and the TCE mass removal rate increased from 700% to 2,300%, depending on the testing configuration. An extended vacuum radius of influence was also observed, which will result in a reduction of the number extraction wells required to remediate the site. The application of PFE should decrease remediation time, and in the case of this site, eliminate the need to excavate or encapsulate the source area.

Work is continuing to expand the applications of pneumatic fracturing to other in situ technologies such as pump and treat, bioremediation, and thermal treatment. Experience is now available in both the vadose and saturated zones, and in several geologic formations including clay, silt, silty sand, cemented sand, fill, sandstone, and siltstone.

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THE REACTOR FILTER SYSTEM: AIR TOXICS CONTROL FOR SOIL THERMAL TREATMENT PROCESSES

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Much of the materials from Superfund sites are sludges, soils and sediments which are contaminated with both toxic organic chemicals and toxic metals. Currently available thermal treatment systems for detoxifying these contaminated media may release products of incomplete combustion (PICs) and volatile toxic metals. Extensive air pollution control devices (APCDs) are then required to prevent release of air toxics to the atmosphere. Because of physical size and utility requirements APCDs are frequently not suitable for transport and remote installation at Superfund sites. The Reactor Filter System (RFS) is designed to avoid some of the logistical problems associated with conventional APCDs . The RFS will exploit the potential for a fabric filter installed immediately downstream of a thermal treatment process to capture toxic metals, particulate matter and unburned organic solids. The RFS process involves three steps:

1) Thermal treatment of the soils, sludges or sediments in a primary chamber that could be any one of a number of devices including a rotary kiln, fluidized bed unit, or other chamber designed to thermally treat sludges or solid materials.

2) Injection of a low cost sorbent containing silicates, such as kaolinite, into the flue gases at temperature near 1300 °C (2370 °F). These sorbents will react with volatile metal species such as lead, cadmium, selenium and arsenic in the gas stream forming insoluble (nonleachable) silicate complexes similar to cementitious species.

3) Fabric filtration using an advanced high temperature (up to about 1000 °C, 1830 °F) filter medium designed to provide additional time for the sorbent particles to react with the metals and provide additional time for the destruction of organics that are associated with the particulate matter. Because of the well established relationship between PIC formation and particle chemistry, this process can virtually eliminate polychlorinated dioxin formation

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REDUCTIVE PHOTO-DECHLORINATION OF HAZARDOUS WASTES

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Waste streams containing hazardous chlorinated hydrocarbons are treated with an innovative process designated **"Reductive Photo-Dechlorination" (RPD)**. This RPD process uses ultraviolet light in a reducing atmosphere to remove chlorine atoms from organo-chlorine waste streams at low to moderate temperatures. Because chlorinated organics are destroyed in a reducing environment under mild conditions, process products include environmentally benign hydrocarbons and hydrogen chloride.

The RPD process is designed specifically to treat volatile chlorinated wastes in the liquid or gaseous phase. Applications include in-situ treatment of wastes discharged from soil venting extraction (SVE) operations, and in-situ regeneration of activated carbon canisters saturated with chlorocarbons. The process can also be used for direct treatment of off-gas streams containing chlorocarbons as well as for pretreatment of gas streams entering catalytic oxidation systems, reducing chlorine content and hereby protecting the catalyst against poisoning.

This poster will focus on photo-thermal remediation of 1,1,1-trichloroethane (TCA) yielding greater than 99% conversion. It will describe bench-scale experimental results, kinetic modeling predictions, and selected design parameters for an on-going pilot-scale demonstration unit employing a unique UV lamp.

The RPD process was developed under the EPA/Small Business Innovation Research (SBIR) program, and in late 1992 was accepted to the EPA-SITE Emerging Technology Program.

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REMEDIATION OF CHLORINATED VOLATILE ORGANIC COMPOUNDS IN GROUNDWATER USING THE ENVIROMETAL PROCESS

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Historic discharges of spent chlorinated industrial solvents resulted in groundwater contamination at a small industrial site in Wayne Township, New Jersey. Dissolved chlorinated volatile organic compounds present in the shallow bedrock aquifer include tetrachloroethene (PCE) at concentrations of 10 to 20 mg/L, and trichloroethene (TCE) at concentrations of up to 1 mg/L. The use of the EnviroMetal process (metal enhanced reductive dehalogenation) is being evaluated as an innovative technology alternative to a conventional pump and treat system.

Bench scale studies were completed to confirm that the PCE and TCE in the groundwater would indeed be degraded using this technology, and to develop design parameters for field application. Groundwater from the site was pumped through laboratory columns containing the reactive media (metallic iron and silica sand). Half-lives (the time required to remove one-half the contaminant mass) of 0.4 hours for PCE and 0.5 hours for TCE were measured in columns containing 100% reactive iron. Small amounts (less than 10%) of cis-1,2-dichloroethene and vinyl chloride were produced as a result of PCE and TCE degradation, but these also subsequently degraded.

Based on these favourable results, an above-ground pilot-scale field test will be initiated this year at the facility. If successful, this will be followed by installation of a full-scale *in-situ* treatment zone in the shallow bedrock.

For more information, contact John Vogan, EnviroMetal Technologies Inc., 42 Arrow Road, Guelph, Ontario, Canada, N1K 1S6. EnviroMetal Technologies Inc. acknowledges the support of SL Industries of Mount Laurel, New Jersey in contracting for the EnviroMetal process to be demonstrated at this site.

REMOVAL OF DISSOLVED HEAVY METALS USING FORAGER™ SPONGE

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Forager™ Sponge, comprised of a chelating polymer disposed within an open-celled cellulosic matrix, selectively absorbs multivalent heavy metals in cationic and anionic states. The following affinity sequence is generally exhibited:

$$Cu^{++} > Pb^{++} > Cd^{++} > Hg^{++} > Fe^{+++} > CrO_4^{++} > AsO_4^{+++} >> Ca^{++}$$

This affinity sequence enables the Sponge to abstract trace quantities of heavy metals in the presence of vast concentrations of commonly abundant ions such as Na, Ca, Al and Mg. Certain metal ions can be removed to non-detectable levels. The Sponge is not adversely affected by dissolved organics, oils, or suspended matter. In fact, the Sponge can be utilized to remove metals from thick sludges.

In the form of $^1/_2$" cubes, the Sponge is employed in columns, fishnet enclosures, rotating drums, or stirred tanks. In column operations, removal efficiencies range to 99% at flow rates of 0.1 bed volume/minute.

The Sponge is used to remediate groundwater by either pump-and-treat operations employing absorption columns, or by in situ operations wherein fishnet enclosures containing the Sponge are emplaced vertically within wells, or horizontally within trenches. When saturated with metals, the enclosures are retrieved, and replaced with fresh units. The in situ technique involves no capital investment and does not require electrical power.

Because fishnet containers filled with the Sponge present essentially no impedance to flow of water, they are also suited for use in stormwater treatment.

The metal-saturated Sponge can in some instances be eluted and re-used. Alternatively, the saturated Sponge can be incinerated or compacted to an extremely small volume to facilitate disposal.

The cost effectiveness of the Sponge is dependent upon factors such as the nature of the metals absorbed, the total chemistry of the water, number of cycles of use, and ultimate disposal method. In general, costs may range between about 10¢ and 90¢ per gram of metal removed.

For More Information: contact N. B. Rainer at the above address.

REMOVAL OF ORGANICS FROM SOILS USING CF SYSTEMS®SOLVENT EXTRACTION TECHNOLOGY

Susan Erickson
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CF Systems patented soil treatment process involves the use of liquified gases as solvents to extract and separate organic contaminants from soils and sludges. The unique physical properties of liquified gas solvent, such as their low viscosities, densities and surface tensions. result in significantly higher rates of extraction compared to conventional solvents. These enhanced physical properties also accelerate the rate of gravity settling of the soil/solvent mixture following extraction of the organics, which broadens the applicability of the process to include the treatment of fine clays and silty sediments.

This paper discusses the results of several bench- and pilot-scale treatability studies, using CF Systems Solvent Extraction process, to remove organic contaminants from a variety of soil types. Technical data will be presented from treatability studies performed on samples from various Superfund Sites including wood treating sites, PCB contaminated sites, and pesticide/dioxin contaminated sites. The discussion will include the significance of process operating variables and the effect of different solvents/co-solvents on the removal efficiency.

Regulatory agencies use a variety of factors, such as risk to human health, future use of the site, and type of organic contaminant, to set the remedial goals for a contaminated site. CF Systems has successfully demonstrated its ability to achieve the required treatment goals for a wide range of organic-contaminants in a variety of soil matrices. As a results of bench and pilot-scale work performed at one particular Superfund site, CF Systems has been awarded a contract to remediate 95,900 tons of creosote contaminated soil.

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The Rochem DT process

The Rochem DT process is a membrane separation technology which allows the removal of hazardous constituents from water. The technology is a concentration process for the volume reduction of hazardous materials.

The patented Disc Tube system consists of a series of membrane cushions stacked between spacer discs. The membranes and discs are then inserted into a pressure vessel to allow operation at high pressures. The open channel flow path and the hydraulic design of the module allow efficient operation with minimal fouling. When fouling does occur, the module cleans easily and completely, without disassembly.

Originally developed for desalinating water, Rochem currently has commercial systems treating landfill leachate at over 25 landfills in Europe. The first installation has operated successfully since 1988. The largest installation to date processes in excess of 1 million gallons per day of leachate discharging 98% of the stream as purified water. The hazardous components are concentrated to 2% of their original volume, solidified and returned to the landfill.

The Disc Tube system is currently in use at the French Limited Superfund site in Crosby, Texas. This unit, which has been in operation since May, 1993, discharges an average of 120 gallons per minute of water directly into the San Jacinto River at a fraction of the cost of alternative means.

A SITE demonstration is scheduled for early summer.

The poster will give a complete description of the technology and will include analytical data from both French Limited and leachate processing.

For further information, please contact:

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SAREX® CHEMICAL FIXATION PROCESS FOR ORGANIC CONTAMINATED SLUDGES AND SOILS

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The SAREX® Chemical Fixation Process (CFP) is a lime-based process that utilizes a physical-chemical reaction between proprietary reagents and the hydrocarbon, water, and solids to produce a physically stable waste product resistant to chemical leaching. Additionally, a heat of hydration reaction between the lime and interstitial water promotes volatilization of volatile organic compounds (VOCs).

CFP is ideally suited for heavy organic sludges and soils that also contain elevated levels of metals. Typical applications include lube oil acid sludges, refinery sludges, tars, F-waste plating sludges, and halocarbon/metal-impacted soils.

CFP can be utilized either in an "open" or "closed" process configuration. The "open" configuration is ideally suited for materials that have minimal volatile emissions. The "closed" configuration is ideally suited for materials where VOC emissions need to be contained. The "closed" process includes a material feed and slurry system, followed by a secondary reagent feed and mixing system. Vapors (moisture, organics, and particulates) are captured in a specially designed vapor recovery system (VRS). The VRS contains direct contact cooling, condensation, and vapor phase carbon polishing.

SRS has successfully treated over 30,000 cubic yards of waste using the SAREX® CFP. In all cases CFP rendered the oily wastes into a treated soil-like product with favorable construction and compaction properties. Recent bench-scale testing on sludge and soil samples have resulted in over 98 percent removal of benzene and trichloroethene (TCE) to levels meeting necessary treatment objectives.

SRS will conduct the SITE demonstration for CFP at a New Jersey Superfund site in the summer of 1994. This site contains surface impoundment sludges containing elevated concentrations of VOCs, semiVOCs and metals.

For More Information Contact:

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SITE EO5: REMOVAL OF HEAVY METALS WITH A CENTRIFUGAL JIG

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Gordon Ziesing
Montana Tech

TransMar, Inc. is the owner of all rights and patents for the Campbell Centrifugal Jig (CCJ) which is a major advance in well proven technology for gravity separation of fine heavy metal particles from background material. The CCJ is a combination of two widely used methods of heavy particle separation - jigging and centrifuging. Mineral jigs have been used for many years to separate solids of different densities in a fluid medium through gravity induced differential settling. For heavy particles (> 150 microns) the standard gravity jig has the advantage of high capacity and continuous material flow. However, it is ineffective for finer particles which tend to remain suspended in the fluid. Centrifuges are very effective in separating solids from liquids, but not for the differential separation of solids in a slurry.

The CCJ combines the effectiveness of the continuous flow of the standard mineral jig with the high "g" forces of the centrifuge to effectively segregate and concentrate particles from 150 microns down to 1 micron, if they have a specific gravity at least 20% greater than the background material. No chemical are needed to effect separation. Slurry material is fed to the CCJ through a vertical hollow shaft and is thrown radially outward by the vanes on a diffuser plate which distributes it over the rotating screen which is covered with oversize material to make a "bed". This bed is intermittently fluidized by pulses of water in a direction opposite to the "g" force and acts as a one way valve for heavy particles. Heavy particles migrate through the bed and screen and enter the hutch to be recovered through the discharge ports as concentrate. Lighter particles are flushed downward across the jig bed and become tailings. The CCJ was originally developed for fine gold recovery. However, it has demonstrated the capability to separate and concentrate a wide variety of materials ranging from 28x100 mesh pyritic sulphur in fine coal cleaning down to 1 micron particles in gold recovery. In recent DOE sponsored experiments it demonstrated concentration ratios of over 100:1 in removing a bismuth surrogate for plutonium, from Nevada Test Site soil.

The EO5 Grant was made to Montana Tech and is being conducted in their Research Facility by Montana Tech and TransMar in conjunction with Hydro Processing and Mining, Inc. the operator of the facility. Materials from four different sites - Ramsey Flats, Colorado Tailings, Cyprus Tailings and the Contact Tailings have been tested to date. Ramsey Flats material was unsuitable because the contained Cu,Pb, and Zn were present as alteration /oxidation products and not liberated from the gangue.The Colorado and Cyprus tails posed similar problems. Much better results were obtained with the Contact Tailings from Phillipsburg, MT. Preliminary results are encouraging with recovery of 64% in a single pass and 77% in two passes (rougher with 20 mesh and scavenger with a 50 mesh screen). To obtain these results required changing the CCJ screen from 50 to 20 mesh since heavy metals constituted 13.3% of the feed. Testing is continuing on similar "Block P Tailings" from near Monarch, MT.

SPOUTED BED REACTOR

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The Spouted Bed Reactor (SBR) technology utilizes the unique attributes of the "Spouting" fluidization regime, which can provide heat transfer rates comparable to traditional fluid beds, while providing robust circulation of highly heterogeneous solids, concurrent with very aggressive comminution (particle size reduction through abrasion). The primary spouted bed provides a zone for volatilization, pyrolysis, and gasification reactions. The gaseous products can then be applied to highly efficient oxidation/incineration in conventional combustion equipment or, alternatively, gasification products can be used as syn-fuel or chemical products can be recovered through synthesis of the off gas. Thus, gasification provides much greater opportunity for product recovery through Advanced Recycling.

An operating pilot plant has been constructed consisting all of the critical system components. Solids are comminuted and gasified at medium temperature (1000-1600°F) in a primary vertical reactor. Large solids remain in the bed until they are reduced in size through attrition, pyrolysis, and gasification reactions.

Steam is used as the spouting fluid, highly superheated by a small in-line oxy-fuel burner. Superheated steam provides heat for endothermic pyrolysis reactions, along with partial oxidation of wastes which react with sub-stoichiometric levels of oxygen injected into the spouted bed primary.

In the presence of excess steam at high temperature, toxic organic compounds that may result during low or medium temperature waste pyrolysis are reduced to H_2, CO, CO_2, and H_2O. Subsequent purification of the $H_2/CO/CO_2$ gas stream can be accomplished using conventional particulate and scrubbing technologies.

The SBR Advanced Recycling technology is primarily applicable to waste with significant heat content that are contaminated with toxic organic compounds and heavy metals. The heat content of the waste may range from 3,000 to 12,000 Btu per pound. Soils contaminated with coal tar residues, petroleum refinery wastes, and municipal solid wastes are appropriate for processing in the SBR Advanced Recycling system. Chemical waste, munitions and rocket propellants are also candidate feed materials.

Accomplishments to date have included the design, construction, shakedown, and preliminary operation of a pilot scale SBR facility capable of processing 1000-1500 lb/hr of waste. Trouble-free feeding of "raw" unsegregated Auto Shredder Residue (ASR) plastics has been accomplished at a feed rate of 1400 lb/hr. Limited gasification data obtained during test runs have demonstrated the conversion of ASR to hydrocarbon rich process gas (330-480 Btu/scf), with negligible tar formation, and with 1-2% carbon remaining in the ash constituents. ASR product ash analysis (recovered from the hot cyclone) indicated metals leachability below regulated limits; lead and cadmium, the two metals of primary concern in ASR, were 0.4 and 0.06 mg/l respectively, the limits being 5.0 and 1.0.

Advanced recycling (thermochemical conversion) of high Btu content wastes can generate a variety of end products. These include pyrolysate liquids, olefins, and syn-gas. EER's SBR technology can be operated at low, medium, or high temperature in order to generate these respective end products. Bed materials tested to date include 1/16" and 1/4" silica sand, 1/4" alumina balls, and 1 mm steel shot. The interaction of bed materials and reactive additives with feed materials requires careful characterization.

FOR FURTHER INFORMATION

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STEAM ENHANCED EXTRACTION FOR *IN SITU* SOIL AND GROUND WATER TREATMENT

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The acceleration of recovery rates of second phase liquid contaminants from the subsurface during gas or water pumping operations is realized by an increase in soil temperature. Of the various methods of delivery of thermal energy to soils and ground water, steam injection appears to be the most economical and versatile technique for soils with sufficient permeability. The use of steam injection to recover volatile, semi-volatile, and non-volatile contaminants from the subsurface also allows the exploitation of various thermodynamic and hydrodynamic mechanisms. These mechanisms include vaporization of liquids with boiling points below that of water, enhanced evaporation rates of semi-volatile components, physical displacement of low viscosity liquids, dilution and displacement of aqueous contaminants, and removal of residual contaminants from low permeability zones by depressurization and vacuum drying.

A recently completed field-scale demonstration of the patented steam enhanced extraction technology to remove gasoline at a site at Lawrence Livermore National Laboratory confirms the effectiveness of this technique and its applicability to contaminants found above and below the water table. Approximately 90,000 cubic meters of soil were treated with this process. Steam was injected into six wells surrounding the plume. The steam injection could occur in each well at two different locations: one in the vadose zone and the other below the water table. After 35 days of injection, the target soils were at a relatively uniform temperature of 100° C. Gasoline extraction rates were limited by the aboveground gaseous phase treatment system. Approximately 1,700 gallons of gasoline were recovered.

An additional 25 days of cyclic steam injection was then applied to the site with continuous pumping of vapors and liquids for a period of 42 days. Recovery rates increased by an order of magnitude over that measured during the first phase. Rates were observed to decrease during steam injection and increase when the steam injection was intermittently ceased. This performance is attributed to steam generation within the lower permeability zones during the depressurization mode of operation. Soil borings at the end of this phase showed that soils both above and below the water table were clean in the high permeability zones with residuals remaining deep in the low permeability clay zones.

A final 35 days of vacuum extraction and ground water pumping was then applied with an additional 1000 gallons of gasoline removed. Recovery rates dropped significantly during this final phase. The total gasoline volume recovered exceeded 8000 gallons. The initial estimate of the gasoline at the site was 6200 gallons. Hydrocarbon degrading biological activity was found in the zones subjected to steam temperatures indicating that the technology did not leave the site sterile.

For More Information: Kent S. Udell, Berkeley Environmental Restoration Center, 6165 Etcheverry Hall, University of California, Berkeley, CA, 94720, (510) 642-2928.

SULCHEM PROCESS - DESTRUCTION OF ORGANICS AND STABILIZATION OF HEAVY METALS

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The patented Sulchem Process reacts contaminated liquids, soils and sludges with elemental sulfur at elevated temperatures. All organic compounds react with sulfur. Hydrocarbons are converted to an inert carbon-sulfur powdered residue and hydrogen sulfide gas. Chlorinated hydrocarbons also produce HCl. The acid gases can be treated to recover sulfur for reuse.

In addition to destruction of the contained organic compounds, heavy metals are converted to the sulfides and thereby rendered less leachable. Thus, the Sulchem Process offers the potential to stabilize heavy metals in the same process step as the organics destruction.

Under a Cooperative Agreement with the U.S. EPA, under the Emerging Technologies E05 Program, the Center for Hazardous Materials Research (CHMR) is developing the Sulchem Process for metals stabilization and organics destruction. The process is anticipated to use two reactors. In the first reactor, the solids are mixed with sulfur and heated to destroy organics and immobilize metals. In the second reactor, the off-gases from the first reactor (which may contain desorbed organics) are further reacted with sulfur to destroy the remaining organic compounds.

During the first year of the program, CHMR examined various heavy metals spiked in different soil blends as well as soils spiked with hydrocarbons. Immobilization of heavy metals is determined by the concentration of the metals in the Toxicity Characteristic Leaching Procedure (TCLP) leachate compared to the EPA TCLP regulatory limits. Cadmium, copper, lead, nickel and zinc were found to provide significant reduction in the TCLP values following treatment of the soil by the Sulchem Process. Copper TCLP values were reduced most effectively by this treatment. Lead TCLP values were reduced below regulatory targets when concentrations in the original soil were below about 10,000 ppm. Cadmium TCLP values were reduced below TCLP limits for runs at different process conditions with starting concentrations ranging from below 1000 ppm to above 3000 ppm depending on soil type.

Tests with hydrocarbons of varying boiling points have demonstrated that a minimum reaction temperature of 250°C is required and that for compounds with boiling points from 250°C to about 320°C there is competition between desorption and reaction in the first stage reactor. Compounds with boiling points below 250°C tend to desorb and will need to be treated in the second stage reactor. Compounds with boiling points above about 320°C were effectively destroyed in the solids reactor. Preliminary tests of this second reactor indicate it is capable of destroying organics in the vapor phase.

For more information: A. Bruce King, CHMR, 320 William Pitt Way, Pittsburgh, PA 15238, (412) 826-5320.

THE SVVS® BIO-SPARGING TECHNOLOGY

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The SVVS® biosparging technology (U.S. Patent Nos. 5,221,159; 5,277,518) was developed in response to a requirement to cost effectively and timely remediate soils and ground water contaminated by petroleum hydrocarbons. The technology was proven and commercially developed in New Mexico, with original testing, theoretical concepts and design development in the late 1980's. The technology was praised by EPA Office of Underground Storage Tanks, and was sought out by the EPA for inclusion in the SITE program.

The SVVS® technology uses both positive and negative air pressures and flows to simultaneously attack and remediate all phases of contamination (dissolved, free phase, soil residual and vapors). Two processes, physical and biological are stimulated and enhanced to remediate the site. The system can use single and multiple pumps/blowers to deliver air to injection points and remove vapors from vacuum wells. Air is normally injected below the water table, and vacuum removal can take place in the vadose zone. Injection/withdrawal points are placed in lines of sub-surface reactor nests throughout a site depending upon a number of design criteria and site specific characteristics, such as depth to water, soil permeabilities, contaminant type and extent, etc.

The SVVS® technology is now in place at over 50 hydrocarbon and chlorinated solvent sites worldwide, with up to 100 planned and or designed, and pending regulatory approval. A typical site is normally taken to soil and ground-water standards not arbitrary clean-up levels, within three years, a substantial improvement over competing technologies.

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TERRA-KLEEN SOLVENT EXTRACTION SYSTEM FOR CONTAMINATED SOIL AND DEBRIS

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The Terra-Kleen technology employs a mobile batch process system that uses a proprietary solvent blend at ambient temperature and pressure. Soil and debris are loaded into the system with standard earth moving equipment. Oversized material need not be separated from finer soils. Debris up to 5 feet in length, width, and depth can be co-processed with the soil. The soil and debris are mixed with a solvent blend that extracts contaminants from the soil. The contaminated solvent is then removed from the soil and pumped through a proprietary separation process which removes organic contaminants from the solvent. The clean solvent is then used again in a closed loop process. The soil, with the organic contaminants removed, can then be left at the site.

The components of the solvent blend used by Terra-Kleen has been approved by the US Food and Drug Administration as food additives for human consumption. Because of this, the Terra-Kleen process is accepted not only by regulators, but also by communities with problems to solve. The technology has been used at two Superfund sites, and has been demonstrated to the US EPA Superfund Innovative Technology Evaluation (SITE) program, the Naval Environmental Leadership Program (NELP), and the Chemical Regulations Branch, Office of Pesticides & Toxic Substances, US EPA.

The compounds successfully removed by Terra-Kleen include Polychlorinated Biphenyls (PCBs), Pentachlorophenol (PCP), Chlorinated Dibenzo-(p)-dioxins, Chlorinated Dibenzofurans, Polycyclic Aromatic Hydrocarbons (PAHs), DDT, Toxaphene, Endrin, and other chlorinated pesticides.

The poster display will document findings by the EPA SITE team on the successful removal of PCB from soils at the North Island Naval Air Station, Coronado Island, California. For more information:

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THREE-PHASE FLUIDIZED BED BIOLOGICAL WASTE WATER TREATMENT SYSTEM

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Introduction: The Bio-Dynactor, developed independently by Denka Consultant & Engineering Co., Ltd, is a three-phase fluidized bed biological waste water treatment system. The system has been in use since 1988 and has handled the industrial waste water of eight types of industries at 17 locations. The picture shows a Bio-Dynactor with a net volume of 300m^3 installed at a paper mill. The treated water capacity of this Bio-Dynactor is 12,000m^3.

Purpose: The Bio-Dynactor is designed to be a compact unit using a simple system to supply general waste water treatment with no maintenance, and low initial and running costs. The unit's mechanisms are explained in a structural diagram.

Methodology: Independently developed carriers that immobilize bacteria consist of composite particles of inorganic powder and polymer. A model of the carrier and a table of the particle characteristics are shown.

Applications: The Bio-Dynactor is designed to meet specific needs and is capable of a variety of functions including direct processing of source water, microorganism neutralization, chemical and microorganism coagulation, sludge-less simultaneous removal of heavy metals, denitrification, dephosphorization, and decoloration. The basic block flow diagram and engineering data are shown. The bacteria immobilizing particles are used in the biological odor removal equipment of public sewage plants at five locations.

Results: The first apparatus won the Presidential Award for Excellence of the Japan Industrial Machine Industry Association. A comparison between this unit and other methods is shown.

Conclusion: The Bio-Dynactor technology has been well received both in Japan and internationally. The technology has been licensed to two domestic manufacturers, and three Korean engineering firms are in the process of negotiating its acquisition.

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THE TREATMENT OF HIGH CONCENTRATION INDUSTRAL NOx WASTE GAS BY DRY METHOD

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In industry, the catalyst production, metallic surface treatment and some other nitriding processes often generate a large amount of high concentration NOx waste gas. NOx is one of major air pollutants. Now, NOx is treated usually by base solution absorbing method, and sometimes by catalytic reducing method. Generally, the investment of base solution absorbing method is high and its absorbing efficiency is low. The investment of the catalytic reducing method is also high, moreover this method need ammonia as reducing agent, so its operating cost is high. It is difficult to use this technology to the discontinuous discharge processes. Owing to the adsorption capacity of many adsorbents is low, high concentration NOx waste gas can not be treated by the adsorption method.

High concentration industral NOx waste gas dry treatment technology developed by us has applied to the industry. By using this method high concentration NOx waste gas can be treated by a treatment agent under the condition of no aqueous solution present, and we need only a equipment which can be manufactured by ourselves, so the investment cost is low (it is only about 40-45% of base solution absorbing method). As it dose not need the catalyst and the treatment agent is cheap and easily available, its operating cost is low (4-5 Chinese yuan per 1000m^3 waste gas). The purification efficiency of this technology is above 99%, no matter how high NOx concentration in the waste gas is, after one time of treatment NOx concentration in the discharged gas can reach the national discharge standard, discharged gas becomes non-colur. This technology dose not cause the second pollution, there are not the pollutants required to carry out further treatment. The technology can treat both NOx waste gas discharged continuously and discontinuously.

This dry treatment technology is not suitable for very large flow rate of NOx waste gas.

TREATMENT OF MIXED WASTE CONTAMINATED SOIL

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Mixed waste represents one of the most challenging waste treatment and disposal problems. Traditionally, hazardous and radioactive materials have been regulated by separate agencies and federal and state regulations. A result of this situation is that there are disposal options for hazardous waste or for low level radioactive waste but no disposal options for combined or mixed wastes.

Soil contaminated by both hazardous and radioactive constituents are a significant fraction of the mixed waste problem in the United States. Contamination by these substances has resulted from disposal of waste residues to the land and from accidental spills and leaks at many of the Department of Energy, Department of Defense, electrical generation and industrial manufacturing facilities. The technologies, to be evaluated in this pilot program, thermal desorption, gravimetric separation and water treatment with ferrate ion, provide simple, cost effective methods of removing from soil three contaminant classes found at these sites. The removal of these contaminants, hazardous organics, radionuclides, and heavy metals, will allow the decontaminated soil to be left at the site. The contaminants are collected as concentrates for recovery or off-site disposal at commercial hazardous or radiological waste facilities. The focus of the project is on the many sites where all three types of contamination exist; the data generated will also be applicable to sites with only one type of contamination.

This project includes both bench- and pilot-scale testing of the three technologies. While bench-scale testing will require less than 10 kilograms of soil, up to 1000 kilograms will be needed for the pilot-scale work. The soil for these tests will be obtained from the RCRA storage facility for the Y-12 oils land farm soil at the DOE Oak Ridge Facility. This material contains hazardous organics, heavy metals, and radionuclides.

The goal of the bench-scale tests is to identify optimum operating conditions and performance for the various treatment technologies. The pilot-scale tests will provide additional performance and scale-up data needed for evaluation of the potential for full-scale application of these technologies.

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Treatment of Wood-Preserving Waste by Lignin-Degrading Fungi

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The ability of lignin-degrading fungi to detoxify by means of degradation or transformation a wide range of hazardous organic pollutants has provoked research leading to a more complete understanding of the use of these organisms in soil remediation technology. As part of a comprehensive program to judge the merits of the emerging fungal technology, a series of three field evaluations have been undertaken. The last two studies were conducted at the former Brookhaven Wood Preserving Facility located 70 miles south of Jackson, MS.

The first of these two studies, completed in 1991, was designed to evaluate the performance of a number of selected fungal strains to degrade pentachlorophenol (PCP) and the polynuclear aromatic hydrocarbons constituents of creosote. Treatment by an inoculum of Phanerochaete sordida demonstrated the largest decrease in the PCP concentration (89%) in soil having an initial concentration of 672 mg/Kg PCP. Loss observed in the "no treatment" control was 14% of the initial PCP concentration.

The following year, the fungal technology was tested in a twenty-week demonstration at the Mississippi site employing the P. sordida treatment. Initial soil concentrations ranging from 1058 mg/Kg to 1210 mg/Kg PCPwere encountered for this study. The field study design was composed of three soil bed plots: one 30.5 m by 30.5 m (treatment plot) and two 7.6 m by 15.25 m (control plots). The treatment plot received an application of P. sordida at a rate of 10% inoculum to soil on a dry weight basis. One control was a "no treatment" control, and the other control was amended with the sterile standard substrate (solid growth substrate for the fungal inoculum) at a rate of 10% on a dry weight basis.

After 20 weeks, the PCP concentration in the treatment plot was decreased by 64%, whereas decreases of 19% and 30% were observed for the "no treatment" and "sterile substrate" controls, respectively. Assessment of viable fungal biomass by means of an ergosterol assay on the soil at the beginning of the study showed a significantly diminished quantity of fungal biomass leading to a lag in and a reduction of treatment. Weather was another significant factor in this field evaluation. Excess precipitation prohibited tillage of the experimental plots on the prescribed schedule which led to poor aeration of the soils on occasion.

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TREATMENT ON SOILS CONTAMINATED WITH HEAVY METALS AND VOCs

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Metals and volatile organic compounds (VOCs) are two types of contaminants that are often found in soils at Superfund sites. Frequently, soils are contaminated with both metals and VOCs. Since no existing technologies address both metals and VOCs, a two-stage process is required. This report presents the results of a bench-scale study, a pilot-plant demonstration, and an engineering assessment for a two-stage physical separation process for the treatment of soils contaminated with VOCs and heavy metals. Three actual Superfund soils were tested to provide performance data for different soil matrices.

The two technologies tested were batch steam distillation for the separation of VOCs from the soil, followed by a multistage, countercurrent extraction with hydrochloric acid (HCl) to remove the heavy metals, and finally neutralization and precipitation of the spent acid. The treated soils, after batch steam distillation and extraction, passed the Toxicity Characteristic Leaching Procedure (TCLP) for volatile organics and heavy metals.

The process demonstrated a removal efficiency of greater than 95 percent for the VOCs and for most metals, (with the exceptions being mercury, chromium, and nickel). A removal efficiency of 95 percent shows that a multistage process provides a method for remediating Superfund soils contaminated with VOCs and heavy metals.

An engineering assessment was also performed to assess the cost of a full-scale treatment plant using each of these technologies to treat Superfund soils. The capital cost estimated for a VOC removal system ranged from $150K for 500 ton/year to $670K for a 2500 ton/year system. Operating cost for these two systems was estimated to be $300 and $230 per ton of soil. The capital cost for heavy metals extraction was $230K for a 500 ton/year system and $990K for a 2500 ton/year system. Operating costs were $382 to $339 per ton.

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TWO-STAGE FLUIDIZED-BED/CYCLONIC AGGLOMERATING COMBUSTOR

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IGT's two-stage combustor (AGGCOM) permits one-step treatment of soils contaminated with both organic and inorganic compounds. The two-stage combustor combines advances in fluidized-bed combustor technology with those of cyclonic combustor technology. This advanced combustor efficiently destroys organic contaminants and encapsulates inorganic contaminants within benign, glassy agglomerates suitable for disposal in an ordinary landfill.

The first AGGCOM stage is a sloping-grid, agglomerating fluidized-bed reactor that can operate under either substoichiometric or excess air conditions. In addition to the sloping grid, the first stage incorporates a central jet and classification section. Fuel gas and air enter the central jet while only air is admitted through the grid and the classifier. Contaminated soils are admitted directly into the fluidized bed. With a unique distribution of fuel and air, the bulk of the fluidized bed is controlled at a temperature of 1500° to 2000°F, while the temperature at the central jet can be varied from 2000° to 3000°F. This feature is the key to the combustor's ability to produce benign agglomerates. Upon introduction of contaminated soils in the bed, the organic fraction is immediately volatilized and partially combusted. The inorganic fraction undergoes melting and subsequent agglomeration.

The volatilized organic compounds are thermally converted in the second AGGCOM stage. This stage is a cyclonic combustor, which provides intense mixing to ensure complete combustion of the organic compounds. Either secondary air or a mixture of natural gas and air is fed to this stage to maintain a temperature in the range of 1800° to 2400°F. The destruction and removal efficiency (DRE) of organic contaminants in this system exceeds 99.99%. Fine particulates collected in the cyclonic stage are returned to the fluidized-bed stage for assimilation in the agglomerates.

A multiyear program is underway to develop a data base for application of the AGGCOM combustor technology at Superfund sites. In the first phase of the program, a bench-scale unit was constructed and operated to determine the operating conditions required for soil agglomeration. During the second phase of the program, a 6-ton/d AGGCOM pilot plant was constructed at IGT's Energy Development Center with funding from EPA and IGT's Sustaining Membership Program. Shakedown has been completed and tests are in progress. This pilot plant provides a natural gas-based thermal treatment solution for contaminated soils and a wide variety of industrial wastes. Future efforts will concentrate on specific treatment demonstrations in the pilot plant.

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THE ULTROX® UV/OXIDATION PROCESS

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The Ultrox® process, which utilizes a combination of ultraviolet light, ozone and/or hydrogen peroxide, can be applied to a number of groundwater, wastewater, industrial waste water, leachate and process water problems for the removal of organic chemicals.

Though historically each component of the process has an application in drinking or wastewater treatment, used in combination, they provide a powerful oxidizing regime which exceeds the ability of any one of the individual components to destroy organic contaminants in water. This was successfully demonstrated when Ultrox participated in the U.S. EPA SITE Program in 1989. Full scale installations are currently installed at industrial sites, Superfund sites and Department of Defense and Department of Energy locations.

The energy-efficient, low maintenance Ultrox® systems are most effective when dealing with higher flow rates (i.e. above 50 gpm). Such difficult-to-treat man made compounds as PCBs and chlorinated solvents, TCE, PCE, PCBs, pentachlorophenol and chlorobenzene, which are not broken down by natural processes in the environment, are easily destroyed or converted into non-toxic chemicals such as carbon dioxide, water, various salts or harmless organic acids, in an efficient and cost-effective way, without creating a need for sludge removal or off-site hauling. Other compounds which respond particularly well to the Ultrox® process include explosives, pesticides (including DBCP), benzene, toluene, ethyl benzene, xylene, MTBE, nitrophenols, phenols, chlorophenols, creosote, chlorinated or phosphonated PAHs, dioxin, methylene chloride, cyanides and vinyl chloride.

If volatile organic compounds are present, Ultrox has developed a patented, low temperature, catalytic system called D-TOX™ for destroying VOCs in air by oxidizing the compounds through the use of ozone and a proprietary catalyst.

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USE OF SECONDARY LEAD SMELTERS FOR THE RECOVERY OF LEAD FROM LEAD CONTAMINATED MATERIALS

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The EPA has estimated that there are over 3,000 sites across the United States contaminated with lead. Techniques to remediate these sites include stabilization/disposal technologies, reclamation of lead, extractive washing, and biological removal technologies.

Under a Cooperative Agreement with the U. S. EPA, the Center for Hazardous Materials Research (CHMR) and Exide Corporation have investigated the use of secondary lead smelters for the recovery of lead from materials found at Superfund sites and other waste materials. The objective of the project was to determine whether existing lead smelting technology could be used to recover lead from materials containing between 3 and 70 percent lead, and to determine the process economics.

Exide's Reading, PA, facility typically processes waste lead acid batteries using reverberatory and blast furnaces. The facilities primary feedstocks include lead-acid batteries. Both the plastic cases and the lead in the batteries are recycled at the facility.

During the study, CHMR and the smelter reclaimed lead from five sources of materials, including two Superfund sites with primarily battery cases, and one battery breaker/smelter site with a variety of lead-containing materials. Batches of between 20 and 1500 tons of these materials were mixed with typical furnace feeds and fed to the furnaces, while the research team assessed the effects on furnace operation and performance. Two additional sets of materials, from the demolition of a house containing lead-based paint, as well as spent bridge blasting abrasive material from work on a bridge coated with lead paint, were also processed in the smelter. The results showed that it was technically feasible to use the secondary lead smelter to reclaim lead from all of the materials.

CHMR also assessed the economics of using secondary lead smelters to reclaim lead from Superfund sites, and developed a method for estimating the cost of reclaiming lead. This method develops cost as a function of material excavation, transportation and processing costs combined with cost benefits received by the smelter (in the form of recovered lead, reduced fuel usage and/or reduced iron usage). The overall remediation costs using secondary lead smelters for the sites and materials studied varied between $57 and $230 per ton, based on current market prices for lead. The costs were primarily a function of lead concentration, the market price for lead, distance from the smelter, and the ash concentration in the material. Materials with high concentrations of lead were significantly less expensive to remediate than those with low concentrations. The cost to remediate materials which left few slag residues in the furnace was significantly lower than the cost to remediate materials which contained significant slagging components.

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VITRIFICATION OF HEAVY METAL CONTAMINATED SOILS

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There are currently several treatment methods available for the processing of heavy metal contaminated soils. The most common practice is the solidification of these wastes with the addition of cement forming reagents. The treatment of heavy metal contaminated soils via vitrification has a number of important advantages over cementation processes, in that vitrified products have substantially superior long-term chemical and physical stability, provide more effective resistance to leaching of the heavy metal contaminants, and, in general, have a smaller volume relative to the waste materials being treated.

The major impediments to the use of vitrification over cementation has been the high operating costs and relatively low operating capacities of conventional vitrification processes. Vortec Corporation, a leader in high temperature process technology development, has developed an advanced vitrification process which is competitive in both cost and capacity with solidification processes. An important advantage of the Vortec vitrification process is that it can be used for the treatment of soils which contain both heavy metal and organic contaminants.

In May 1991, Vortec's technology was accepted by the U.S. Environmental Protection Agency's (EPA) SITE Emerging Technologies Program. Vortec Corporation has now completed a two-year experimental program to demonstrate its vitrification technology. The poster will summarize the results and conclusions of several tests performed under Vortec's EPA SITE program. The program verified the effectiveness of the Vortec Combustion and Melting System (CMS) to produce a fully-reacted, stable vitrified product which immobilized the heavy metal contaminants found in hazardous soils. The program also demonstrated the CMS's flexibility in processing both dry and wet contaminated soils.

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WARREN SPRING LABORATORY SOIL WASHING PROCESS

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Warren Spring Laboratory has developed a soil separation and washing process under the SITE Emerging Technology Program. This poster presents results of a pilot scale test conducted on soil from a gas works site that was contaminated with PAHs, petroleum hydrocarbons and heavy metals. The soil was investigated in the laboratory to characterize the distribution of contamination on the basis of soil particle size, density, magnetic susceptibility and hydrophobicity. This information was then used to design the pilot-scale flowsheet.

The main contaminants in the soil were: arsenic (> 30 mg/kg), lead (> 800 mg/kg), PAH (<200 mg/kg) and petroleum hydrocarbons (> 600 mg/kg). The pilot scale circuit was operated for a period of some four weeks. The nominal throughput rate was 1 ton per hour with about 40 tons being treated. The soil was treated as a water based slurry with minimal reagents used as additives. The major operations involved were size separation, washing and attrition, separation based on combined size/density differences, flotation and magnetic separation.

The pilot test generated the following product streams:

* > 50 mm clean gravel product
* 10 - 50 mm clean fine gravel product
* 10 - 1 mm product that may require further treatment
* < 1 mm coarse sand from the hydrosizer that may require further treatment
* < 10 μm contaminated product from the hydrocyclones that will require treatment or disposal
* < 1 mm - > 500 μm contaminated light gravity concentrate from screen after hydrosizer
* froth concentrate with organic contamination
* froth concentrate with metal contamination
* magnetic concentrate with metal contamination (optional)
* < 1 mm treated material.

Data reduction and evaluation provides a material balance around the complete process flowsheet for soil, individual contaminants, and process water. Performance determination for the complete process as well as for some individual unit operations is presented. The percentage removal for each contaminant in any clean products is determined by comparison with the original soil. For each contaminated product stream further treatment or disposal is recommended.

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