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DEPARTMENT OF ENERGY · UNITED STATES OF AMERICA

Office of Environmental Management

Office of Technology Development

VOCs in Arid Soils

Technology Summary

MASTER

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VOLATILE ORGANIC COMPOUNDS IN ARID SOIL INTEGRATED DEMONSTRATION (VOC-ARID ID)

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OFFICE OF TECHNOLOGY DEVELOPMENT OVERVIEW

The Department of Energy (DOE) established the Office of Technology Development (EM-50) (OTD) as an element of Environmental Restoration and Waste Management (EM) in November, 1989 (see Figure A). The organizational structure of EM-50 is shown in Figure B.

EM manages remediation of all DOE sites as well as wastes from current operations. The goal of the EM program is to minimize risks to human health, safety and the environment, and to bring all DOE sites into compliance with Federal, state, and local regulations by 2019. EM-50 is charged with developing new technologies that are safer, faster, more effective and less expensive than current methods.

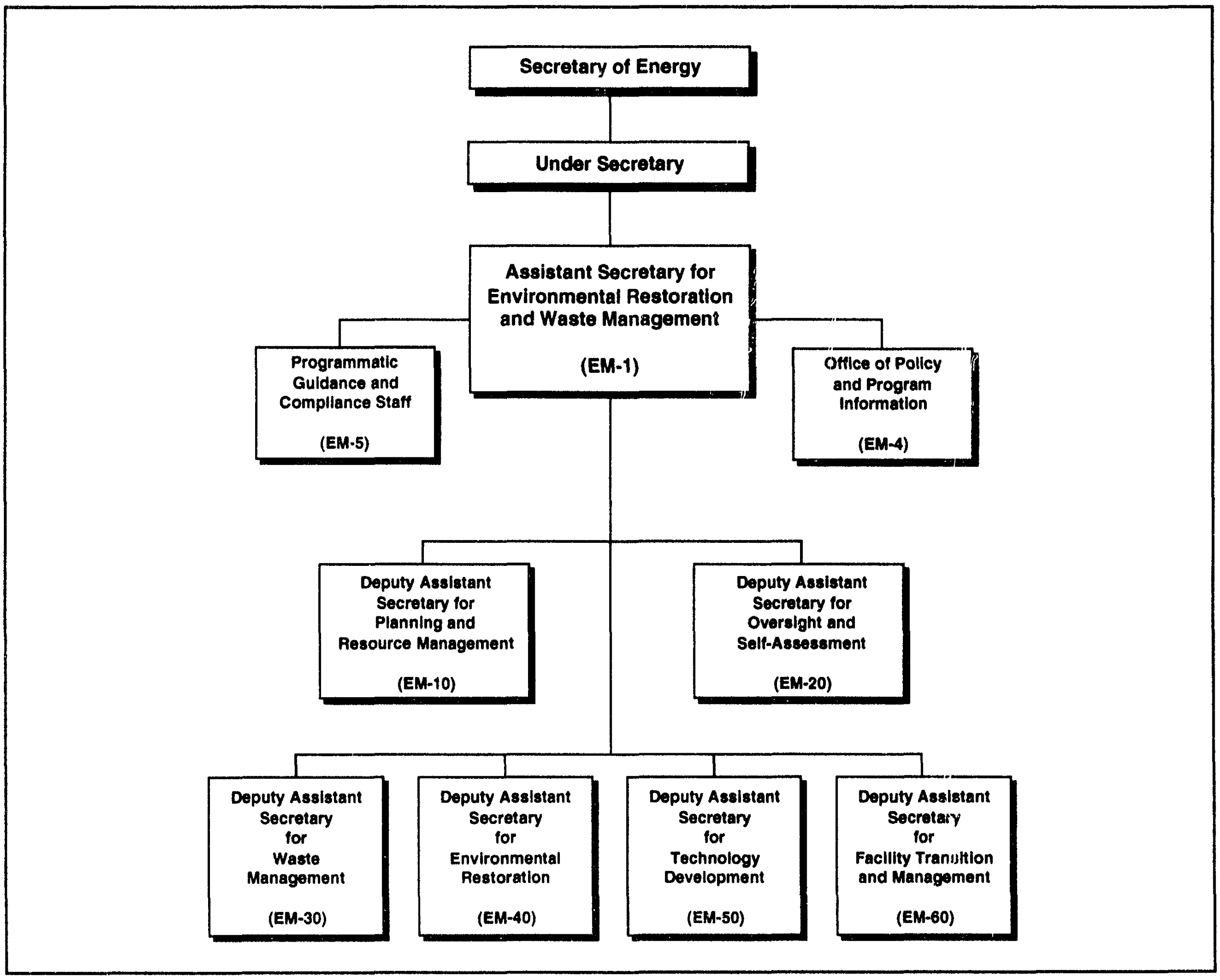

Figure A. DOE Organizational Structure as of June 1993.

In an effort to focus resources and address opportunities, EM-50 has developed **Integrated Programs (IP)** and **Integrated Demonstrations (ID)**. An *Integrated Program* focuses on technologies to solve a specific aspect of a waste management or environmental problem and it can be either unique to a site or common to many sites.

An *Integrated Program* supports applied research to develop innovative technologies in key application areas organized around specific activities required in each stage of the remediation process (e.g., characterization, treatment, and disposal).

An *Integrated Demonstration* is the cost-effective mechanism that assembles a group of related and synergistic technologies to evaluate their performance individually or as a complete system in correcting waste management and environmental problems from cradle to grave.

The Volatile Organic Compounds in Arid Soils Integrated Demonstration (VOC-Arid ID) (the subject of this report) is part of EM-551, the Development, Testing, and Evaluation Division of EM-55.

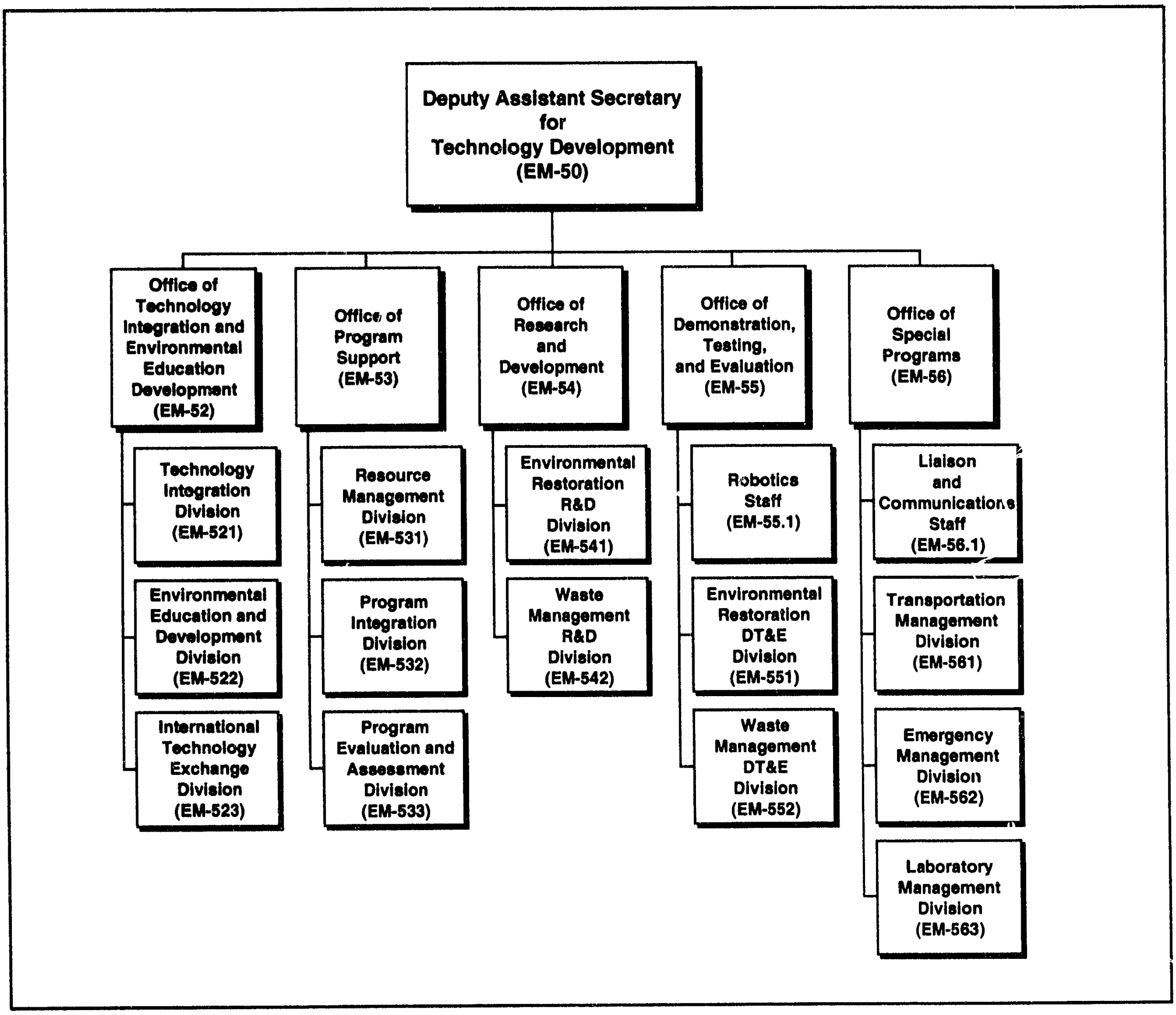

Figure B. Office of Technology Development Organizational Structure as of June 1993.

VOLATILE ORGANIC COMPOUNDS IN ARID SOILS INTEGRATED DEMONSTRATION OVERVIEW

PURPOSE

The Volatile Organic Compounds In Arid Soils Integrated Demonstration (VOC-Arid ID) focuses on technologies to clean up volatile organic compounds and associated contaminants in soil and groundwater at arid sites. The initial host site is the 200 West Area at DOE's Hanford site in southeastern Washington state (see Figure C). The primary VOC contaminant is carbon tetrachloride, in association with heavy metals and radionuclides. An estimated 580-920 metric tons of carbon tetrachloride were disposed of between 1955 and 1973, resulting in extensive soil and groundwater contamination.

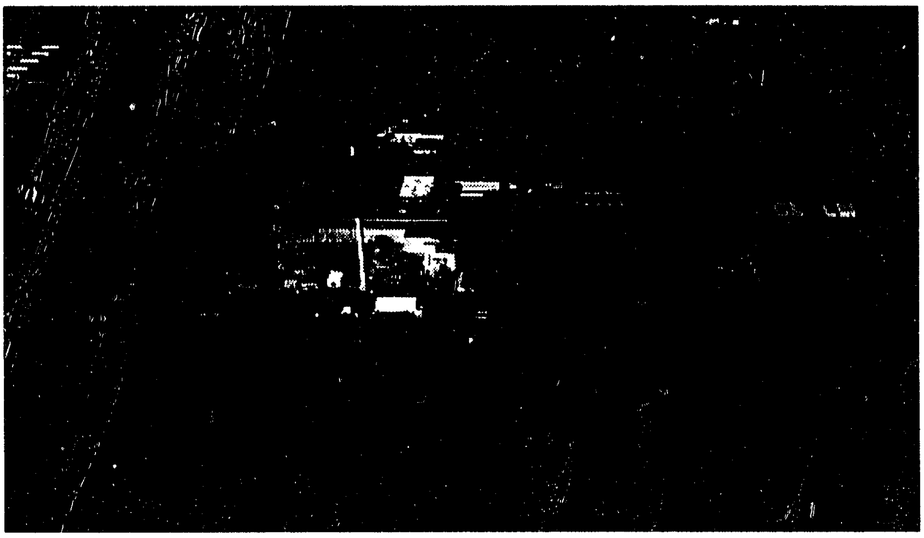

Figure C. 200 West Area.

The VOC-Arid ID schedule has been divided into three phases of implementation. The phased approach provides for:

- rapid transfer of technologies to the Environmental Restoration (EM-40) programs once demonstrated;
- logical progression in the complexity of demonstrations based on improved understanding of the VOC problem; and
- leveraging of the host site EM-40 activities to reduce the overall cost of the demonstrations.

During FY92 and FY93, the primary technology demonstrations within the ID were leveraged with an ongoing expedited response action (ERA) at the Hanford 200 West Area, which is directed at vapor extraction of VOCs from the vadose (unsaturated) zone. Demonstration efforts are underway in the areas of subsurface characterization including: drilling and access improvements, off-gas and borehole monitoring of vadose zone VOC concentrations to aid in soil vapor extraction (SVE) performance evaluation, and treatment of VOC-contaminated off-gas. These current demonstration efforts constitute **Phase I** of the ID and, because of the ongoing vadose zone ERA, can result in immediate transfer of successful technologies to EM-40.

In **Phase II**, demonstration of techniques to enhance and control (e.g., contain or direct) the transport of VOC vadose zone contaminants is a primary goal because a significant percentage of the VOC contamination resident at the Hanford host site, and other DOE sites, is still held up in unsaturated soils. Emphasis will be placed on demonstrating enhanced techniques for VOC removal and control in vadose zone soils, and improved methods for accessing the subsurface to reduce the cost of characterization and improve the likelihood for success of in situ treatment technologies. The baseline technology, SVE, will have been operating at the host site for a sufficient period of time before Phase II to allow for adequate analysis of cost and technical performance (see Figure D). Monitoring technologies for VOCs will be developed and demonstrated throughout Phase I to ensure availability for Phase II remediation technology demonstrations. With baseline technology performance, and availability of monitoring tools, demonstrations of innovative remediation technologies can then be effectively conducted.

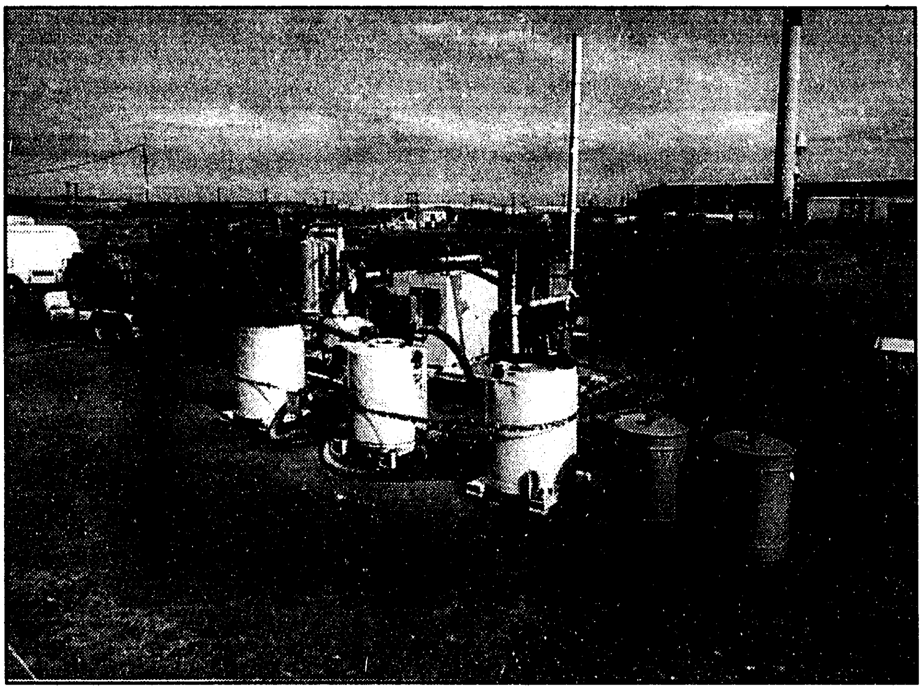

Figure D. Soil Vapor Extraction.

Phase II will also expand the focus of the demonstrations to groundwater contamination, which is consistent with the general strategy of the Environmental Restoration program. EM-40 moved forward with a proposed ERA for groundwater treatment in FY93, and will continue in FY94, therefore, there will again be a direct transfer route for demonstrated technologies to environmental restoration. In anticipation of this, the ID has supported Research and Development (R&D) activities that focused on groundwater remediation.

With the initiation of a new ERA and opportunities for leveraged work activities, the VOC-Arid ID is moving more aggressively to support technologies in FY93 and FY94 for the enhanced removal and treatment of groundwater contaminants. Pump and treat is an unacceptable baseline approach for extracting groundwater VOCs; unfortunately, it is currently the only available method. Unlike vadose zone remediation using SVE, groundwater remediation is an extremely expensive option with the current baseline.

Investments in groundwater remediation will have significant cost benefits. Technologies for in situ treatment of groundwater, and to a lesser extent, more cost-effective treatment of extracted groundwater, will be developed and demonstrated. Characterization and monitoring technologies will continue to be developed to ensure that the necessary tools are available as the focus shifts from bulk contaminant VOC removal from soil to enhanced techniques for VOC residuals removal and groundwater treatment.

Phase III of the VOC-Arid ID will begin to address issues related to co-contaminants within the VOC plume. Specifically, emphasis will be placed on developing and demonstrating technologies for containing, mobilizing for recovery, and/or immobilizing metals and radionuclides in both soil and groundwater. Phase III will build on the base characterization and VOC treatment programs conducted during the first two phases of the program to focus efforts on high-priority areas.

Efforts will primarily focus on in situ treatment or enhanced recovery techniques for americium and plutonium in soils, and uranium and chromium in groundwater. These contaminants represent common VOC co-contaminants at DOE sites and are significant problems at the host site. The focus on metal and radionuclide contamination in Phase III is consistent with EM-40 program needs and the general schedule for restoration activities associated with these plumes in the 200 West Area of the Hanford site. These efforts will build on applicable technology development and demonstration activities associated with the Mixed Waste Landfill Integrated Demonstration (MWLID) and integrated programs focusing on in situ treatment, in situ monitoring, and metals treatment technologies.

The VOC-Arid ID will develop and demonstrate technologies in all phases of the program. Technologies ready for demonstration at or near the onset of the ID program were demonstrated in FY93 if they were technically and/or logistically consistent with the goals of Phase I. Longer term development efforts were initiated in FY92 and FY93 to ensure that the technologies were ready for transition from integrated programs to the ID for demonstration in Phases II and III. Technologies supporting the objectives of Phase I and II will continue to be demonstrated over the duration of the ID as they become available.

The VOC-Arid ID is demonstrating technologies for all phases of remediation, including:

- drilling;
- site characterization and monitoring;
- retrieval of contaminants;
- above-ground treatment of contaminants; and
- in-ground treatment of contaminants.

Drilling: Techniques are needed that can gain access to underground contamination to obtain samples, place monitoring sensors, retrieve contaminants, or treat contaminants in place. Cable tool drilling is the current baseline technology being used at many arid sites. Techniques are being pursued that are faster, easier to use, and safer. Two techniques that have successfully met these criteria through demonstration are the cone penetrometer and sonic drilling (see Figure E). A heavy-weight cone penetrometer has been deployed at Hanford site and will be transferred to other arid sites. Sonic drilling has been adopted by the Hanford Environmental Restoration Program and is being transferred to other sites. A third innovative technology, directional drilling, was demonstrated in FY93, and will continue in FY94. This technology enables access to areas that vertical drilling cannot reach (e.g., under a building).

Site Characterization and Monitoring: To design an effective method for site cleanup, an engineer must know the types, location and concentration of contaminants, and the hydrogeology and microbiology of the site. Typically, site characterization and monitoring techniques are time intensive (e.g., samples are sent offsite for analysis) and expensive. Several technologies have been successfully demonstrated at the VOC-Arid ID that can accelerate characterization and monitoring. For example, the unsaturated flow apparatus is a centrifuge system that measures the movement of contaminants in arid soils. It is much faster than standard techniques available (e.g., days rather than months to years to generate a single data point) and has been validated by the Environmental Protection Agency (EPA). An industrial partner has been found to produce the system and it has been transferred to Hanford site, Los Alamos National Laboratory (LANL), and industry.

Retrieval of Contaminants: Techniques are needed to more effectively remove VOCs and other associated contaminants from soils and groundwater. Two technologies, soil heating and in-well vapor stripping, are being prepared for demonstrations in FY94. Heating enhances volatilization of VOCs from unsaturated soils and improves the performance of soil vapor extraction. This technology was demonstrated in late FY93 through the VOC-Non Arid ID, and will be tested for arid soil applications in FY95 In-well vapor stripping removes dissolved VOCs from groundwater without the added cost and difficulty of extracting large volumes of water.

Above-Ground Treatment of Contaminants: Once retrieved from soils and groundwater, effective and economical methods for treating contaminants are required. For VOCs, granular activated carbon (GAC) canisters are currently used to trap the contaminants for subsequent off-site destruction. Steam reforming and membrane separation are two technologies being demonstrated in FY93 to reduce the cost of off-site GAC

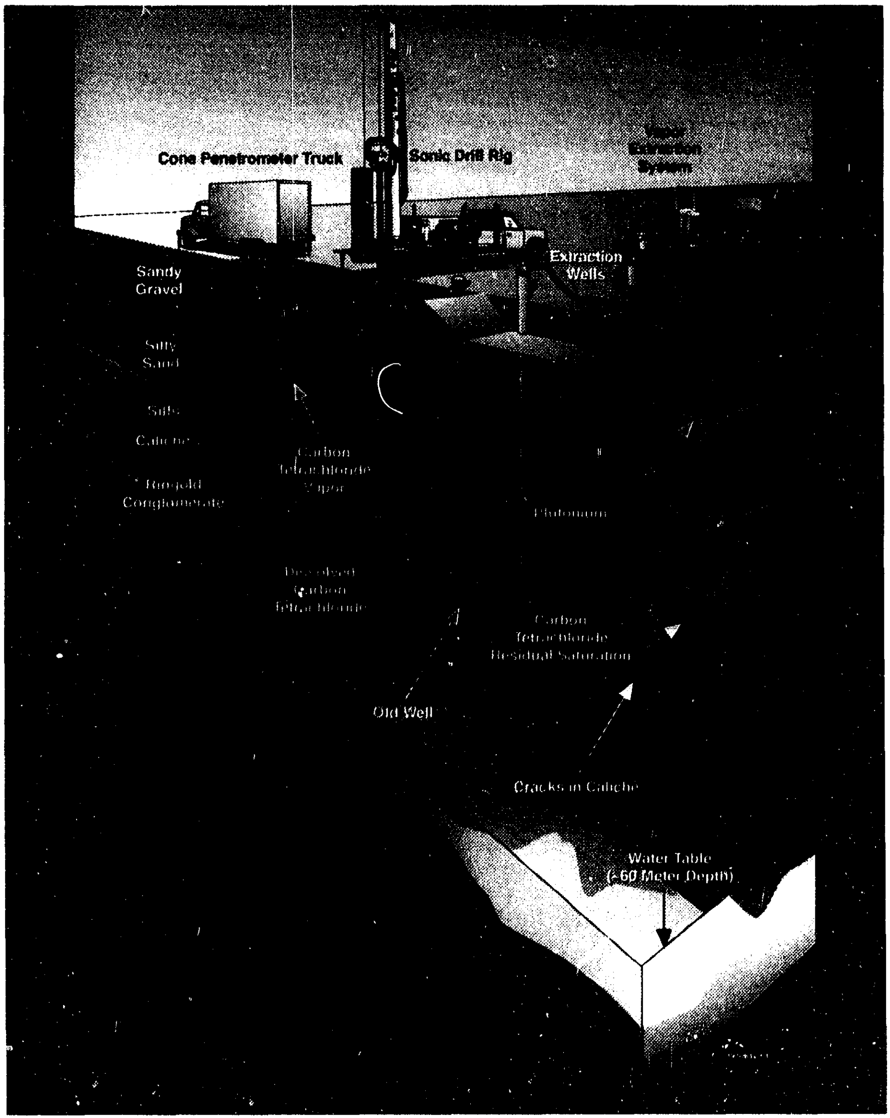

Figure E. Cross Sectional Conceptual Model of the VOC-Arid ID Site.

regeneration. Other destruction and separations technologies, such as an on-line tunable hybrid plasma (low energy E-beam) system, are being readied for demonstration in FY94 and FY95.

In-Ground Treatment of Contaminants: A longer-term goal of the ID is to develop and demonstrate in-ground treatment technologies that destroy organics, and immobilize or contain other contaminants. In-ground treatment offers significant economic and performance benefits over retrieval and treatment. Bioremediation is one example of an in-ground process for destruction of VOCs and nitrates in groundwater that is being developed for demonstration in FY94 and FY95 at the host site.

A technology will be judged as ready to be deployed in a cleanup if it is technically sound and acceptable to the regulators and the public. Success of an integrated demonstration will be realized if such technologies are transferred, for immediate use, to DOE environmental restoration personnel and private industry. In addition, such transfer will help address environmental concerns at other sites and make U.S. industry more competitive in the global marketplace.

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Drilling

Section 1.0

1.1 HEAVY-WEIGHT CONE PENETROMETER

TASK DESCRIPTION

The objective of the heavy-weight cone penetrometer is to provide a cost effective source detection tool. The heavy-weight cone penetrometer will be used to characterize contamination, install monitoring points, and collect chemical and radiological data. The goal is a transferrable technology that:

- reduces overall characterization costs and schedule;
- minimizes waste generated; and
- consistently achieves required depths.

Current activities are focused on enhancing the heavy-weight cone penetrometer efficiency in the aggressive Hanford gravels. This will require:

- further upgrading of the thrusting capacity of the truck and reinforcing tools to withstand this force;
- minimizing waste from down hole tool decontamination;
- evaluating the use of mechanical forces to facilitate penetration through gravels; and
- improving sensors such as radiation detection devices.

TECHNOLOGY NEEDS

At hazardous waste sites, vertical drilling allows access to the subsurface to take soil and groundwater samples and to help monitor the site. Information gained from drilling is used to characterize the subsurface environment and to allow measurements of the types and extent of contamination at a site.

BENEFITS

The cone penetrometer is a quick tool for initial evaluation of the extent of groundwater and soil contamination present at potential environmental restoration sites. It is less costly than drilling, and does not result in contaminated soils being brought to the surface. Cone penetrometers may be used to deploy many different state-of-the-art line sampling and instrument devices. Additionally, effectiveness of the cone penetrometer is unaffected by weather conditions. Compared to traditional drilling methods, the cone penetrometer minimizes worker exposure to potential industrial and chemical hazards and is very mobile.

PROCESS DESCRIPTION

The cone penetrometer is a truck-mounted device that rapidly penetrates into the ground to collect characterization data (see Figures 1.1 a&b). It has been used for approximately 50 years for geotechnical applications, but use in environmental restoration is relatively new. The cone penetrometer rod has a conical tip of up to 2 inches in diameter. It is pushed hydraulically into the ground with a pressure up to 80,000 pounds. The hole generated by the cone penetrometer retains the outside diameter of the rod and can be grouted to prevent the escape of contaminants as the probe is withdrawn. As the rod progresses into the ground, a computer reads data from sensors located in both the tip and the side of the probe. The cone penetrometer can monitor for contaminants as the probe is advanced or can leave monitors in place as the rod is withdrawn. The cone penetrometer can advance through fine-grained soil at a rate of 40 to 50 feet an hour. However, adapting this tool for full use in the gravel/cobble subsurface common to arid sites required upgrading the thrusting capacity of the truck, reinforcing tools associated with the penetrometer to withstand the additional force, and evaluating the use of mechanical forces to facilitate penetration through gravel. Successful development, demonstration, and deployment of the cone penetrometer system as a source detection tool will provide cost-effective site characterization and remediation by reducing the number of drill holes required, minimizing secondary waste, and reducing potential worker exposure to contaminated materials. Cone penetrometers can be designed to collect several types of data in addition to collecting groundwater samples. This allows for a real-time print out of the soil and contaminant characteristics in the subsurface.

ACCOMPLISHMENTS

At this time the reliability of the cone penetrometer varies with soil type. When used in gravel the cone penetrometer maintains approximately 100% reliability (minimal refusal) with two attempts in gravels to depths of 50 feet. In gravels to 100 feet the percentage drops to approximately 50-75%. In soft soil the cone penetrometer maintains near 100% reliability.

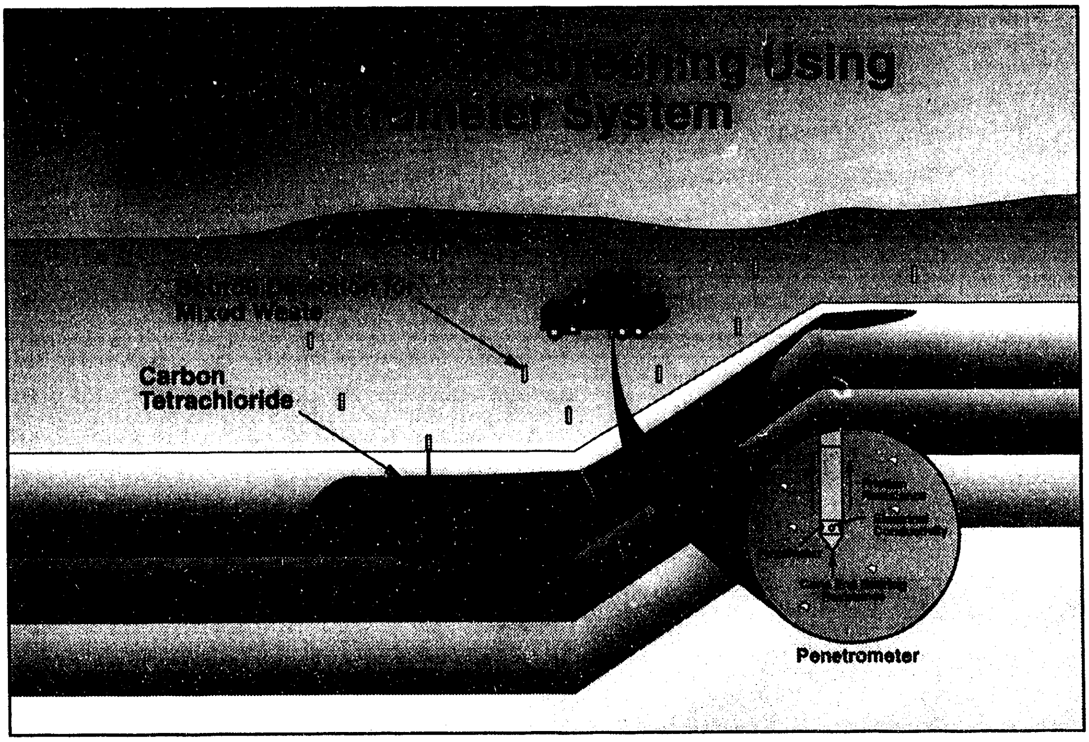

Figure 1.1a. Source Detection Screening Using Cone Penetrometer System.

COLLABORATION/TECHNOLOGY TRANSFER

This technology is being developed by Argonne National Lab (ANL), Pacific National Lab, and Westinghouse Hanford Company through a contract with Applied Research Associates. Any environmental remediation at sites where the generation of airborne contaminants or effluents during drilling is not acceptable, will also be interested in evaluating the use of the cone penetrometer technology. In addition, there is potential for this technology to be linked with portable acoustic wave sensors or other real-time monitoring systems. Applied Research Associates is the only firm which has successfully used a cone penetrometer in gravels and cobbles.

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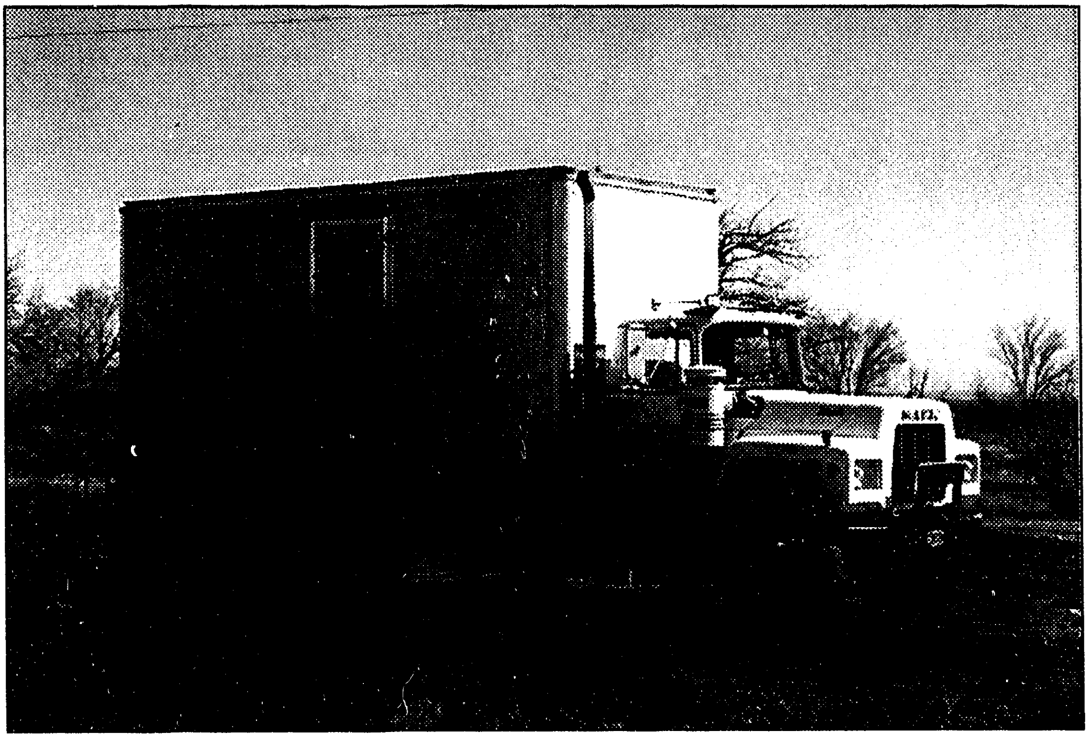


Figure 1.1b. Cone Penetrometer Truck.

1.2 DIRECTIONAL DRILLING

TASK DESCRIPTION

The objective of this task is to install directional wells that meet data quality objectives, minimize secondary waste generation, and reduce costs for drilling while minimizing operational and contamination exposure hazards to personnel. A secondary objective both during drilling and following the completion of a boring or well, is to support the deployment of instruments, sensors and other devices to the subsurface for characterization, remediation and monitoring purposes. Accuracy/placement of these boreholes is also an important factor. Several systems have been tested in the past two years at the Savannah River, Sandia and Hanford sites, including the short radius system, mud rotary system; Eastman Christensen hybrid system; slant compaction rig (Ditchwitch™); and the river crossing system. Currently two methods of directional drilling are being tested at Hanford, air rotary and air hammer drilling.

TECHNOLOGY NEEDS

In order to characterize the nature and extent of contamination at DOE sites, wells are drilled for sampling and monitoring. The ability to construct horizontal wells or wells that are not vertical in contaminated soils will increase the ability to accurately assess the levels of contamination under structures. The directional drilling project will focus on increasing the ability for:

- the installation of subsurface treatment systems such as vapor extraction, leaching, and microbial treatment;
- barrier installations - applications include obtaining access holes beneath cribs, ditches, ponds, trenches, and structures; and
- characterization and/or monitoring, which commonly would involve soil sampling, and the installation of sensors, packers, and instrumentation.

Advanced and improved drilling technologies are needed to:

- reduce costs;
- minimize waste from drilling;
- maintain containment of drill cuttings and effluents while drilling; and
- improve well completion technologies.

BENEFITS

A horizontal drilling method which uses air as the circulating fluid could allow drilling in unsaturated soils such as those at Hanford. By using air rather than drill mud, fluid loss to the formation and contaminant mobilization is minimized.

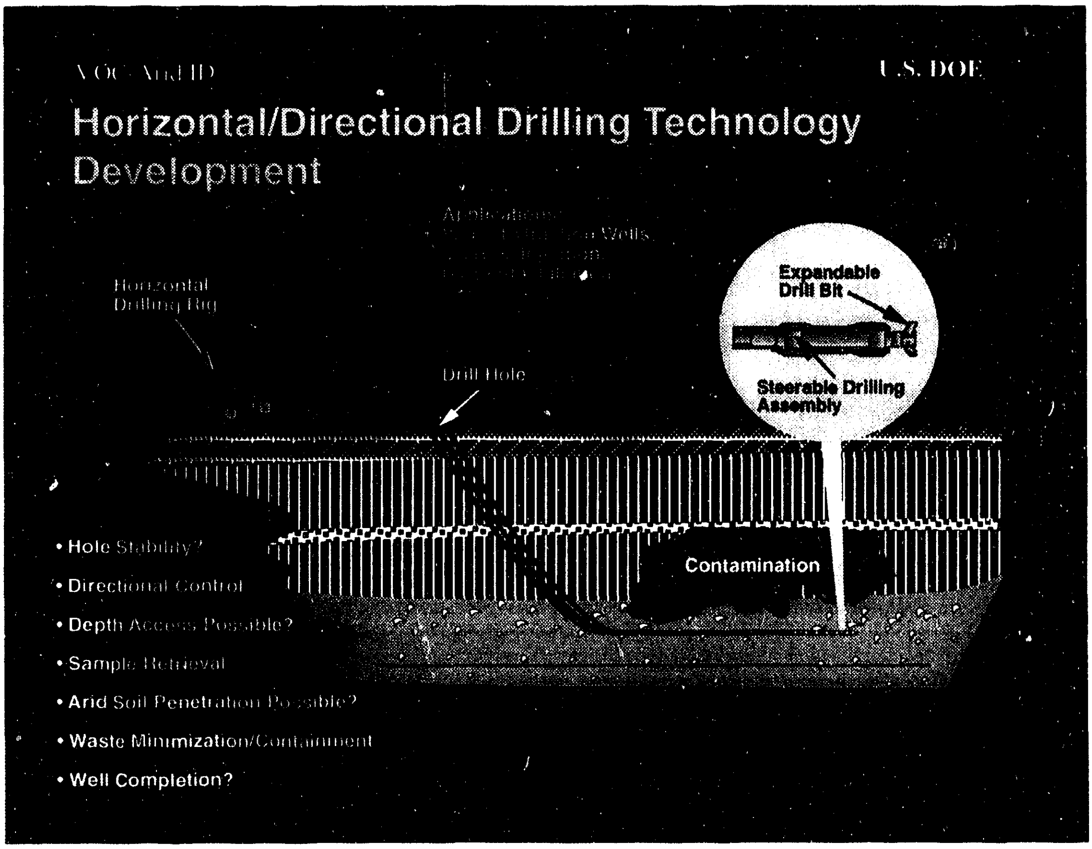
PROCESS DESCRIPTION

Directional drilling can be accomplished using an asymmetric drill bit or a bent drill pipe. The directional drilling processes currently being investigated begins with an angle or vertical hole which can be directed to bend in any direction. Steering is accomplished by using a slightly bent section of pipe, called a bent sub. When the outer casing, including the bent sub, is rotating, the hole will go straight, but when it is not rotating, the bent sub will cause the hole to naturally veer off in one direction (see Figures 1.2 a&b). As soon as the desired turn has been made, casing rotation is resumed and the drill bit cuts a straight path again, but in a new direction. Similarly, directional drilling using an asymmetric drill bit rotates to drill straight, but uses the asymmetry of the drill bit to steer instead of a bent pipe.

Two methods of directional drilling are currently being investigated at Hanford, air rotary drilling and air hammer. Both use down hole motors or hammers connected to an interior drive train to drive the drill bit and an outer casing with a bent sub which can be rotated independent of the inner drive train. Both use air circulation to cool the drill bit and remove cuttings. A vacuum method is being developed to contain the cuttings and filter circulation air to prevent contaminant spreading.

ACCOMPLISHMENTS

Horizontal drilling was initiated in the oil industry during the 1940s to improve production from oil wells. Environmental horizontal drilling was initiated in 1986 to increase volatile extraction capability from a remediation



VOC-Arid ID

U.S. DOE

Horizontal/Directional Drilling Technology Development

- Hole Stability?
- Directional Control
- Depth Access Possible?
- Sample Retrieval
- Arid Soil Penetration Possible?
- Waste Minimization/Containment
- Well Completion?

Figure 1.2a. Horizontal/Directional Drilling Technology Development.

area at the Savannah River Site. To date, five horizontal boreholes (four mud drilled, one shallow hole using no circulation fluid) have been installed at the Savannah River site. Vapor extraction volume has exceeded that which would be anticipated from several vertical boreholes. Horizontal boreholes have also been drilled using mud rotary techniques at Department of Defense sites across the United States. In addition, mud rotary horizontal drilling has been used in the river-crossing industry since the early 1970s.

COLLABORATION/TECHNOLOGY TRANSFER

Work on the development of an air turbine drilling system is being developed in cooperation with the New Mexico Institute of Technology. A plan to interest other commercial partners is also currently under development.

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Figure 1.2b. Directional Drilling Rig.

1.3 RESONANTSONIC^{SM} DRILLING

TASK DESCRIPTION

The objective of this task is to enhance the sonic drilling method to obtain representative geologic samples that meet data quality objectives. Furthermore, secondary waste generated will be minimized and costs for drilling will be reduced through increased productivity. Minimizing operational and contamination exposure hazards to personnel is also a requirement of this task. An additional goal is the deployment of instruments, sensors and other devices to the subsurface for characterization, remediation and monitoring purposes.

While the ResonantSonic^{SM} drilling method (see Figures 1.3 a&b) has produced improvements to baseline methods, a definite area for improvement is the minimization of downtime which is directly related to equipment failures both in the drill head and drill pipe. Currently sonic drilling is rated as marginal; however, recently tested enhancements in industry applications will increase the reliability to an acceptable level. The goal is to reduce overall down time from equipment failure and drilling related problems to less than 10%. Reduction of downtime rates to levels consistent with other drilling methods will result in significant cost reductions compared to the current baseline.

The major challenge of this project is the development of reliable drill pipe for resonant sonic drilling. A resonance monitoring system will provide valuable input in determining the threshold energy levels for the drill pipe design basis. In addition, an accurate measurement system to determine the thermal effects from the bit to the core sample is necessary to develop bits which will maintain temperatures of the

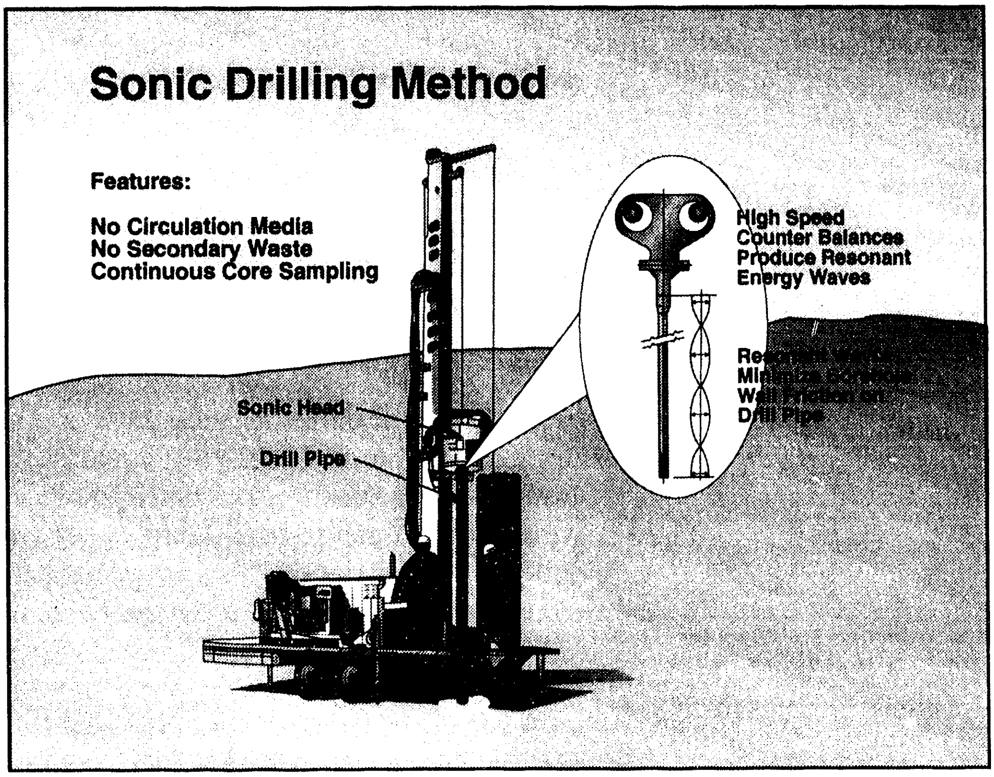

Figure 1.3a. ResonantSonic^{SM} Drilling.

contaminants being characterized at acceptable levels (e.g. to avoid volatilizing organics), while maintaining acceptable penetration rates. Resonant sonic methods for directional drilling applications are also being pursued, as is driving of casings up to 10 foot diameter.

TECHNOLOGY NEEDS

Advanced and improved drilling technologies are needed to:

- reduce costs;
- minimize waste from drilling; and
- maintain containment of drill cuttings and effluents while drilling.

ResonantSonic^{SM} drilling is a promising method for several drilling applications including: characterization boring, groundwater monitoring wells, vapor and water extraction wells, and barrier installation holes, vertical to horizontal continuous coring, or any type/size earth penetration with a steel pipe.

BENEFITS

The key advantages of the resonant sonic drilling method are:

- increased rate of drilling;
- containment of drill cuttings;
- minimization of secondary drilling waste;
- sample quality in formations where the baseline method cannot retrieve high quality samples (e.g., caliche, boulders); and
- increased safety due to less hands on exposure to physical hazards and waste contaminants.

Additionally, ResonantSonic^{SM} drilling minimizes contamination to supplemental drilling components (which occurs with systems which require a circulation media), and maintains excellent contamination control at the collar of the borehole. Drilling at any angle from horizontal to vertical is also possible.

PROCESS DESCRIPTION

ResonantSonic^{SM} drilling has three major components: a drill rig with the sonic head, drill pipe, and a core retrieval system. The drill head uses offset counter-rotating weights to generate sinusoidal wave force energy, and operates at frequencies close to the natural frequency of the steel drill column (up to 150 cycles per second). This causes the column to vibrate elastically along its entire length. In the resonant condition, drill pipe acceleration rates exceed 500 g's and forces up to 200,000 lbs per cycle are efficiently transmitted to the drill bit face to create a very effective cutting action.

As the pipe moves through the ground during drilling, the walls of the steel pipe expand and contract helping to reduce dampening of the vibrations caused by ground swelling. The drill bit can be designed to either push all the soils into the borehole wall or modified to allow a continuous core to enter into a core barrel. High quality core samples can be continuously retrieved by using either a wireline latch or small inner rod retrieval assembly, or acquisition of data can take place via down hole probes and sensors. No circulation medium is required with the resonant sonic method; therefore, unused core samples are the only secondary by-product from drilling. On a typical well (8 inch hole diameter) this relates to 1 drum of cuttings for every 60 feet drilled. This results from the fact that the resonant energy causes sands, gravels, cobbles and even clays to displace into the adjacent formation just enough to permit the drill pipe to advance into the formation.

ACCOMPLISHMENTS

Preliminary testing of sonic drilling at the Hanford site in 1991 resulted in a cost reduction of approximately 15-20% over 11 holes. Testing in 1993 with a redesigned sonic drill head has reduced downtime to less than 1% and resulted in significant improvements in core quality, core temperature reduction, use of robotic arms, and greatly reduced secondary waste generation. Angle drilling at 45 degrees and well completion were accomplished to 170 feet as per plan.

COLLABORATION/TECHNOLOGY TRANSFER

Development of the resonant sonic drilling method is being accomplished in coordination with Water Development Corporation (WDC). The DOE is currently operating under a CRADA with WDC. Due to the relatively unknown nature of the resonance impacts to drill pipe, teaming with an industry lead contractor for this system is a positive step toward solving it and other equipment reliability issues. WDC currently has all the patents, documentation files, and previous sonic drilling equipment from the resonant drilling system developed by Albert Bodine, the inventor of sonic drilling.

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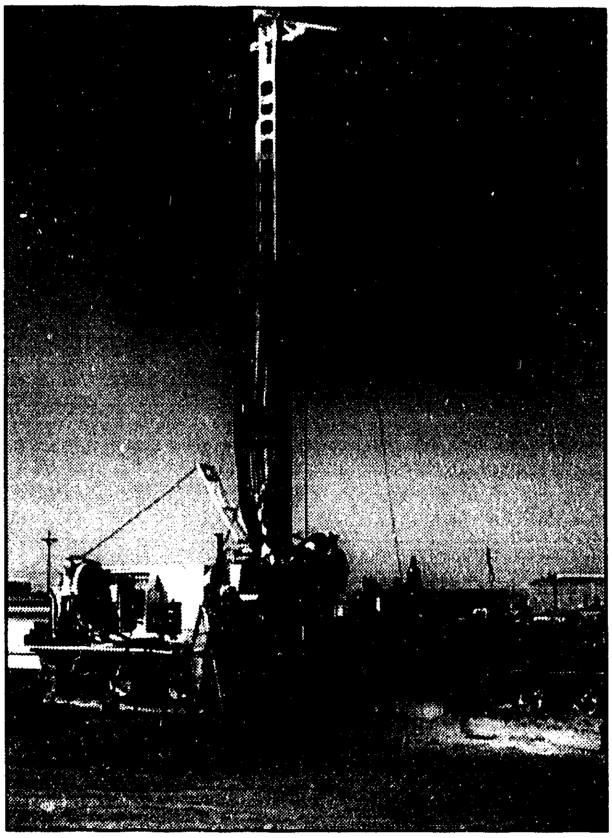

Figure 1.3b. Sonic Drilling Rig.

Characterization and Monitoring

Section 2.0

2.1 BOREHOLE SAMPLER

TASK DESCRIPTION

The focus of this task is to complete a field demonstration of the borehole soil-gas and aquifer sampling and testing device (BoreSampler). The BoreSampler will be applied for both soil-gas and groundwater sampling during characterization activities for in-situ remediation technologies. Technology transfer and commercialization through an industry partner are planned for 1994.

TECHNOLOGY NEEDS

Many of the DOE sites require characterization of contaminants in both the vadose zone and saturated zone in vertical profile. Improved capabilities are needed to determine subsurface contaminant concentrations and distributions. The BoreSampler is designed to collect soil-gas and groundwater samples underground during well drilling (see Figure 2.1). This technology provides an alternative to current methods, such as chemical analysis of retrieved sediment or the use of a packer systems for soil-gas sampling and bailed groundwater samples and chemical analysis of a retrieved water samples.

BENEFITS

Some techniques are available for obtaining ground-water samples during drilling, and some of these can obtain depth-discrete samples. However, each method has limitations, as discussed below. Formation water

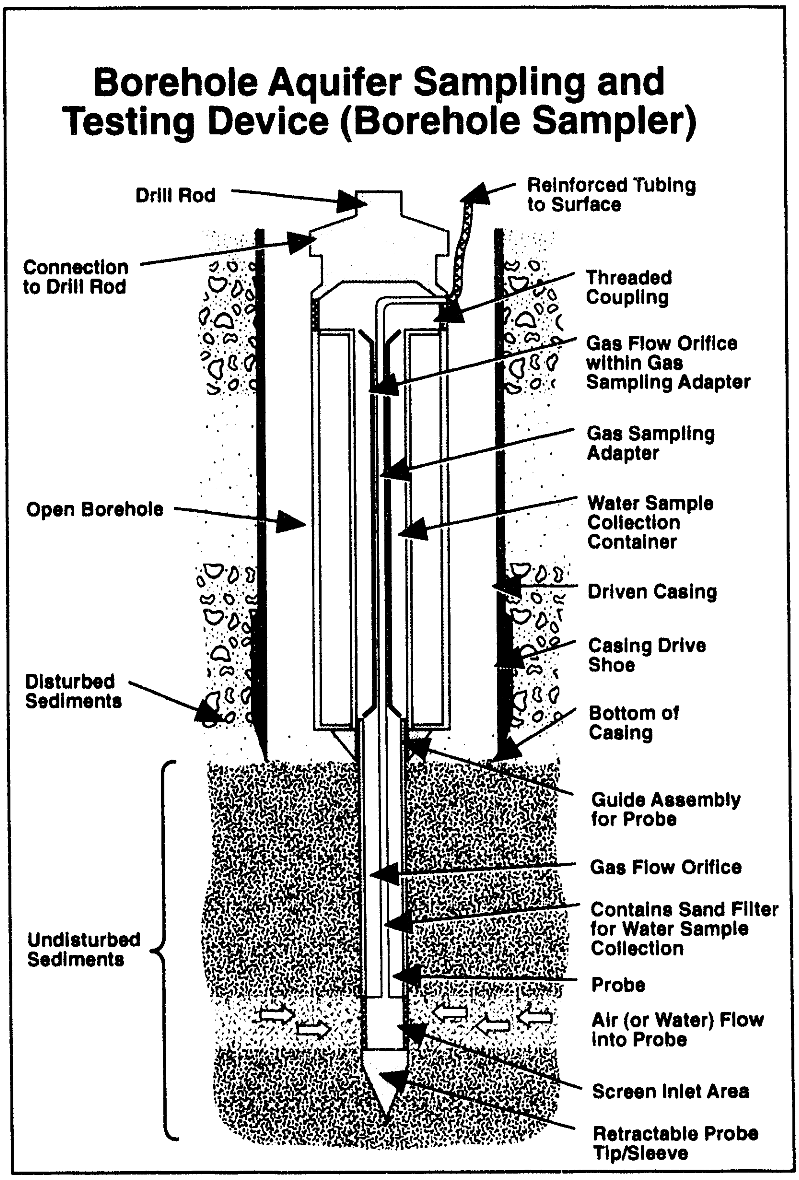

Figure 2.1. Borehole Soil-Gas and Aquifer Sampling and Testing Device (Bore Sampler).

samples can be collected by bailing or pumping water directly from the borehole; however, the samples are not representative of a discrete level in the formation, but rather of borehole fluids from which the precise depth of origin is unknown. In addition, borehole fluids contain solids which may compromise the representativeness of the water sample.

Screened augers are also used to collect water samples during drilling (Taylor and Serafini 1988); however, this method is applicable only during auger drilling.

Water samples can be obtained by in situ sediment samplers [e.g. split-spoon or other samplers (Zapico, Vales, and Cherry 1987, Hoffman and Dresen 1990)]. The disadvantage of this method is that water then has to be extracted from the sediment for analysis. Limited volume of water can be obtained by this method, and the subsampling and/or extraction process may affect the representativeness of the sample for some constituents, especially volatile organics.

A Hydropunch™ sampler can be used in conjunction with a cone penetrometer or with drill rods (Edge and Cordry 1989). This sample method is limited to water sampling and is also limited in some applications because drive rods need to be assembled and driven.

The BAT Enviroprobe can be used to collect soil-gas and water samples; however, a small sample volume is collected (500 ml maximum). In addition, drive rods need to be assembled to drive and retrieve the sampler.

Shallow-depth soil-gas sampling systems are readily available; however, they are severely limited in depth capability and generally allow only a single measurement for each sample hole.

The BoreSampler can be used between drilling runs during the drilling phase of borehole or well completion to obtain depth-discrete, representative soil-gas or groundwater samples in the undisturbed aquifer materials below the bottom of the borehole. It is a single device that is modular. It can easily be modified to collect either soil-gas or groundwater samples. Assembly of drive rods is not necessary. A larger volume groundwater sample can be collected than from other methods. A continuous soil-gas flow is pulled that can allow real-time monitoring and unlimited volume.

PROCESS DESCRIPTION

The BoreSampler is designed to obtain depth-discrete soil-gas and aquifer water samples, thus providing a means to characterize contaminant concentrations vertically without installing multiple wells. The device accesses the target zone between drilling runs by pounding or pushing a probe below the disturbed zone of drilling in order to collect the desired sample; the probe is removed after the sample has been collected. The BoreSampler is currently designed only for use and demonstration with cable-tool drilling. Future improvements of the system may include allowing use with other drilling methods by use of a wire-line with a drive head or driving rods.

The prototype BoreSampler currently consists of a reinforced probe and intake protruding from the bottom of a larger carrier. The carrier holds a sample container, provides excess volume retention for groundwater sample purging, provides valves for excess air discharge, and is currently designed to attach to drilling cable leading to the surface. For water sample collection, the device operates by driving the probe into undisturbed sediments below the bottom of a borehole. The sleeve that covers the access holes is opened, which then allows water to flow into the probe and through the system until the sample container is full. Before the container fills, excess water passes through the container and fills the carrier; this provides for a purging of the water that first enters the system.

A reinforced vacuum line leading to the surface is used for soil-gas sampling. A gas-flow orifice is placed in the probe. The groundwater sample container is removed and the reinforced line is connected directly to the probe before deployment. The probe is driven into the sediments below the borehole and the sleeve is opened in the same manner as for water sampling. Gas-sampling apparatus (pump, flow meter, sample containers) are located at the surface to control and collect soil-gas from the unsaturated zone.

The soil gas sample is withdrawn through the sample line and concentrations of soil gas are measured on site with field screening instruments, and samples are collected for laboratory analysis. Water sample is collected in the container and retrieved from the borehole, transferred to sample containers, and sent to a laboratory for analysis. Residuals that are generated include soil gas released to the atmosphere.

ACCOMPLISHMENTS

The field demonstration of the BoreSampler for soil-gas sampling was completed in 1993. A partnership plan was written, but a commercial partner has not yet been identified. The technology was transferred to the ER Program at the Hanford site for their application. Design changes were made to allow more flexibility and to make it easier to deploy.

COMMERCIALIZATION/ TECHNOLOGY TRANSFER

At the present time the BoreSampler is being developed without the participation of a commercial partner; however, a partnership plan has been prepared. Plans for 1994 include locating a commercial partner for commercialization.

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2.2 HALOSNIF

TASK DESCRIPTION

HaloSnif was designed to monitor carbon tetrachloride vapor in the vadose zone at the Hanford Site (see Figure 2.2). However, it is capable of measuring any volatile chlorinated compound in air, gas, or water. HaloSnif has been evaluated at Hanford as a real-time monitoring system for measuring carbon tetrachloride concentrations in soil gas being extracted at the Vapor Extraction Site (response to an Expedited Response Action) at the 200 West Area.

Targeted toward environmental cleanup, HaloSnif was developed as a monitoring system capable of providing real-time concentration data for volatile chlorinated hydrocarbons. One specific application included interfacing HaloSnif to a cone penetrometer rig to provide profiles of carbon tetrachloride concentrations as a function of depth. A second application at Hanford included using HaloSnif as a real-time monitor for carbon tetrachloride concentrations in soil gas extracted and subsequently cleaned up. Just recently in the laboratory, HaloSnif has been used to monitor real-time concentrations of trichloroethylene, tetrachloroethylene, and carbon tetrachloride in water samples. With this most recent development, HaloSnif may be useful for process or facility monitoring at DOE or industrial sites.

BENEFITS

HaloSnif is a chlorinated compound class-specific sensor system capable of providing real-time measurement capability for numerous environmental and process application relating to air, gas, or water monitoring. HaloSnif's response is insensitive to moisture and other non- chlorinated compounds present in the sample stream. The most important advantages are response, reversibility of response, and range, as explained below.

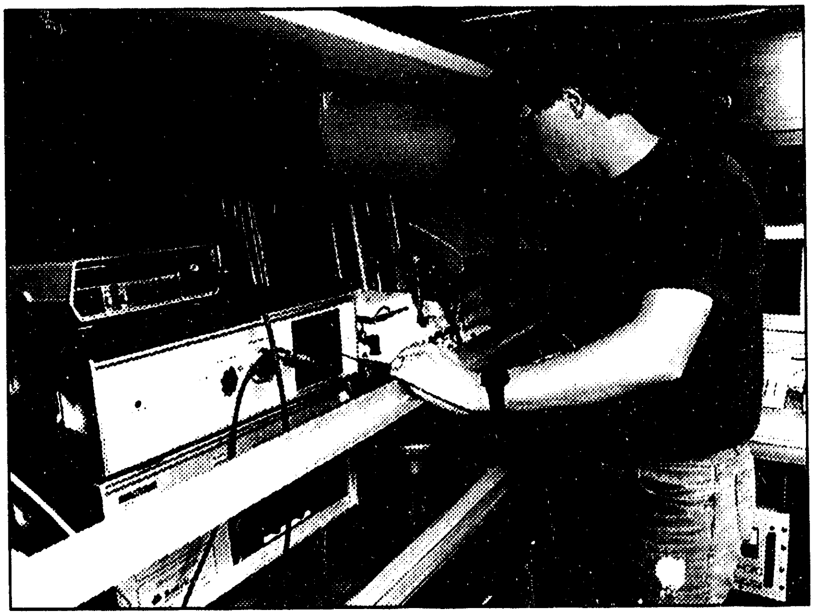

Figure 2.2. HaloSnif.

Instrument Response: HaloSnif is considered a real-time monitor, responding immediately to the presence of chlorine-containing compounds. Equilibration times normally are less than 1 minute to reach 90% of full scale. Short-term (2-4 hours) baseline drift is approximately ± 5 ppm.

Reversibility: HaloSnif's response is completely reversible when the source of chlorinated compound(s) is/are removed. Thus, it is immediately ready for re-use.

Range: HaloSnif's response to chlorinated species is linear from its detection limit to the compound (i.e., 4 ppm for carbon tetrachloride) to approximately 10,000 ppm.

TECHNOLOGY NEEDS

New technologies are needed to better evaluate subsurface characteristics of geohydrological features and contaminant distribution for more cost-effective sampling strategies using remote, in situ or on-site field screening methods. These techniques will enable an improved understanding of subsurface variability by achieving high-density data acquisition, with high-resolution, and real-time monitoring instrumentations. Furthermore, this technology will provide low-cost data on a real distribution of contaminant during characterization and cleanup activities, and efficient monitoring for post-closure of a site.

PROCESS DESCRIPTION

During monitoring operation, HaloSnif operating at sub-ambient pressure (40 torr) continuously draws an air sample through a critical orifice into the plasma excitation chamber where it is mixed with helium and excited with a radio-frequency signal inductively-coupled to the plasma chamber. The plasma chamber is coupled via a fused silica optical fiber to the signal processor unit. The optical emission of the plasma is filtered with an narrow band pass filter designed to monitor the 837.6 nm emission line from the excited chlorine atom. The intensity of the chlorine emission is directly proportional to the concentration of chlorine containing species in the sample gas. The detection sensitivity for carbon tetrachloride is 5 ppmv. The response of the system is linear from the detection limit to 10,000 ppmv. The detection limit for other chlorine containing compounds can be estimated by determining the ratio of chlorine in the compound of interest to that of carbon tetrachloride.

Data acquisition is achieved using a LabView™ data acquisition software package mounted on a Macintosh computer system. The data acquisition system is interfaced to the electro-optical signal processing module via a 1 to 10 volt analog output. Real-time concentrations of total chlorinated compounds are displayed on the monitor for observation by on-site personnel. All data is stored in computer memory for post-run processing and analysis.

ACCOMPLISHMENTS

HaloSnif has been successfully demonstrated at DOE's Savannah River site and Hanford Site. At Savannah River, HaloSnif was used to measure the concentrations of tetrachloroethylene and trichloroethylene in vadose zone monitoring wells and soil gas being extracted for catalytic destruction. At Hanford, HaloSnif was used as a real-time monitor for carbon tetrachloride concentrations in soil gas before and after cleanup with activated charcoal. HaloSnif was interfaced with a cone penetrometer rig to provide real-time measurements for carbon tetrachloride concentrations as a function of depth during site characterization activities. HaloSnif was also used to conduct long-term monitoring at several vadose zone test points installed with the cone penetrometer.

COMMERCIALIZATION/ TECHNOLOGY TRANSFER

HaloSnif was developed at Pacific Northwest Laboratory (PNL) and covered under U.S. patent 5,085,499 "Fiber Optics Spectrochemical Emission Sensors" issued in February 1992. Prototype HaloSnif systems have been further refined through a joint effort of PNL and Quanta Physik. Presently, two units constructed by Quanta Physik have been secured by standard purchase requisitions. A third Quanta Physik system has been ordered, with an expected delivery date of April 1994. The third system will be totally integrated to include a power supply, vacuum/gas handler, and electro-optical processing unit.

A solicitation for transferring the HaloSnif technology for commercialization was entered in the May 15 Commerce Business Daily (CBD). Fifteen firms requested additional information as a result of the CBD solicitation.

One HaloSnif unit has recently been transferred to Westinghouse Hanford Company, Richland, Washington, (EM-40) for independent evaluation at the Hanford VOC ERA site during soil vapor extraction in an area around the Plutonium Finishing Plant in 200 West Area.

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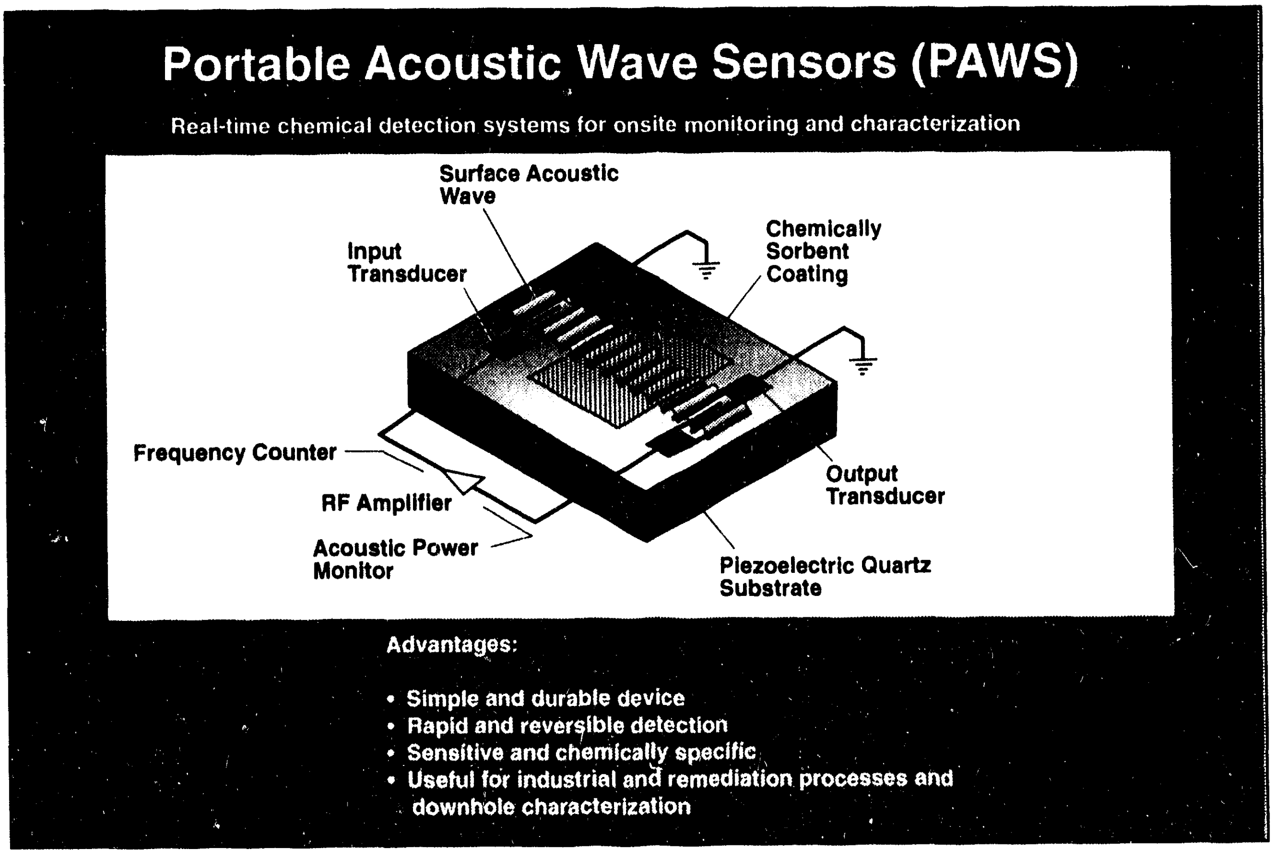
2.3 PORTABLE ACOUSTIC WAVE SENSOR

TASK DESCRIPTION

The objective of this project is to develop, test, and demonstrate field monitoring systems capable of quantitative detection of volatile organic contaminants found in vadose zone soils and in groundwater.

Current activities are focused in three areas. First, the down hole probe, successfully demonstrated in July 1993 at the Hanford Carbon Tetrachloride Site, will continue to be evaluated. As part of this evaluation, this down hole probe system will be transferred to Hanford Site environmental restoration personnel for their use on site over several months. The other two activates focus on the above ground version of the Portable Acoustic Wave Sensor (PAWS) technology (currently contained in a module about the size of a shoebox) (see Figures 2.3 a&b). One task involves providing a PAWS module to Hanford site personnel for their ongoing use as a real-time, continuous monitor of carbon tetrachloride in the off-gas streams from the soil vapor extraction systems. The final task involves developing an environmental sampling system using preconcentrators and semi-permeable membranes that will enable the PAWS system to be used to monitor the residual carbon tetrachloride after on-site destruction in off-gas streams. These treated streams have high acid contents



Portable Acoustic Wave Sensors (PAWS)

Real-time chemical detection systems for onsite monitoring and characterization

Advantages:

- Simple and durable device
- Rapid and reversible detection
- Sensitive and chemically specific
- Useful for industrial and remediation processes and downhole characterization

Figure 2.3a. Portable Acoustic Wave Sensor (PAWS).

making them a special challenge for a monitoring system.

Hardware miniaturization is especially important if the PAWS is to be used with the cone penetrometer. Development of coatings and pattern recognition for characterizing multiple chemical species simultaneously is also important. Another challenge is to decrease the detection limits based upon improved coatings and environmental sampling techniques. The development and evaluation of semi-permeable membranes for groundwater analysis, and for monitoring of residual contamination in acidic treated streams is also being examined.

In some situations the current level of accuracy may need to more sensitive. For groundwater measurements, the sensor may need to operate in the ppb range. There appear to be no major technical issues associated with dropping the order of magnitude of the sensors, i.e., making the sensor more sensitive.

TECHNOLOGY NEEDS

Many DOE sites have been contaminated with volatile organic compounds, such as the carbon tetrachloride and TCE that are found at the Hanford site. To characterize this contamination sensors are needed that can be put down into monitoring wells or holes drilled for characterizing a site. One example of these sensors is PAWS. Using a downhole sensor allows for characterization of a site in real time, instead of waiting for a laboratory to analyze every sample.

BENEFITS

PAWS can perform continuous, on-line or in situ monitoring, with rapid and reversible response. In comparison to offsite grab sample analysis, PAWS will perform real-time monitoring of carbon tetrachloride. This can be beneficial when conducting remediation activities. The sensor can be placed down a hole for in-situ monitoring, and can be automated to provide chemical information to site remediation workers on the distribution and concentration of contaminants. PAWS has capabilities for determining both molecular species and concentration of isolated chemicals. It is faster, cheaper, and as safe as a gas chromatograph or infrared analyzer.

PROCESS DESCRIPTION

PAWS involves monitoring down-hole contaminant levels for volatile organic compounds using acoustic wave sensors. These sensors will be used with on-site monitoring wells or placed in the ground using a technology such as a cone penetrometer (see the fact sheet on the cone penetrometer).

The sensor module contains:

- a coated sensor;
- gas handling equipment; and
- electronics to operate the device.

The PAWS system monitors changes in the speed and power of the wave as it travels across the sensor. These changes occur because a film coating the sensor softens and becomes heavier when it absorbs the contaminant.

Coatings have been developed that respond to VOCs. Using one coating material, polyisobutylene, the PAWS system is able to discriminate carbon tetrachloride from many other contaminants based on a comparison of the two sensor responses. This and other coatings will be tested and used with the probe.

ACCOMPLISHMENTS

Two basic sensor systems have been developed and tested in five field demonstrations at the Hanford Carbon Tetrachloride Site. One is an above ground system for on-line monitoring, while the other is a down hole probe for in-situ characterization of VOC contaminants in the vadose zone. Both systems provide sensitive and accurate (within 2%) analysis, rapid response (few seconds) for real-time monitoring, wide dynamic range (10-50,000 ppm for carbon tetrachloride), an ability to provide molecular discrimination of isolated species based on a patented dual output technique, simple set-up and operation, and low maintenance.

Using the above ground system, on-line monitoring of contaminant concentration for soil vapor extraction systems was demonstrated at both Savannah River and Hanford. Based on the success of these tests, a PAWS system is being provided to Hanford environmental restoration personnel for their on-going use. Demonstrations were also performed showing the potential for real-time analysis of gas samples as a cone penetrometer probe is pushed into the soil at a contaminated site.

The PAWS down hole probe has been demonstrated at the Hanford site as part of the VOC-Arid ID. The probe was placed in six different wells with diameters from four to eight inches. Concentrations from below 10 ppm to over 20,000 ppm were successfully observed during the demonstration, illustrating the wide range of concentrations these systems can monitor.

COMMERCIALIZATION/ TECHNOLOGY TRANSFER

A key component of this program is the transfer of the PAWS monitoring technology to industry. PAWS systems are currently being evaluated by two U.S. companies for other markets including industrial waste applications. One potential commercialization partner has already completed tests exploring PAWS performance characteristics. Another partnership focuses on developing and demonstrating a more advanced PAWS system to provide on-line chemical information for a VOC recovery and recycling system. In addition to these interactions, a recent commerce business daily announcement has been published seeking additional industrial partners for the use, development, and manufacturing of monitoring systems based on the PAWS technology. Thirty respondents have expressed interest in commercialization of this technology. Information exchanges are in progress.

A patent has been issued to DOE and transferred to Sandia National Labs. The PAWS is covered under patent number 5,076,094.

Similar work is being done by universities and private industry but no sensors have dual output. In addition to its application for environmental restoration, this technology could have applications in industry for real-time, on-line monitoring of exhaust stacks, or work place environments. Sensors could be integrated into on-line process control systems to optimize process operations.

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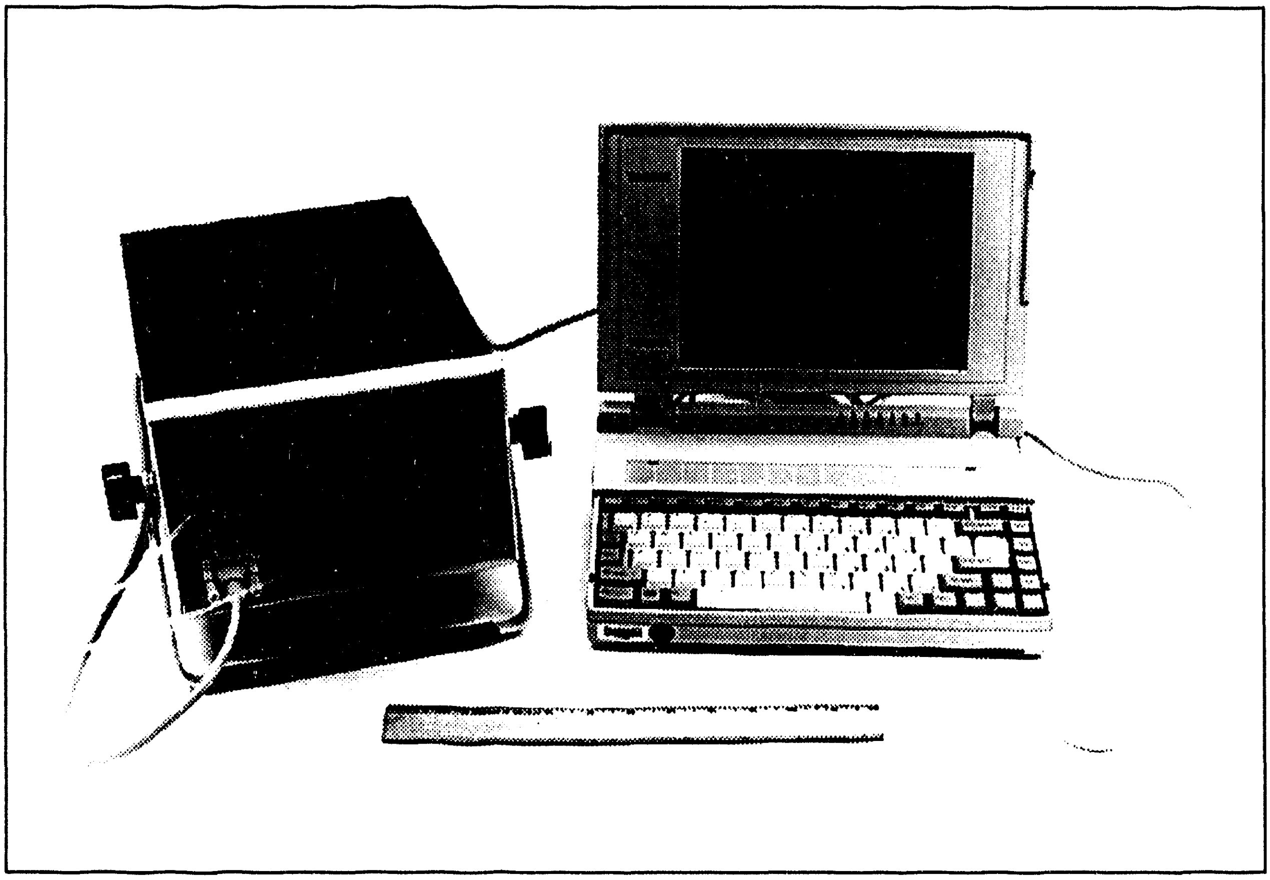

Figure 2.3b. Bench-Top Portable Acoustic Wave Sensor.

2.4 UNSATURATED FLOW APPARATUS

TASK DESCRIPTION

This task is focused on developing the Unsaturated Flow Apparatus (UFA) method and instrument for use as a laboratory technique that simulates the migration of VOCs, microbial nutrients, and water in the subsurface environment of arid sites (see Figures 2.4 a& b). Instead of taking weeks or years to obtain hydraulic transport data on unsaturated environments, the UFA method can generate this information in several hours. The UFA method can address any flow transport problem involving almost any fluid in any porous media under almost any condition.

One of the major challenges facing the UFA method is the preparation of the sample, i.e., obtaining undisturbed samples. Special handling may be required for some applications to prevent drying, and to maintain original structures.

TECHNOLOGY NEEDS

A method is needed to determine contaminant distribution and behavior in subsurface environments at the VOC-Arid ID. In addition, there is a need for remote, in situ, and other on-site methods that increase the safety and cost

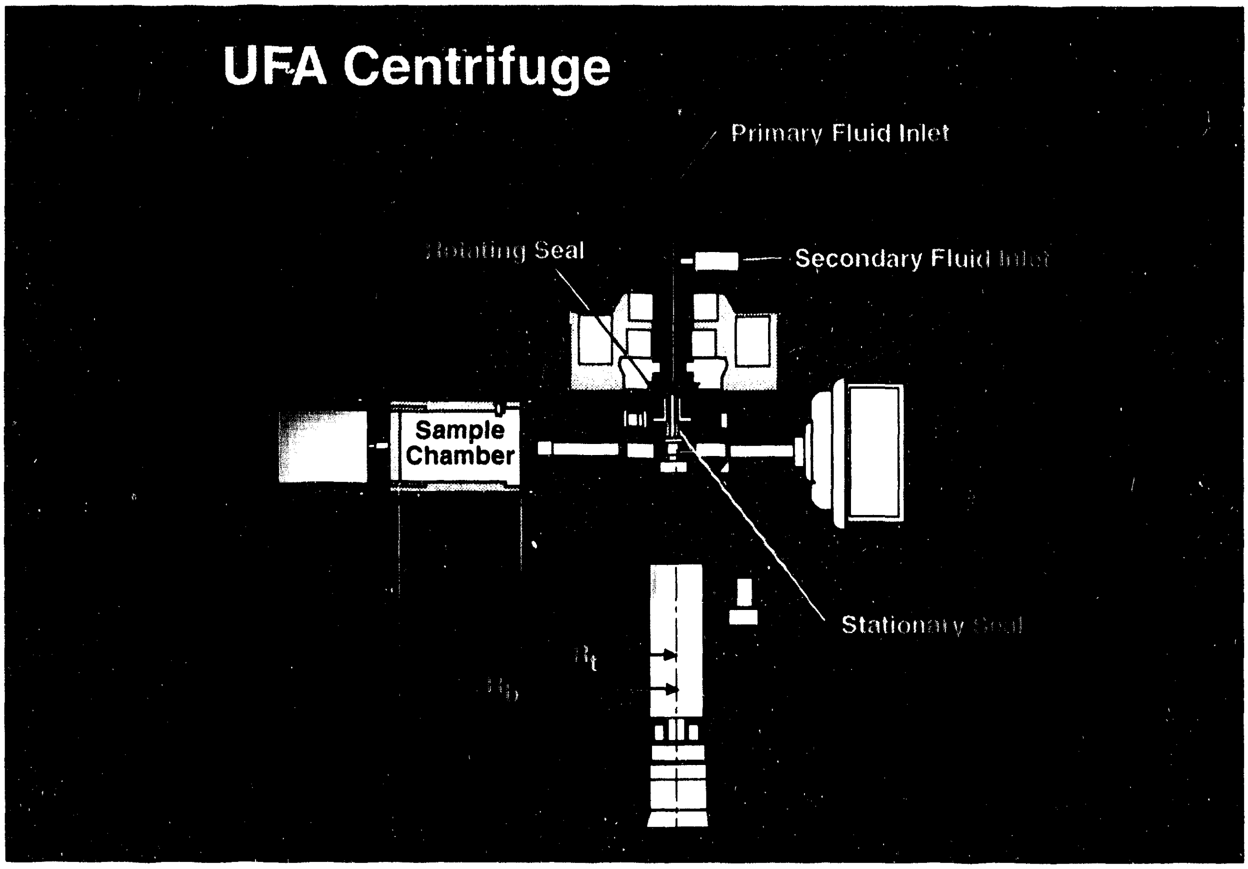

Figure 2.4a. Unsaturated Flow Apparatus.

effectiveness of local contaminant characterization.

The alternative to the UFA method is dependence on less reliable assumptions (e.g., data based on wetter vadose zone conditions) to extrapolate contaminant behavior. This could result in choosing a restoration strategy which is less appropriate for this region of the subsurface. Inadequate predictive capability in this area will lead to loss of time, money, and credibility and will hinder DOE meeting its long-term environmental restoration goals.

BENEFITS

The major benefit of this technology is rapid, direct measurement of VOC transport and, therefore, improved predictive capabilities of VOC migration, greater probability of choosing successful restoration strategies, improved remediation schedules, and a reduced need in the future for lengthy experimental programs. Cost savings, based on the time and effort spent on experiments alone, is expressed in orders of magnitude, since transport data can be obtained by the UFA in hours as opposed to months or years by more conventional methods.

The UFA method directly measures transport parameters at water contents well below those measured by any existing method. As an example, hydraulic conductivities have been measured in soils with water contents ranging from fully- saturated down to highly-unsaturated (water content is only a few percent and hydraulic conductivities are 10^{-10} cm/s) in three days. This technology can also be used to do quick screening. The UFA can provide data to describe field conditions which cannot be obtained under normal conditions.

PROCESS DESCRIPTION

Soil samples are collected from the site using cable tool drilling/split spoon sampler technology. The soil or bedrock samples are transferred to a specially designed titanium canister and subjected to as much as 20,000 g's in an open-flow centrifugation device. A rotating seal assembly fitted to the canister allows an ultra-low flow pump to deliver liquid or gas to the sample surface during centripetal acceleration. When steady state conditions are reached (within a matter of hours), transport parameters can be evaluated, e.g., hydraulic conductivity to measure permeability, diffusion coefficient, and breakthrough retardation. Data specific to remediation site sediments is then compiled.

The carbon tetrachloride introduced into the UFA samples will be collected in the effluent collection chamber. It is anticipated that during one year, no more than one liter of carbon tetrachloride will be used in UFA analyses. In addition to the carbon tetrachloride, any remaining water (e.g., pore water) that exists within the soil will also be collected in the effluent collection chamber.

The UFA method supports the development of restoration technologies such as vapor extraction (e.g., estimate vapor migration rates) or bioremediation (e.g., estimate nutrient delivery rates) for unsaturated soils. In addition, data obtained using the UFA can be used to validate predictive models of subsurface contaminant migration and to screen the performance of various remediation technologies in the field.

ACCOMPLISHMENTS

The major accomplishment of this project related to the initial goals has been the direct, rapid measurement of the flow behavior of uncontaminated soils and sediments beneath the Z-plant at Hanford site from completely saturated to the highly-unsaturated conditions that exist at Hanford. This has never before been accomplished. Specific accomplishments were:

- The prototype UFA was modified to accommodate VOCs and other non-aqueous phase liquids.
- A new UFA system is being designed that is much less expensive and has low-temperature capabilities for frozen soils work.
- One UFA unit has been purchased outside this project and several other outside parties have expressed the desire to purchase UFA units over the next year. A brochure has been printed for marketing and sales of the UFA.
- The project is preparing a short course to be given at the 1994 annual meeting of the Geological Society of America in Seattle, Washington, entitled "Measurement of Unsaturated Transport in Porous Media."

Several new characterization techniques have been developed based upon the UFA method that were not anticipated at the outset of this project. These techniques have provided significant increases in our fundamental understanding of the subsurface environment at the Hanford site and these techniques can be used at any site:

- Data gathered using the UFA method was used in combination with data on field moisture contents to map artificial recharge in the subsurface associated with contaminant plumes and surface discharges to disposal cribs and trenches.
- The UFA method, together with borehole samples, was used to construct a hydrostratigraphic map of the subsurface that predicts, in detail, the transport and flow behavior of the soils and beneath the Z-plant. This significantly enhanced the conceptual model of the site and our knowledge of where the contaminant plume has migrated.
- The UFA instrument was successful in extracting pristine pore water from unsaturated samples, including highly unsaturated soils. This marked the first time that pristine pore water was obtained from the vadose zone at any site.

COMMERCIALIZATION/ TECHNOLOGY TRANSFER

The UFA instrument is being developed in a joint effort with Beckman Instruments, Inc. Beckman developed the rotating seals for the UFA instrument based on existing technology used to spin oil out of whole rock shales. A CRADA has been put in place between Beckman and PNL that addresses all intellectual property rights. Beckman is providing prototype instruments for PNL use. PNL will use the instruments to develop and refine the technology and its applications.

Environmental companies may be very interested in working with PNL to test the performance of their technologies on arid soils. There may be a need for UFA specialists to work with principal investigators who are assessing the feasibility of laboratory user facilities for site remediation.

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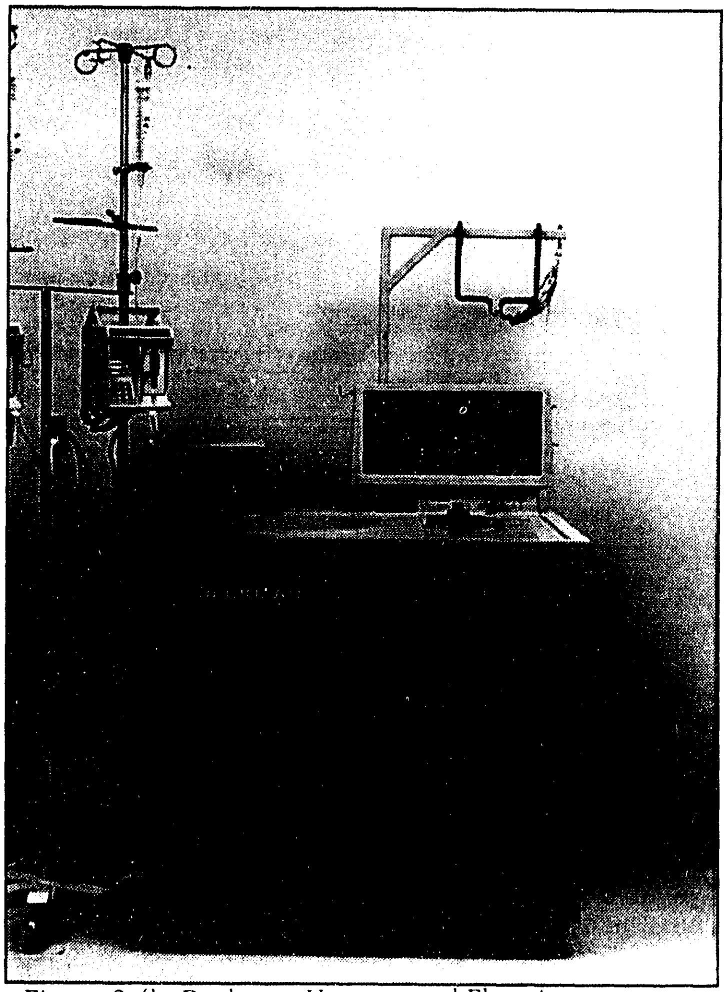

Figure 2.4b. Beckman Unsaturated Flow Apparatus.

2.5 SUPERCRITICAL FLUID EXTRACTION/FIELD DETECTION

TASK DESCRIPTION

The performance of a commercially available Supercritical Fluid Extraction (SFE) system was compared to baseline extraction technology (Soxhlet extraction) in laboratory tests conducted in the latter part of FY93 at PNL (see Figure 2.5). The tests incorporated Hanford site sediments spiked with tributylphosphate and lard oil, organic chemicals co-disposed with carbon tetrachloride in large quantities to the ground at Hanford's 200 West Area. During the conduct of the tests, additional data was compiled (e.g., capital and supply costs, space and facility requirements) in the event that a cost evaluation comparing SFE and Soxhlet processes was desired. Results of the study will be made available to interested industrial parties for use in refining existing commercial SFE systems.

The FY93 study evaluated only one SFE design on the commercial market and therefore the data may not be fully representative of the performance of all SFE systems on the market relative to the baseline technology. An additional test has been proposed that evaluates the performance of a system that contains a variable restructure and sorbent trap collection device in order to provide a broader base of data on which SFE technology application and purchase decision-making can be made.

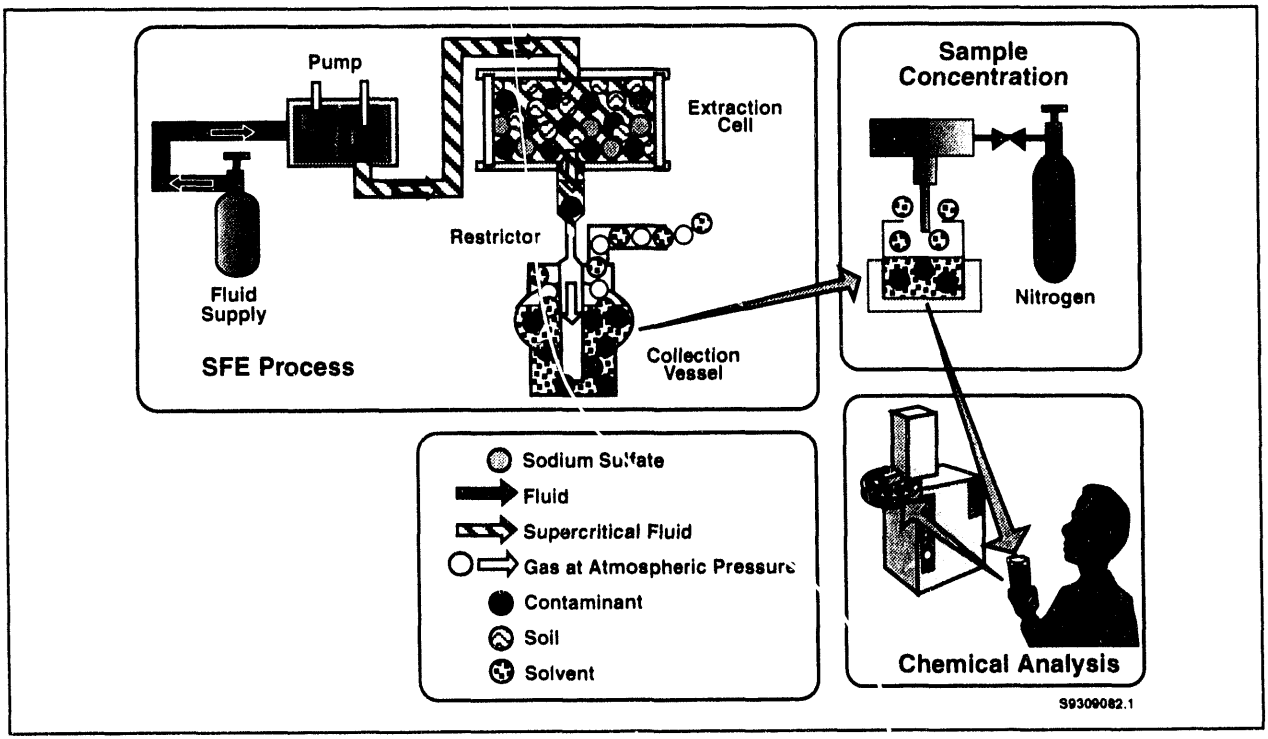

Figure 2.5. Typical Characterization Scheme using Supercritical Fluid Extraction (SFE).

Results of the FY93 tests suggest that improvements are needed to some commercial SFE systems in the areas of pumping capacity, restructure design and analyte trapping efficiency. Improvements in system design are also needed to eliminate solvent emissions during SFE operation, a factor that will likely become important as facility emission regulations become more restrictive. Application of SFE to the characterization of organic contaminants in radioactive mixed waste and environmental samples will require additional technology development.

TECHNOLOGY NEEDS

Technologies are needed that speed up the availability of characterization data necessary for waste management and remediation decisionmaking while reducing costs (e.g., in many cases over 60% of the cost of organic contaminant characterization of soils, sediments or solid wastes can be attributed to lengthy and laborious liquid solvent-type extractions); reducing the amount of toxic waste generated; and reducing/eliminating environmental, safety and health concerns associated with technology application.

Technologies are needed for the characterization of organic contaminants in radioactively-contaminated wastes, soils and sediments for application in laboratory and field environments.

Because of proposed and promulgated regulatory drivers (e.g., Montreal Treaty), Soxhlet extraction and other extraction methods (e.g., sonication) that require the use of solvents become less desirable as standard characterization tools. A solution to this situation would be to adopt emerging technologies that significantly reduce or eliminate the use of organic solvents. However, many analytical laboratories cannot afford the change-over to methods that require more sophisticated instrumentation. Methods that use less solvent, such as automated Soxhlet extraction are being evaluated as short-term solutions until optimization and regulatory acceptance of alternative emerging technologies (e.g., SFE) is achieved.

BENEFITS

As the technology matures, SFE when coupled with standard measurement tools may offer a safer and more cost effective replacement to Soxhlet extraction for the characterization of semi-volatile and non-volatile organic contaminants in soils, sediments and solid wastes. SFE systems are field transportable and process components will take up considerably less space in a mobile laboratory than conventional extraction technology. Application in the off-line mode allows extracts of samples to be analyzed by a variety of field transportable chromatographic and spectrometric techniques, enhancing the characterization of field laboratories. It is anticipated that increased cost savings will be realized when advanced systems are applied to radioactive mixed waste and environmental samples where use of excess solvents is prohibitive (e.g., solvents used in hot cells have to be treated as radioactive mixed waste). In addition, SFE may prove to be effective for the characterization of waste and environmental samples containing toxic or unstable compounds (e.g. explosives) common to DOE sites

PROCESS DESCRIPTION

SFE is a technology which uses a solvent with properties between that of a gas and a liquid to more efficiently extract contaminants from solid matrices such as wastes, soils and sediments. The solvent, or supercritical fluid, most commonly consists of pure, non-toxic carbon dioxide or carbon dioxide that contains small quantities of modifiers to enhance extraction of some contaminants. Modifiers typically include organic chemicals such as methanol or acetonitrile.

In the SFE process, a fluid is passed through a pump and raised to its supercritical temperature and pressure. This supercritical fluid enters a high pressure stainless-steel extraction cell containing the solid matrix (e.g., soil, 0.5-30 grams) co-mixed with a drying agent such as sodium sulfate. Organic contaminants sorbed to the soil rapidly dissolve in the supercritical fluid while water in the soil (which can adversely effect contaminant extraction and recovery and can be a factor in restructure plugging) is retained by the sodium sulfate. The supercritical fluid containing dissolved contaminants exits the extraction cell and passes through a restructure into a collection vessel containing a small amount of organic solvent (2-30 ml).

As the fluid passes through the restructure, the fluid cools and expands to a gas at atmospheric pressure. The restructure is either fixed or variable in design and is required to allow fluid flow while allowing supercritical fluid conditions to be retained in the extraction cell. As an alternative to trapping in an organic solvent, some commercial systems collect the contaminants on sorbent traps that may be cryogenically cooled.

The contaminant extract in the collection vessel is further concentrated under a stream of nitrogen gas may then subjected to several different preparative steps (e.g., chromatographic cleanup or filtration) prior to being subjected to a variety of possible chromatographic, spectroscopic and/or spectrophotometric measurements (e.g., gas chromatography, gas chroma-tography/mass spectrometry and infrared spectroscopy). The extraction process typically takes less than an hour. Sample cleanup can be facilitated through the application of programmed fractionation capabilities.

ACCOMPLISHMENTS

Based on 34 SFE and 64 Soxhlet extractions conducted in the FY93 tests, a commercial SFE system was found to give mixed performance relative to Soxhlet extraction. SFE was found to be less labor intensive (15 min/sample vs 85 min/sample) and provided more rapid turn-around time (2 hrs vs 27-35 hrs) than Soxhlet extraction. In addition, while it was shown that Soxhlet extraction produced significant liquid waste (2,560 ml of solvent/8 samples) and some solid hazardous waste (40 g/8 samples), the SFE process did not produce a liquid waste, and its solid waste is likely to be non-hazardous. Soxhlet extraction produced significantly more solvent releases to the atmosphere than SFE (640 ml/8 samples vs 105 ml/8 samples).

However, both systems tested released significant concentrations of hazardous chemicals to the air during their time of operation. Adjustments need to be made to SFE system design to eliminate solvent releases to the atmosphere as pollutant discharge limits for research facilities are promulgated and so that a hood would not be required for its operation.

While SFE extraction efficiency of analytes from aged soils was demonstrated to be high and comparable to Soxhlet extraction, recovery of the analytes by SFE was low relative to Soxhlet (40-54% lower) due to poor solvent trapping efficiency. Improvements are needed to the SFE system hardware that employ solvent collection (e.g., pumping capacity, restructure design, and analyte trapping) to achieve consistent analyte recovery performance observed with Soxhlet extraction.

COMMERCIALIZATION/ TECHNOLOGY TRANSFER

A partnership is actively being pursued at this time with a Cooperative Research and Development Agreement (CRADA) development and implementation anticipated in FY94. A partnership is needed to leverage DOE/industry capabilities to develop, test and commercialize advanced systems.

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Retrieval of Contaminants

Section 3.0

3.1 IN-WELL VAPOR STRIPPING

TASK DESCRIPTION

The objective of this project is to demonstrate the In-Well Vapor Stripping system in the field at the Hanford site for extracting VOCs from groundwater. The demonstration will primarily show the effectiveness and efficiency of the method to remove carbon tetrachloride from the groundwater on a continuous basis. The system will first be demonstrated for groundwater remediation, but a combined soil vapor extraction and groundwater remediation system will also be demonstrated. The combined system can remove VOCs contained in both the vadose zone (soil) and the saturated zone (aquifer).

The in-well vapor stripping method, as currently envisioned, will not remove non-volatile compounds from the groundwater. If wells are not properly located, it is possible to spread the partially remediated (lower concentration) plume by recirculating partially treated water beyond the radius of influence of the well. Discharges to the vadose zone may also mobilize pockets of contaminant in the vadose zone, adding to the total mass of contaminants in the aquifer, but these can be captured by the in-situ VOC removal well. Current efforts to improve this system are focused on resolution of these issues.

TECHNOLOGY NEEDS

Many DOE sites have aquifers where groundwater is contaminated with VOCs. Carbon tetrachloride, chloroform, and trichloroethylene are found at the Hanford site. It is expensive to bring the water to the surface for treatment. Furthermore, if the water contains tritium, as at the Hanford site, surface storage and disposal of the tritiated water is a major problem. Using the In-Well Vapor Stripping, the VOCs are removed from the aquifer without removing the contaminated water. The system provides a means to convert a groundwater contamination problem into a vapor stream, which can be easily treated at the surface.

BENEFITS

The In-Well Vapor Stripping system can continuously remove VOCs from groundwater without lifting the water to the surface or removing the water from the ground. It has the advantage of being an in-situ method (see Figure 3.1). It avoids the need for handling contaminated water above the ground surface and for disposing or storing partially treated water.

There is no need for an above-ground air-stripping tower or storage tanks to contain the tritiated water that is free of VOCs. Compared to the baseline pump-and-treat method, where reinjection of tritiated water was permitted, the in-well VOC removal system would not require the expense of drilling injection wells. The method has the further advantage of enabling recirculation of chemical aids to groundwater remediations, such as surfactants and catalysts. Finally, it also has the advantage that a single well can be used for extraction of soil vapors and for groundwater remediation. The baseline technology would require sepa-

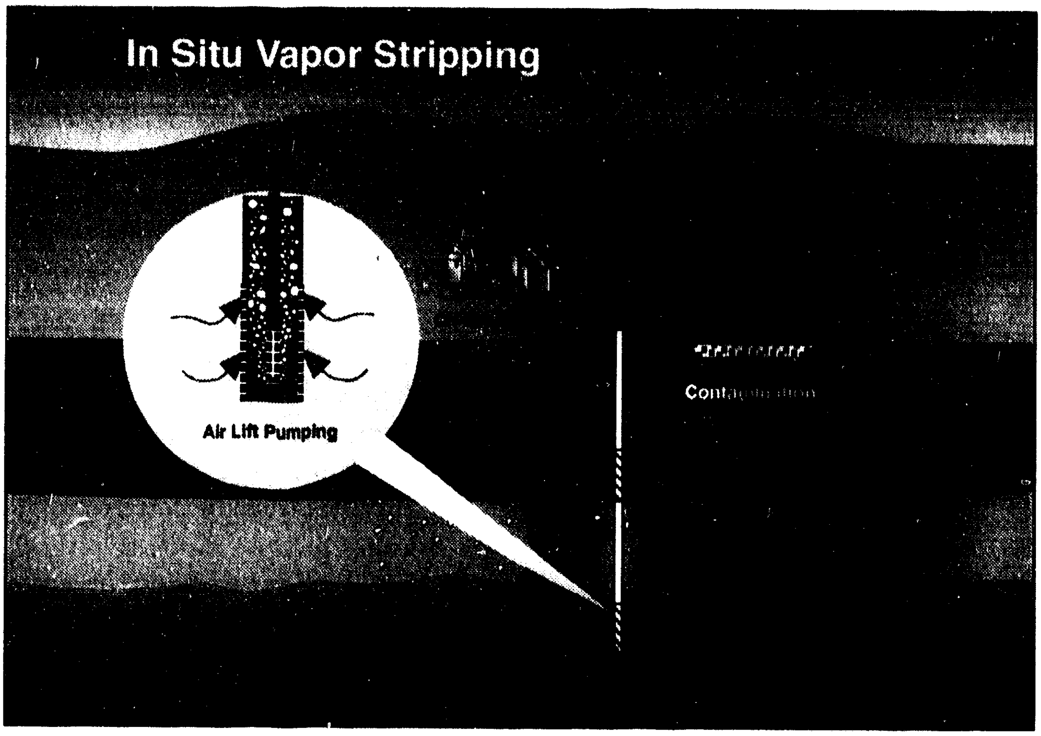

Figure 3.1. In-Well Vapor Stripping.

rate pump-and-treat wells and soil vapor extraction wells. The in-well VOC removal system is cheaper, safer, and as fast as pump-and-treat and soil vapor extraction.

PROCESS DESCRIPTION

The In-Well Vapor Stripping system creates an in-well air stripper, which volatilizes the VOCs contained in the groundwater, and removes these contaminants as a vapor. The vapor is then extracted under a vacuum and treated at the ground surface. The system consists of a special well design that consists of a well within a well. The inner well extends from the ground surface into the saturated zone and is screened in the zone of contamination. The outer well extends from the ground surface through the vadose zone and may terminate above the water table. This outer well may be screened in the vadose zone so it can be used for soil vapor extraction. A gas injection line is placed in the inner well and releases bubbles in the well at an elevation beneath the zone of contamination. The bubbles rise in the well and collect VOCs which are naturally transferred from the liquid phase to the gas bubbles. The bubbles and water rise within the well until they hit a packer which is placed in the inner well above the elevation of the water table. The inner well is screened just below the packer, allowing the water and bubble mixture to escape into the annular space between the inner and outer well. The water falls down the annular space and is returned to the water table. The gas bubbles pop and are vacuumed off via a vacuum line extending from the ground surface into the annular space between the inner and outer well. In this way the VOC-enriched vapor is extracted off and the partially cleaned water is returned to the aquifer. The system creates a recirculation environment for the groundwater through air-lift pumping. In essence, the In-Well VOC Removal System converts groundwater contamination into a contaminated vapor which is then vacuum extracted and treated. At the same time, airlift pumping creates a groundwater circulation cell in which the groundwater becomes sequentially cleaner and cleaner with each pass through the in-well air stripper.

COMMERCIALIZATION/ TECHNOLOGY TRANSFER

In-Well Vapor Stripping is currently being developed in cooperation with NoVOCs, Inc. Stanford University owns the patent for this technology, #5180503; however, the licensing has been transferred from Stanford to NoVOCs which is in the process of seeking industrial alliances in the United States. There has been serious interest from large engineering and oil companies in the environmental remediation area. They are awaiting the results of this demonstration.

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3.2 SIX-PHASE SOIL HEATING

TASK DESCRIPTION

A large-scale field demonstration of Six-Phase Soil Heating (SPSH), also referred to as ERACE, was initiated in November 1993, at the Savannah River Site (SRS) and completed in December 1993. The objective of this demonstration is to show that chlorinated solvents (trichloroethylene, trichloroethane, and tetrachloroethylene) can be removed from a highly impermeable clay soil by SPSH in conjunction with an integral soil vapor extraction (SVE) system, modified to handle the large quantities of steam generated by the heating process (see Figures 3.2 a&b).

At SRS, the contaminated zone extends between depths of 35 and 50 feet below surface, and contains a massive 10-foot thick clay layer contaminated with the solvents. Electrodes installed in a 30-foot hexagonal array at these depths are expected to heat and treat a soil volume of 1050 cubic yards, with equal volumes treated inside and outside of the array. Treatment efficiency will be determined by analyzing core samples obtained before and after the demonstration. This task will be completed with a final summary report on the results of the demonstration and a commercialization plan.

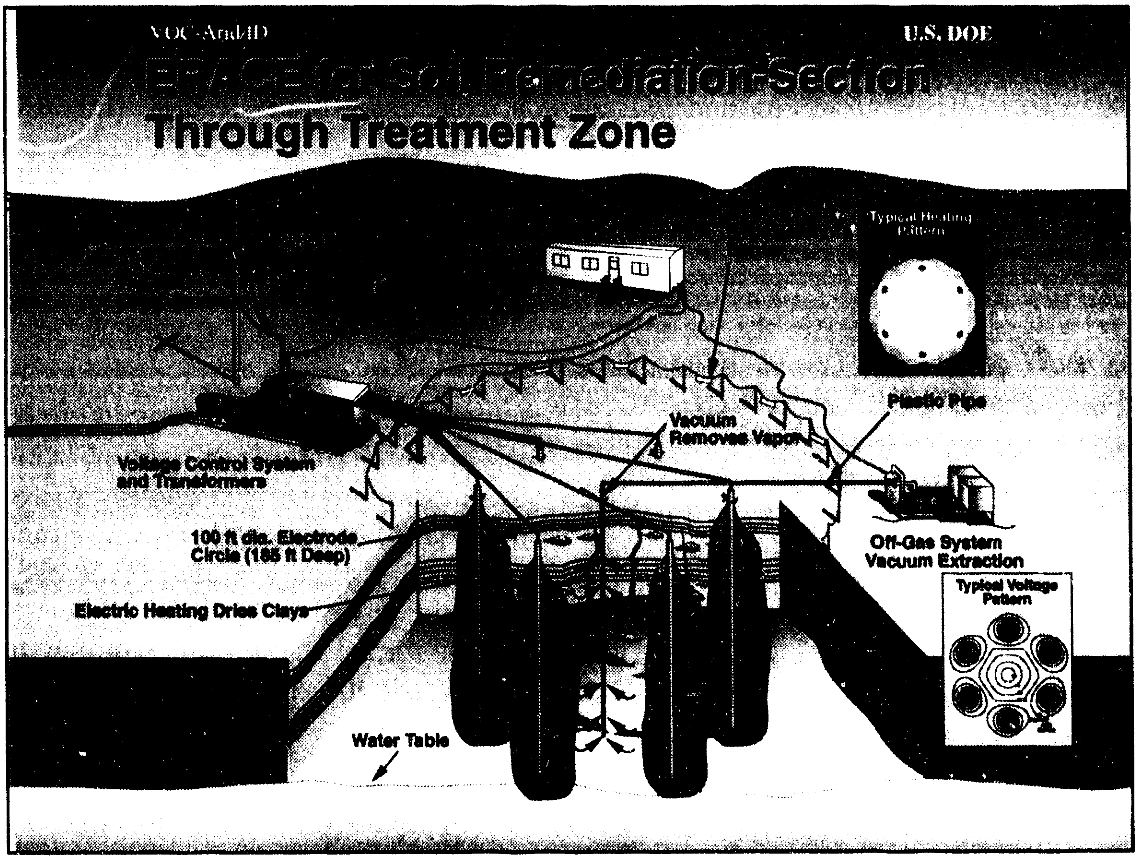

Figure 3.2a. ERACE for Soil Remediation-Section Through Treatment Zone.

In FY94 and FY95, SPSH will be demonstrated at Rocky Flats in cooperation with Environmental Restoration activities.

TECHNOLOGY NEEDS

Most DOE sites have been contaminated with VOCs, including chlorinated solvents like trichloroethylene and tetrachloroethylene, nonchlorinated solvents like methyl ethyl ketone, benzene and acetone, and fuels like gasoline. Techniques being developed for retrieving these VOCs from soils include in-situ vapor stripping, dynamic stripping, radio-frequency heating, Electromagnetic heating and SPSH. The primary baseline technologies are SVE for vadose zone soils and pump-and-treat for groundwater. Both are limited by retardation of VOC movement in the subsurface, especially in fine sediments and clays. Thus, both SVE and pump-and-treat must be operated for long periods of time and may not achieve cleanup standards in low-permeability soils.

The objective of SPSH is simply to enhance SVE by electrically heating the soil. Raising the soil temperature increases the vapor pressure of the VOCs, and creates an in situ source of steam, both of which accelerates VOC removal. SPSH may also enable remediation of semi-volatile organics (SVOs).

BENEFITS

Compared with soil vapor extraction, this technology will accelerate remediation, extend the application of vapor stripping to less volatile contaminants, and allow cost-effective remediation of lower permeability and more heterogeneous soils. Compared to other resistive-heating schemes, the use of six individually controlled electrical phases produces a more ideal heating distribution, requires the same or fewer electrodes, and requires less added moisture to overcome drying at the electrodes. Also, the SPSH system as tested at the SRS is fully transportable, self-contained, and automated for unmanned operation. A third-party economic analysis projects a treatment cost for SPSH of $45 to $50 per cubic yard of soil, which is roughly half the cost of radio-frequency heating, and only twice the cost of steam-injection (which is a highly soil-dependent technology that has little or no applicability to impermeable clays and tight silts).

PROCESS DESCRIPTION

Six electrodes are placed in a circle surrounding a central vent. Conventional three-phase power is transformed to six-phase for distribution to the six electrodes. Heating occurs due to resistive losses in the contaminated zone, producing steam. The steam is removed along with the contaminants through a vertical vent at the center of the electrode array, similar to conventional soil vapor extraction. To maintain soil conduction at the electrodes, the electrodes are backfilled with graphite and moistened via the continuous addition of water containing an electrolyte. For the SRS demonstration, sodium chloride was used as the electrolyte at a total concentration of 500 ppm (within drinking water standards). While more water will be removed by heating than added, further efforts are required to fully understand the regulatory impacts of water addition, and to minimize the quantity of water required, probably through automated control.

Following treatment, the soil is left intact but is dry and sterilized. Soil moisture can be restored if desired along with the indigenous bacterial population, or the soil can be left to eventually return to its original state over a longer time period. For many or most VOCs, the electrodes and any surface cover can be reused or disposed of as unregulated waste. The applicability of SPSH to sites with buried metal objects including pipes is unknown, but can be addressed by numerical modelling and laboratory experiments.

ACCOMPLISHMENTS

Major accomplishments to date include:

- Detailed design, installation, and start-up of full-scale treatment system.
- Completion of pilot-scale laboratory test showing >99.99% removal of chlorinated solvents (trichloroethylene and tetrachloroethylene) from SRS clay.
- Completion of bench test of SPSH combined with In-Situ corona showing >99.999% removal of benzene and >99.994% removal of naphthalene, representing a gasoline/diesel matrix in a tight Hanford silt.
- Completion of bench test of trichloroethylene removal with soil offgases treated by the High-Energy Corona (HEC) process as an integrated system with SPSH.
- Bench-scale demonstration of the ability of SPSH to significantly accelerate biodegradation rates by holding soil at optimum temperature range (30 to 35° C) for microbial growth with relatively small (± 2° C) temperature variation.

COMMERCIALIZATION/ TECHNOLOGY TRANSFER

A relationship with an interested third party is expected to culminate in a licensing agreement with PNL for use of the SPSH at a large number of independently-owned sites. Additionally, a relationship with Riedel Environmental Services, Inc. for PNL to provide the SPSH equipment and expertise in site clean-up operations under subcontract to Riedel is being developed. Successful teamwork is expected to lead to a commercial licensing agreement with Riedel. Due to multiple press releases on the SPSH technology, a very large volume of inquiries from the private sector have challenged the ability to explore any but

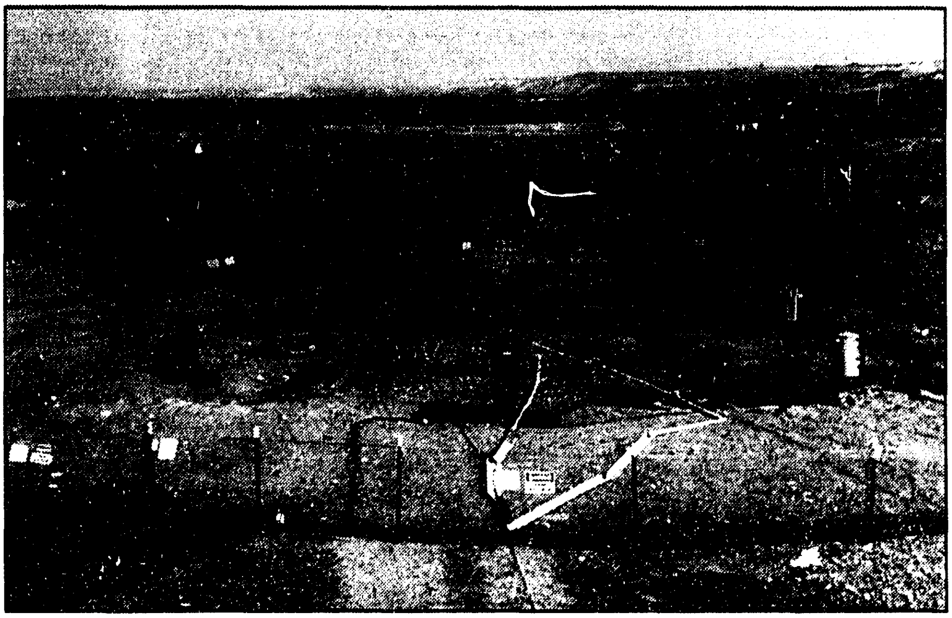

Figure 3.2b. Six-Phase Soil Heating.

a few partnership/licensing opportunities. Thus far, one patent has been obtained for electrical soil heating (US 4,957,393), a second has been allowed and will issue in the next few months, and a third has been submitted. Applications for foreign rights have also been completed.

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Above Ground Treatment of Contaminants

Section 4.0

4.1 OFF-GAS MEMBRANE SEPARATION

TASK DESCRIPTION

The objective of this technology is to preferentially remove carbon tetrachloride and chloroform from a gas stream at Hanford using a vapor membrane separation system (see Figures 4.1 a&b). The waste stream has been obtained by vacuum extraction of VOCs from a contaminated soil site. An existing vendor pilot plant has been modified to remove an 95% of the VOCs in the gas stream. The recovered VOC is in a liquid form, suitable for reuse or for solvent-recycling programs.

There are two major challenges which confront the membrane separation unit project:

- sizing the pilot plant to handle fluctuations in the VOC flows from the well field; and
- preventing fouling of the membrane with other constituents.

Additionally the membrane system does not operate as effectively with trichloroethylene as with carbon tetrachloride. Current activities are focused on resolving these problems.

TECHNOLOGY NEEDS

Cost-effective methods are needed to remove VOCs in the gas stream. The cost of capturing VOCs by carbon adsorption is about $5-15/lb of VOC. Tests indicate that the cost of emissions treatment by membrane technology will be about $2-5/lb of VOC recovered. Also, because of the 1990 Clean Air Act Amendments the direct discharge of VOCs has been significantly reduced. To abate the quantity

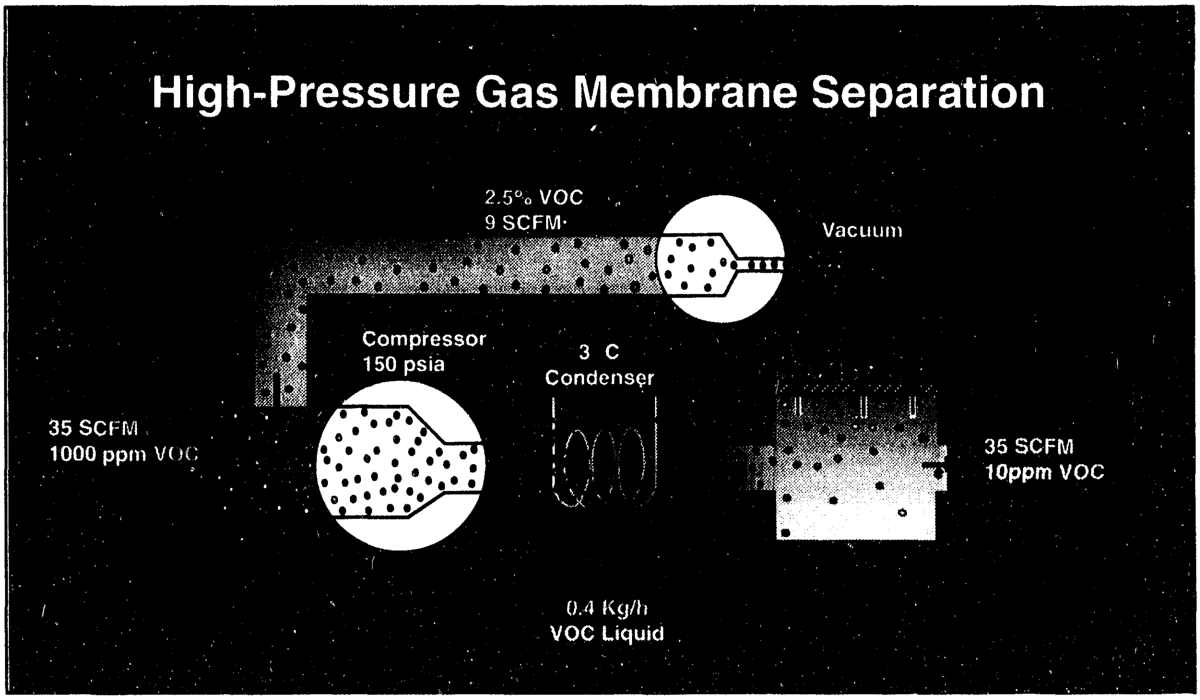

Figure 4.1a. High-Pressure Gas Membrane Separation.

of VOCs discharged to the atmosphere from the soil vented groundwater, this technology or similar technology requires development.

The most common alternative to this technique is using granulated activated carbon (GAC) adsorption. This technique generates secondary waste that requires disposal or regeneration on a regular basis. The proposed membrane system would minimize the secondary waste while providing a recyclable product.

BENEFITS

Membrane separation can remove 95% of the VOCs from the soil vent stream before they are introduced into the GAC, thereby reducing the large amount of secondary waste otherwise generated. The membrane separation technology is less expensive than direct processing with GAC. The cost for capturing VOCs by carbon absorption is about $5-15/lb. of VOC. Present calculations using membrane technology estimate costs of $2-5/lb. of VOC recovered. The membrane system requires very little attention and will operate without operator attention for days or weeks at a time.

Design will be based on a maintenance schedule to check pumps, compressors, replace oil,, etc. approximately three times per month.

PROCESS DESCRIPTION

Vacuum extraction removes the VOCs from the contaminated soil. A high pressure system has been designed to treat feed streams that contain dilute concentrations of VOCs. The organic vapor/air separation technology involves the preferential transport of organic vapors through a non-porous semi permeable gas separation membrane (diffusion process analogous to putting oil on a piece of wax paper). In this system, the feed stream is compressed and sent to a condenser where the liquid solvent is recovered. The condenser bleed stream, which contains approximately 5000-10,000 ppm of the VOC is then sent to the membrane module. The membrane module is comprised of spiral bound modules of thin film membranes separated by plastic mesh spacers. The membrane and the spacers are wound spirally around a central collection pipe. In the membrane module the stream is further concentrated to 3% VOC. The concentrated stream is then returned to the compressor for further recovery in the condenser.

The system concentrates and creates a carbon tetrachloride liquid which is destroyed using the UV Oxidation process. The treated air stream (10-20 ppm VOC) is sent to an activated carbon filter and then to the atmosphere. Approximately 0.4 kg/hr. of residual liquefied VOC (carbon tetrachloride) was removed from the system for organic destruction. The recovered VOC was in liquid form, suitable for reuse or for a solvent-recycling program.

ACCOMPLISHMENTS

A high pressure membrane separation unit of the type proposed for the VOC-Arid ID was operated at Hanford for six months. Based upon a 200-1000 pm effluent concentration, tests have resulted in a 95% removal efficiency on DOE waste streams. No degradation of system performance was evident during the operation of the system. The cost of operation was between $2-5/lb of VOC removed.

COMMERCIALIZATION/ TECHNOLOGY TRANSFER

The development of the gas membrane separation project was conducted with the assistance of Membrane Technology and Research, Inc. (MTR). MTR is primarily a research organization; however, they also manufacture the membrane and skids. Westinghouse Hanford Company is leasing the equipment from MTR.

The biggest cost-sharing opportunity is with companies interested in technology for recycling solvent vapors. British Petroleum is looking for technology to recycle fugitive gasoline storage tank emissions and Texaco has been exploring this area as well. Many other industries have clean-up sites that are contaminated with chlorinated VOCs, including hospitals and refrigeration applications.

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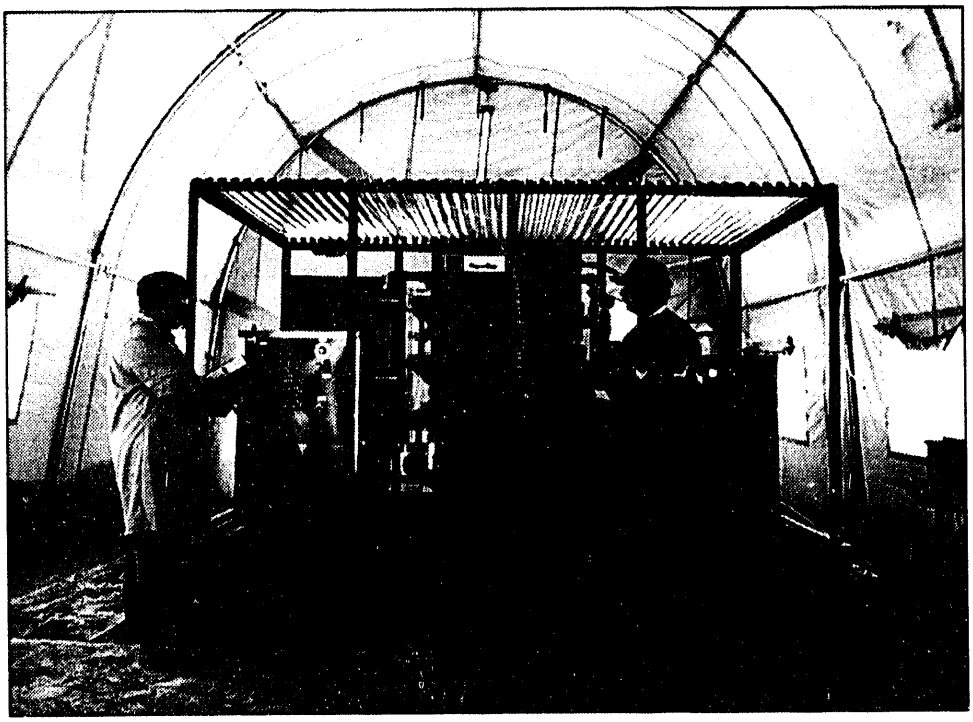

Figure 4.1b. Off-Gas Membrane Separation System.

4.2 SUPPORTED LIQUID MEMBRANES

TASK DESCRIPTION

The current focus of this task is to complete fabrication of the supported liquid membrane groundwater treatment test unit and to transfer this technology to EM-30 & EM-40. Future investigations will examine the potential for improving the capture of extractant in the fiber and reducing the cost of the hollow fiber support module. Additionally, further development is needed if the Supported Liquid Membranes (SLM) is expected to be significantly faster than current baseline technologies (see Figure 4.2).

TECHNOLOGY NEEDS

Over 40 years of processing fissionable isotopes for production of weapons has led to the discharge of liquids containing small amounts of radionuclides and other hazardous chemical compounds into the soil. This waste disposal practice has resulted in contamination of groundwaters with uranium, chromium, technetium, and nitrate at levels sufficiently high to pose a health risk. Groundwater remediation must be undertaken to remove toxic pollutants from the aquifer at these sites.

The SLM removes and concentrates radioactive and hazardous chemicals from contaminated groundwater while producing a small amount of secondary waste. Development of this technology has focused on removing uranium, chromium, and technetium. There is

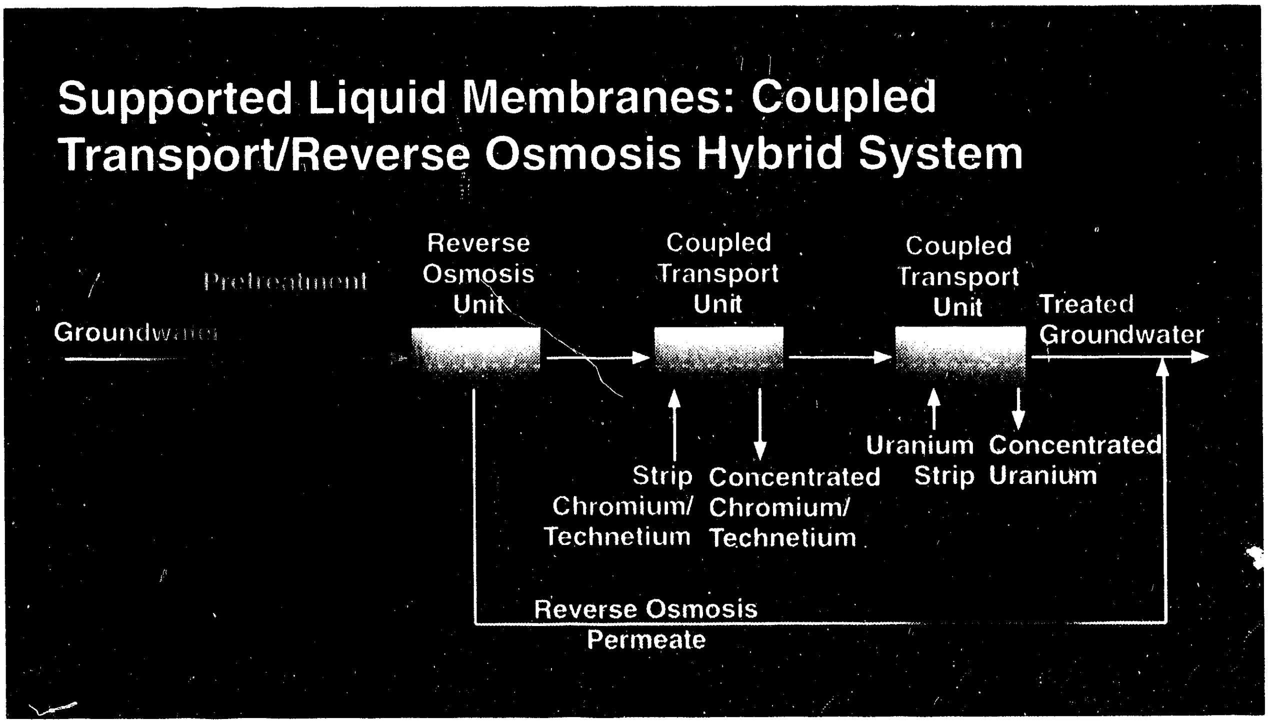

Figure 4.2. Supported Liquid Membranes.

also potential application of this technology to the Uranium Soil ID.

BENEFITS

Unlike other technologies, SLM can remove the toxic components selectively, leaving the nonhazardous components behind. Other technologies remove all of the dissolved ions. Since the concentration of all toxic metals in contaminated groundwater typically total well below 10 ppm and the concentrations of dissolved solids is typically 5000 ppm, the amount of solid secondary waste generated by SLM system followed by precipitation is about 1/500 that generated by non-selective technologies.

PROCESS DESCRIPTION

A feed solution containing a mixture of metal ions is pumped through a hollow fiber membrane. The hollow fiber supports a liquid membrane containing a commercially available complexing agent which binds to the metal ion as it comes in contact with the membrane. As the metal ion is transported through the membrane, a hydrogen ion is released to the waste stream. The metal containing complexing agent comes in contact with a stripping solution at the opposite wall. When this occurs, the metal ion is released to the stripping solution through the membrane and a hydrogen ion takes its place (coupled transport). The exact mechanism of transport varies depending on the metal ions being removed and the species of the ions. The stripping agent for chromium and technetium is dilute sodium hydroxide, while the stripping agent for uranium is VDPA (1,1-vinylidene diphosphonic acid) or HEDPA (1-hydroxy-ethane-1,1-diphosphonic acid). Several pretreatment and post-treatment steps may be required.

ACCOMPLISHMENTS

Bench scale testing and laboratory demonstration of the process was successfully completed. Secondly, design data for development of a groundwater test unit has been created, as well as completing the design of a 1 gallon per minute groundwater test unit.

COMMERCIALIZATION/ TECHNOLOGY TRANSFER

The SLM is currently being developed in cooperation with Bend Research Inc. and Albright-Wilson Americas Inc. Bend Research will design and manufacture a field unit via subcontract. Albright-Wilson Americas Inc. bought the rights to the stripping agent (VDPA) from Argonne National Laboratory. Bend Research Inc. is also communicating to electroplaters to determine the potential for use of the technology in chrome bath recovery. The removal of chromium is being tested at a shop in Seattle.

Technetium has medical applications and is a corrosion inhibitor. Market applications of Technetium were studied by Westinghouse Hanford Company (WHC) in the early '80s.

The most promising opportunities for industrial collaboration seem to be:

- identify metal finishing companies that would be interested in cost-sharing development work;
- find companies interested in marketing or using technetium (corrosion in-

hibitor, medical applications, antifoulant); and

- find companies interested in testing other types of complexing agents.

Bend Research Inc. has already obtained a patent on the hollow fiber, and spun-off a small company to manufacture modules for water treatment.

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4.3 STEAM REFORMING

TASK DESCRIPTION

The objective of this task is to develop a technology to destroy VOCs (carbon tetrachloride (CCl_4), and chloroform ($CHCl_3$) adsorbed on activated carbon. This will be accomplished by reacting the VOCs with superheated steam (steam reforming), after vaporization from the GAC, by exposure to steam at moderate temperatures (see Figure 4.3).

At this time there is still a need to complete the development and testing of the moving bed evaporator which uses an alkali base to capture acids generated in the bed by gasification of wastes that contain halogenated solvents.

Sandia National Laboratory is developing a chlorocarbon sensor that uses Surface acoustic wave sensing elements for use with the detoxifier. The chlorocarbon sensor will be used to monitor the vaporization of chlorocarbon solvents in the drum feeder and their gasification in the moving bed evaporator.

The spent slurry and salts generated in the Moving Bed Evaporator would be regulated wastes if toxic or inorganic materials are constituents of these wastes.

However, this is not the case for the off-gas being treated in the VOC-Arid ID. In such cases, further treatment of the spent slurry and salts may be required prior to disposal.

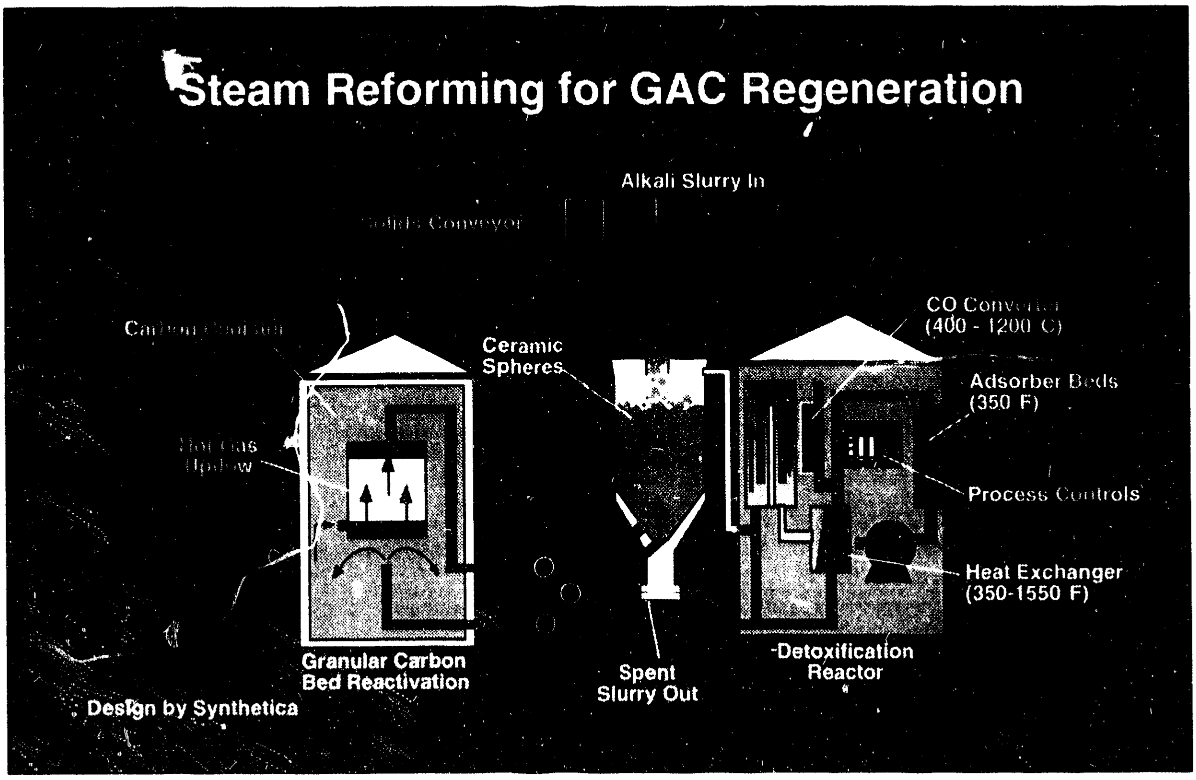

Figure 4.3. Steam Reforming for Granular Activated Carbon Regeneration.

TECHNOLOGY NEEDS

Based on regulator concern over available off-gas treatment technologies, DOE has been required to use expensive GAC beds to remove VOCs from the off-gas stream. GAC currently requires off-site shipment and regeneration at a cost that exceeds that estimated for on-site treatment, if available. Technologies are needed to reduce the cost and potential public exposure associated with GAC treatment and regeneration offsite.

PROCESS DESCRIPTION

Carbon tetrachloride and chloroform stripped from Hanford arid soils will be adsorbed on activated carbon in 55-gallon steel drums. The drums will be placed in a drum feeder and the adsorbed chlorocarbons will be vaporized by exposure to 300° C steam.

The chlorocarbon laden steam effluent from the drum feeder is fed to a moving bed evaporator, that consists of a bed of ceramic spheres coated with alkali base. At the bottom of the evaporator, spheres are removed and transported to the top of the evaporator by a bucket elevator, where they are coated with fresh base and re-injected into the evaporator.

At the 600° C operating temperature of the evaporator, the chlorocarbons will be efficiently decomposed releasing HCl which will be neutralized by the alkali base coating on the spheres. As the spheres settle to the bottom of the evaporator, spent base, and chloride salts formed by the neutralization of HCl, are mechanically scraped off of the spheres and removed from the bottom of the evaporator through a star valve. The star valve allows waste products to exit the bottom of the evaporator, while sending the scraped spheres to a bucket elevator to be re-injected into the top of the evaporator.

The effluent steam stream from the Moving Bed Evaporator is fed to the high-temperature (1200° C) reaction chamber of the steam reforming reactor, where any organic fragments released in the Moving Bed Evaporator are destroyed. Any HCl released in the Detoxifier is removed by adsorption and neutralization by Selexsorb™, a commercial adsorbent. Finally, the effluent from the reactor is passed through a catalytic converter where carbon monoxide (CO) and hydrogen (H_2) are converted to carbon dioxide (CO_2) and water.

BENEFITS

In comparison to SVE using GACs and processing them offsite, Steam Reforming is faster, 75% cheaper, and 99.99% effective in destroying off-gas contaminants. GACs can be processed and re-activated on-site, eliminating the need for shipment and replacement. Because Steam Reforming is not a combustion process, fuel and air are not used and products of incomplete combustion are not generated. The detoxifier can handle a wide variety of waste forms. Liquid and solid wastes in drums are gasified in the drum feeder. Liquid waste streams are flash vaporized in the moving bed evaporator. Solids requiring shredding to enhance gasification are processed using a heated shredder. Contaminated soils are processed using a heated screw feeder.

COLLABORATION/TECHNOLOGY TRANSFER

Steam Reforming is being developed in cooperation with Synthetica Technologies, Inc. The DOE is currently testing the Synthetica Detoxifier for use in DOE Complex cleanup.

Synthetical holds the patents for this technology, #4874587, and steam detoxifier systems are available through them.

A CRADA between Synthetica Technologies and Sandia National Laboratories will support studies of alternative heating methods (e.g., microwave heating) for the detoxifier. Use of steam reforming catalysts in the detoxifier, and the conversion of the synthesis gas effluent from the Detoxifier into light hydrocarbons using Fischer-Tropsch catalysts will also be addressed under the CRADA.

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4.4 TUNABLE HYBRID PLASMA

TASK DESCRIPTION

The objective of this task is to develop an electron-beam generated plasma process for efficient, versatile, on-site treatment of gaseous toxic and hazardous compounds (particularly carbon tetrachloride for the VOC-Arid ID) with minimum creation of undesirable by-products and additional treatment. Present activities consist of designing and building a field demonstration system to be used in 1994 at the Hanford site.

This task will investigate the potential to develop a system to remove carbon tetrachloride and similar toxic gaseous compounds from waste gas streams containing dilute concentrations of toxic gases. The system must include the E-beam reactor and scrubber and a control system to fully automate its operation and be cost competitive with other means for carrying out the same function. The electron-beam window tests carried out to date indicate that titanium can be used and withstands the acid attack due to reaction products.

TECHNOLOGY NEEDS

Soil vapor extraction is the baseline technology for remediating the vadose zone soils. The baseline treatment technology for the extracted gas is granulated activated charcoal adsorption with off-site regeneration and ultimate disposal. Efficient and versatile on-site treatment is an important alternative that should be considered.

BENEFITS

The advantages of this technology include:

- on-site treatment of toxic substances in gas streams with high destruction and removal efficiency;
- capability of eliminating contaminants from high volume waste gas streams with end products of small volumes of solid precipitates and toxic gases;
- relatively low cost;
- minimum pre- and post-treatment requirements;
- ability to treat gases from solid waste treatment systems resulting in non-toxic emissions and small volumes of solid non-toxic residues; and
- versatile operation that can be used to process a wide range of substances and concentrations.

Laboratory tests have demonstrated that all the products of the E-beam dissociation of carbon tetrachloride can be dissolved in an aqueous solution. This solution preferably contains a base such as sodium hydroxide, which combines with the dissolved hydrochloric acid and chlorine to form the sodium chloride (salt). The remaining by-product, carbon dioxide, is released to the atmosphere. The salt is a non-hazardous waste, which can be disposed of in landfills if reduced to a solid. Brine solutions may be amenable to reuse.

PROCESS DESCRIPTION

A moderate energy electron beam (100-300 keV) is injected into atmospheric air containing the organic contaminants. The electrons and free radicals plasma generated from the electron beam interact with the organics in the atmospheric air and the organics are destroyed or oxidized to non-toxic chemicals. In cases where carbon tetrachloride is the main contaminant, dissociative attachment initiates the breakup of the carbon tetrachloride into non-toxic compounds. The electron beam ionizes the air stream; this allows the use of either AC or DC electric fields to further increase the electron and gas temperatures to optimize the treatment processes. The moderate energy electron beam technology is a well established commercial product. It is user friendly, self-shielded, and has a record of high operational availability.

The products of the reaction for carbon tetrachloride destruction are passed through a conventional scrubber. All of these gaseous products; chlorine, hydrochloric acid, and carbon dioxide, dissolve in aqueous solutions or can be passed through the scrubber and released into the atmosphere. The scrubber can contain an aqueous solution with or without a caustic, such as sodium hydroxide. The caustic solution is preferred since it produces sodium chloride and carbon dioxide gas, which can be easily disposed of.

The tunable plasma system utilizes feedback detection to optimize performance and facilitate autonomous operation.

ACCOMPLISHMENTS

Initial studies resulted in removal of carbon tetrachloride below detection limit in lab experiments. The Tunable Hybrid Plasma (THP) technology decomposed carbon tetrachloride into harmless carbon dioxide and chlorine-salt (see Figure 4.4).

The output air stream from the THP reactor has been fully characterized. The carbon balance results in carbon monoxide and carbon dioxide, and the chlorine balance results in carbon tetrachloride going to chlorine and hydrochloric acid.

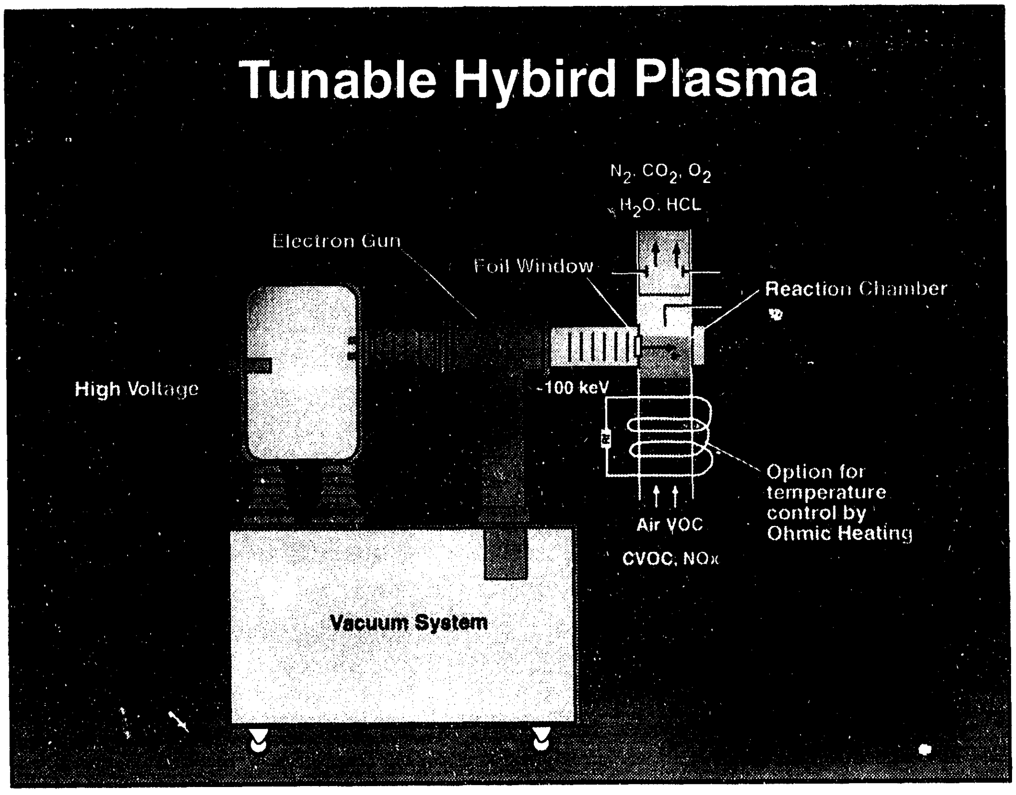

Figure 4.4. Tunable Hybrid Plasma.

Secondly, a preliminary design of the field system has been completed. The electron beam is a commercial unit purchased from Energy Sciences Inc. Negotiations are underway to purchase standard units for the scrubber/stripper to produce salt solutions from the THP reactor exhaust, and the air dryer used to reduce the water content in the off-gas air stream to increase the THP reactor efficiency.

COMMERCIALIZATION/ TECHNOLOGY TRANSFER

Current investigation of this technology is being conducted by PNL, in coordination with MIT. Additionally, THP has gained the interest of Energy Sciences in Woburn, MA., and Ebarra in Japan.

Additionally, preliminary discussions are underway with a licensee for commerciali-zation of the process. The prospective licensee may participate in the demonstration.

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In Ground Treatment of Contaminants

Section 5.0

5.1 IN-SITU BIOREMEDIATION OF GROUNDWATER

TASK DESCRIPTION

The objective of this technology is to stimulate the growth and metabolism of naturally occurring microorganisms to degrade and detoxify chemical contamination in-situ in the sediments and groundwater.

Laboratory studies on carbon tetrachloride degradation kinetics, chloroform production, and confirming soil column studies are underway. The results of these laboratory effort will be used to refine the model/simulator (design tool) and operation at the demonstration. Field demonstration activities are currently planned to begin in May 1994.

The main limitation of this technology when compared with baseline methods is the difficulty in designing and implementing an effective subsurface treatment system for highly heterogeneous media. However, this limitation may be overcome as the technology matures. It is possible that chloroform will be produced as an intermediate in the degradation of carbon tetrachloride; however, the process will be designed to further degrade the chloroform to carbon dioxide.

Several key technical issues have prevented widespread use of bioremediation for organic and inorganic subsurface contaminants, including adequate nutrient delivery systems, effective mixing technologies for contacting microorganisms, nutrients, and contaminants, control of biofouling or excessive microbial growth, and adequate tools for designing, predicting, and monitoring the performance of in-situ technologies in heterogeneous subsurface environments. The goal of this program is to address these technical issues in an integrated laboratory-, bench-, and field-scale demonstration by stimulating native microorganisms and accelerating the natural degradation of nitrates, carbon tetrachloride, and chloroform. Another major challenge of any in-situ remediation process is being able to effectively monitor the process to confirm the effectiveness of the technology.

Although bioremediation is broadly applicable and very versatile, it is also a very site specific technology. Therefore, treatability studies and site-specific testing are needed to implement the technology. The equipment, design tools, and treatability testing protocols are quite versatile and can be used consistently from one site to another (see Figure 5.1).

TECHNOLOGY NEEDS

In order to remediate contaminated groundwater, it currently must be pumped from the ground and treated. This process is difficult and expensive; therefore, more cost-effective and efficient methods, particularly in-situ methods, must be developed. In-situ bioremediation is being developed to stimulate the growth of naturally occurring organisms that can degrade and detoxify chemical contamination in place in soils and groundwater.

BENEFITS

Present estimates indicate that this technology should remediate the Hanford test site in half the time required by conventual pump-and-treat methods.

In-situ bioremediation provides a potentially significant benefit for VOCs and other contaminants that are held up in adsorptive soils or less permeable silts, sediments, and clays that act as sinks. Bioremediation can destroy the VOCs in place and reduce the mass transport limitations associated with VOC adsorption/desorption to sediments, and dissolution into the groundwater that limits pump-and-treat technologies. The time and cost of clean-up could be substantially reduced if bioremediation could be effectively employed alone, or in conjunction with other bulk-contaminant removal technologies. Present conservative estimates (based on very permeable soils, and groundwater with VOC contaminants only, i.e., no nitrate) indicate that this technology will be faster and safer than the baseline methods while costing about the same as pump-and-treat per volume of soil remediated. The increase in safety results because no contaminated media need to be brought to the surface, and the technology provides ultimate on-site destruction of the contaminant; converting the hazardous compounds to non-hazardous products. In addition, use of this treatment method has the potential of reducing further spread of contamination. The increased numbers of microorganisms will reduce the soil permeability, and therefore reduce the rate of migration of VOCs out of and into the contaminated zone. It is expected that if the cost/benefit analysis included the baseline cost of treating nitrates in addition to VOCs, bio-remediation costs would be significantly lower than the baseline. Other advantages include:

- worker exposure to chemical contaminants are decreased;
- the movement of radionuclides in the groundwater may be slowed; and

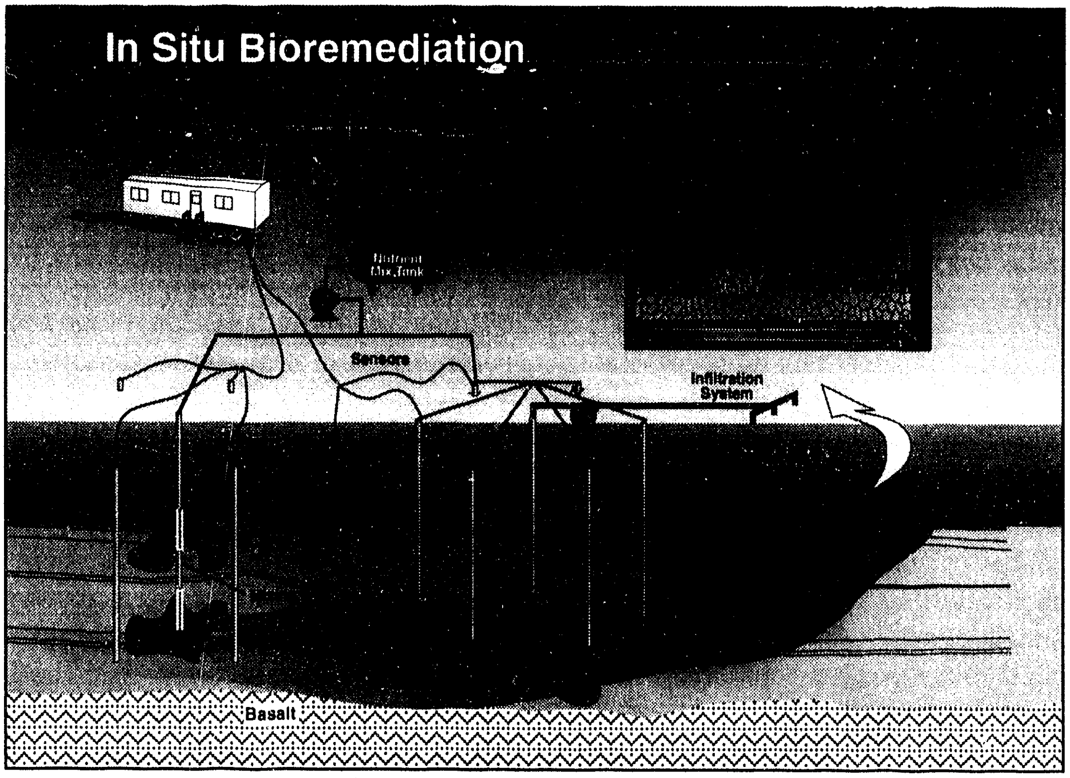

Figure 5.1. In-Situ Bioremediation.

- bioremediation is a natural process with high likelihood for acceptance.

PROCESS DESCRIPTION

Native microorganisms can be stimulated with acetate to consume and degrade carbon tetrachloride and nitrates in soils and groundwater. In laboratory-, bench-, and pilot-scale tests, it has been demonstrated that 99% of nitrates and 93% of carbon tetrachloride contamination in groundwater can be degraded. The insitu bioremediation process injects acetate and nitrate (as needed after initial nitrate levels are depleted) through a series of a) injection wells, or b) injection well screens as part of a multiscreened mixing well. These nutrients are mixed with the groundwater through an appropriate injection strategy to maximize contaminant degradation and minimize excessive microbial growth around the well. The injected nutrients produce an active zone of organisms that will degrade contaminants as they are pumped through the treatment zone. The system can employ a series of injection and extraction wells to mix contaminated groundwater with nutrients and microorganisms or the system can use one or more multiscreened mixing wells to mix the water, nutrients, and microorganisms without extraction to the surface. The residual effect on the aquifer of applying this technology will be elevated levels of naturally occurring microorganisms. If the operating scenario using a series of extraction and injection wells is used (rather than the mixing wells), outputs of the system at the surface would include carbon dioxide, nitrogen gas, and excess biomass (microorganisms).

There are no output streams for this technology because it occurs in-situ. If co-contaminants, such as heavy metals or radionuclides, are extracted with the VOC and nitrate-laden groundwater, then conventional treatment techniques may need to be employed in addition to the bioremediation. These processes would generate additional secondary waste.

ACCOMPLISHMENTS

Through FY93 there have been a number of significant accomplishments in the development and demonstration of in-situ bioremediation of carbon tetrachloride. The test site at Hanford has been partially characterized during the completion of two characterization and monitoring wells. Recently a third well, the mixing well, was completed and additional characterization information for baseline is being collected. The biological degradation of carbon tetrachloride has been demonstrated in the laboratory soil column and the reaction kinetics for these processes were determined for inclusion into a modeling design tool.

A simulation design tool was developed specifically for this in-situ bioremediation process, and a number of simulations have been conducted to help identify critical field operation parameters related to bioremediation and nutrient injection. The modelling design tool has been demonstrated for 2-D, 3-D and multiphase in-situ bioremediation simulations.

Hydrologic testing was conducted on the completed mixing well that will be used to inject and distribute nutrients in the unsaturated zone. The drilling and characterization plan was completed for installation of a third monitoring well and another mixing well at the test site. The plan also covers the remaining baseline characterization work to be completed before beginning the field demonstration.

COMMERCIALIZATION/ TECHNOLOGY TRANSFER

Discussions with several companies are underway; however, there is no commercial partner at this time. In order to ensure successful transfer of the technology to industry and the commercial environmental consulting firms, industrial partnerships are needed. Collaborations are being pursued for both industrial companies desiring the technology for their own clean-up actions, and for industrial consulting or service companies to provide the service to other clients for site cleanup. Because the contaminants and organisms are so site specific in this case, a capability, not a technology is the marketable product. Because of this, the possibility of developing intellectual property is difficult. Sectors of the economy with potential interest in developing bioremediation products and services to cleanup the many thousands of VOC and nitrate-contaminated sites in the U.S. include Allied Signal, DuPont, Kodak, Exxon, GE, Occidental Petroleum, Sybron Chemicals, Westinghouse Electric and biotechnology companies such as Celgene, ECOVA, Envirogen, Genencor, and several companies which sell microbial inocula. Most of the environmental engineering firms are interested in subcontracting with DOE to provide cleanup services.

No single patent exists for the technology. Elements of the technology are the intellectual property of various organizations. Stanford has applied for a patent on the mixing well designs. Rice University has the rights to the design simulation software. Treatability study equipment was developed by PNL and an invention disclosure has been filed. Specific enhancements to the technology have also been described in invention disclosures.

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How to Get Involved

Section 6.0

6.0 HOW TO GET INVOLVED

WORKING WITH THE DOE OFFICE OF ENVIRONMENTAL RESTORATION AND WASTE MANAGEMENT

DOE provides a range of programs and services to assist universities, industry, and other private-sector organizations and individuals interested in developing or applying environmental technologies. Working with DOE Operations Offices and management and operating contractors, EM uses conventional and innovative mechanisms to identify, integrate, develop, and adapt promising emerging technologies. These mechanisms include contracting and collaborative arrangements, procurement provisions, licensing of technology, consulting arrangements, reimbursable work for industry, and special consideration for small business.

Cooperative Research and Development Agreements (CRADAs)

EM will facilitate the development of subcontracts, R&D contracts, and cooperative agreements to work in collaboration with the private sector.

EM uses CRADAs as an incentive for collaborative R&D. CRADAs are agreements between a DOE R&D laboratory and any non-Federal source to conduct cooperative R&D that is consistent with the laboratory's mission. The partner may provide funds, facilities, people, or other resources. DOE provides the CRADA partner access to facilities and expertise; however, no Federal funds are provided to external participants. Rights to inventions and other intellectual property are negotiated between the laboratory and participant, and certain data that are generated may be protected for up to 5 years.

Consortia will also be considered for situations where several companies will be combining their resources to address a common technical problem. Leveraging of funds to implement a consortium can offer a synergism to overall program effectiveness.

Procurement Mechanisms

DOE EM has developed an environmental management technology development acquisition policy and strategy that uses phased procurements to span the RDDT&E continuum from applied R&D concept feasibility through full-scale remediation. DOE EM phased procurements make provisions for unsolicited proposals, but formal solicitations are the preferred responses. The principle contractual mechanisms used by EM for industrial and academic response include Research Opportunity Announcements (ROAs) and Program R&D Announcements (PRDAs).

EM uses the ROA to solicit advanced research and technologies for a broad range of cleanup needs. The ROA supports applied research ranging from concept feasibility through full-scale demonstration. In addition, the ROA is open continuously for a full year following the date of issue and includes a partial procurement set aside for small businesses. Typically, ROAs are published annually in the *Federal Register* and the *Commerce Business Daily*, and multiple awards are made.

PRDAs are program announcements used to solicit a broad mix of R&D and DT&E proposals. Typically, a PRDA is used to solicit proposals for a wide-range of technical solutions to specific EM problem areas. PRDAs may be used to solicit proposals for contracts, grants, or cooperative agreements. Multiple awards, which may have dissimilar approaches or concepts, are generally made. Numerous PRDAs may be issued each year.

In addition to PRDAs and ROAs, EM uses financial assistance awards when the technology is developed for public purpose. Financial assistance awards are solicited through publication in the *Federal Register*. These announcements are called Program Rules. A Program Rule can either be a one-time solicitation or an open-ended, general solicitation with annual or more frequent announcements concerning specific funding availability and desired R&D agreements. The Program Rule can also be used to award both grants and cooperative agreements.

EM awards grants and cooperative agreements if fifty-one percent or more of the overall value of the effort is related to a public interest goal. Such goals include possible non-DOE or other Federal agency participation and use, advancement of present and future U.S. capabilities in domestic and international environmental cleanup markets, technology transfer, advancement of scientific knowledge, and education and training of individuals and business entities to advance U.S. remediation capabilities.

Licensing of Technology

DOE contractor-operated laboratories can license DOE/EM-developed technology and software to which they elect to take title. In other situations where DOE owns title to the resultant inventions, DOE's Office of General Counsel will do the licensing. Licensing activities are done within existing DOE intellectual property provisions.

Technical Personnel Exchange Assignments

Personnel exchanges provide opportunities for industrial and laboratory scientists to work together at various sites on environmental restoration and waste management technical problems of mutual interest. Industry is expected to contribute substantial cost-sharing for these personnel exchanges. To encourage such collaboration, the rights to any resulting patents go to the private sector company. These exchanges, which can last from 3 to 6 months, are opportunities for the laboratories and industry to better understand the differing operating cultures, and are an ideal mechanism for transferring technical skills and knowledge.

Consulting Arrangements

Laboratory scientists and engineers are available to consult in their areas of technical expertise. Most contractors operating laboratories have consulting provisions. Laboratory employees who wish to consult can sign non-disclosure agreements, and are encouraged to do so.

Reimbursable Work for Industry

DOE laboratories are available to perform work for industry, or other Federal agencies, as long as the work pertains to the mission of a respective laboratory and does not compete with the private sector.

The special technical capabilities and unique facilities at DOE laboratories are an incentive for the private sector to use DOE's facilities and contractors expertise in this reimbursable work for industry mode. An advanced class patent waiver gives ownership of any inventions resulting from the research to the participating private sector company.

EM Small Business Technology Integration Program

The EM Small Business Technology Integration Program (SB-TIP) seeks the participation of small businesses in the EM Research, Development, Demonstration, Testing and Evaluation programs. Through workshops and frequent communication, the EM SB-TIP provides information on opportunities for funding and collaborative efforts relative to advancing technologies for DOE environmental restoration and waste management applications.

EM SB-TIP has established a special EM procurement set aside for small firms (500 employees or less) to be used for applied research projects, through its ROA. The program also serves as the EM liaison to the DOE Small Business Innovation Research (SBIR) Program Office, and interfaces with other DOE small business offices, as well.

CONTACT

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EM Central Point of Contact

The EM Central Point of Contact is designed to provide ready access to prospective research and business opportunities in waste management, environmental restoration, and decontamination and decommissioning activities, as well as information on EM-50 IPs and IDs. The EM Central Point of Contact can identify links between industry technologies and program needs, and provides potential partners with a connection to an extensive complex-wide network of DOE Headquarters and field program contacts.

The EM Central Point of Contact is the best single source of information for private-sector technology developers looking to collaborate with EM scientists and engineers. It provides a real-time information referral service to expedite and monitor private-sector interaction with EM.

To reach the EM Central Point of Contact, call 1-800-845-2096 during normal business hours (Eastern time).

Office of Research and Technology Applications

Office of Research and Technology Applications (ORTAs) serve as technology transfer agents at the Federal laboratories, and provide an internal coordination in the laboratory for technology transfer and an external point of contact for industry and universities. To fulfill this dual purpose, ORTAs license patents and coordinate technology transfer activities for the laboratory's scientific departments. They also facilitate one-on-one interactions between the laboratory's scientific personnel and technology recipients, and provide information on laboratory technologies with potential applications in private industry for state and local governments.

Acronyms

Section 7.0

7.0 ACRONYMS

ANL	Argonne National Lab
CBD	Commerce Business Daily
CRADAs	Cooperative Research and Development Agreements (CRADAs)
DOE	U.S. Department of Energy
EM	Environmental Restoration and Waste Management
EPA	Environmental Protection Agency
ERA	expedited response action
GAC	granular activated carbon
ID	Integrated Demonstrations
IP	Integrated Programs
LANL	Los Alamos National Laboratory
MTR	Membrane Technology and Research, Inc.
MWLID	Mixed Waste Landfill Integrated Demonstration
ORTAs	Office of Research and Technology Applications
OSHA	Occupational Safety and Health Administration
OTD	Office of Technology Development (EM-50)
PAWS	Portable Acoustic Wave Sensor
PCE	perchloroethylene
PEL	Permissible Exposure Limit
PNL	Pacific Northwest Laboratories
PRDAs	Program R&D Announcements
RDDT&E	Research, Development, Demonstration, Testing and Evaluation
ROAs	Research Opportunity Announcements
SBIR	Small Business Innovation Research
SB-TIP	Small Business Technology Integration Program

SFE	Supercritical Fluid Extraction
SLM	Supported Liquid Membranes
SPSH	Six Phase Soil Heating
SRS	Savannah River Site
SVE	soil vapor extraction
SVOs	semi-volatile organics
TCE	trichloroethylene
THP	Tunable Hybrid Plasma
UFA	Unsaturated Flow Apparatus
VOCs	volatile organic compounds
VOC-Arid ID	Volatile Organic Compounds In Arid Soils Integrated Demonstration
WDC	Water Development Corporation

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