DOE/RL-95-32

In Situ Remediation Integrated Program

FY 1994 Program Summary

April 1995

U.S. Department of Energy
Office of Technology Development

MASTER

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OFFICE OF TECHNOLOGY DEVELOPMENT
IN SITU REMEDIATION INTEGRATED PROGRAM

PREFACE

The U.S. Department of Energy (DOE) established the Office of Technology Development (EM-50) as an element of the Office of Environmental Management (EM) in November 1989. Figure 1 shows the organizational structure for EM. EM is responsible for waste management and the cleanup of over 100 contaminated installations in 36 states. The goal of EM 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 responsible for managing an aggressive national program of applied research, development, demonstration, testing, and evaluation for environmental cleanup, waste management, and related technologies. The technology development program is designed to resolve major technical issues, to rapidly advance technologies beyond current baselines, and to expedite compliance with applicable environmental laws and regulations. EM-50 is charged with developing new remedial technologies that are safer, faster, more effective, and less expensive than existing technologies.

In an effort to focus resources and address priority needs, EM-50 introduced the concept of integrated programs (IPs) and integrated demonstrations (IDs). An IP is a set of applied research and development activities dedicated to providing technology solutions for a single problem category, such as in situ remediation and characterization technologies. An ID provides a cradle-to-grave system for solving a specific environmental or waste management problem. An ID assembles a group of related and synergistic technologies to evaluate their performance individually or as a complete system.

The In Situ Remediation Integrated Program (ISR IP) focuses research and development on the in-place treatment of contaminated environmental media, such as soil and groundwater, and the containment of contaminants to prevent the contaminants from spreading through the environment. Using in situ remediation technologies to clean up DOE sites minimizes adverse health effects on workers and the public by reducing contact exposure. The technologies also reduce cleanup costs by orders of magnitude by eliminating the need for waste excavation, transport, and disposal, and enable the remediation of relatively inaccessible areas such as the deep subsurface and areas beneath structures. The ISR IP establishes interfaces with fundamental research organizations (e.g., DOE's Office of Health and Environmental Research and the U.S. Environmental Protection Agency) to link these activities with applied research and development programs, and provides developed technologies to three primary customers for evaluation and demonstration: the IDs, the Office of Environmental Restoration, and the Office of Waste Management.

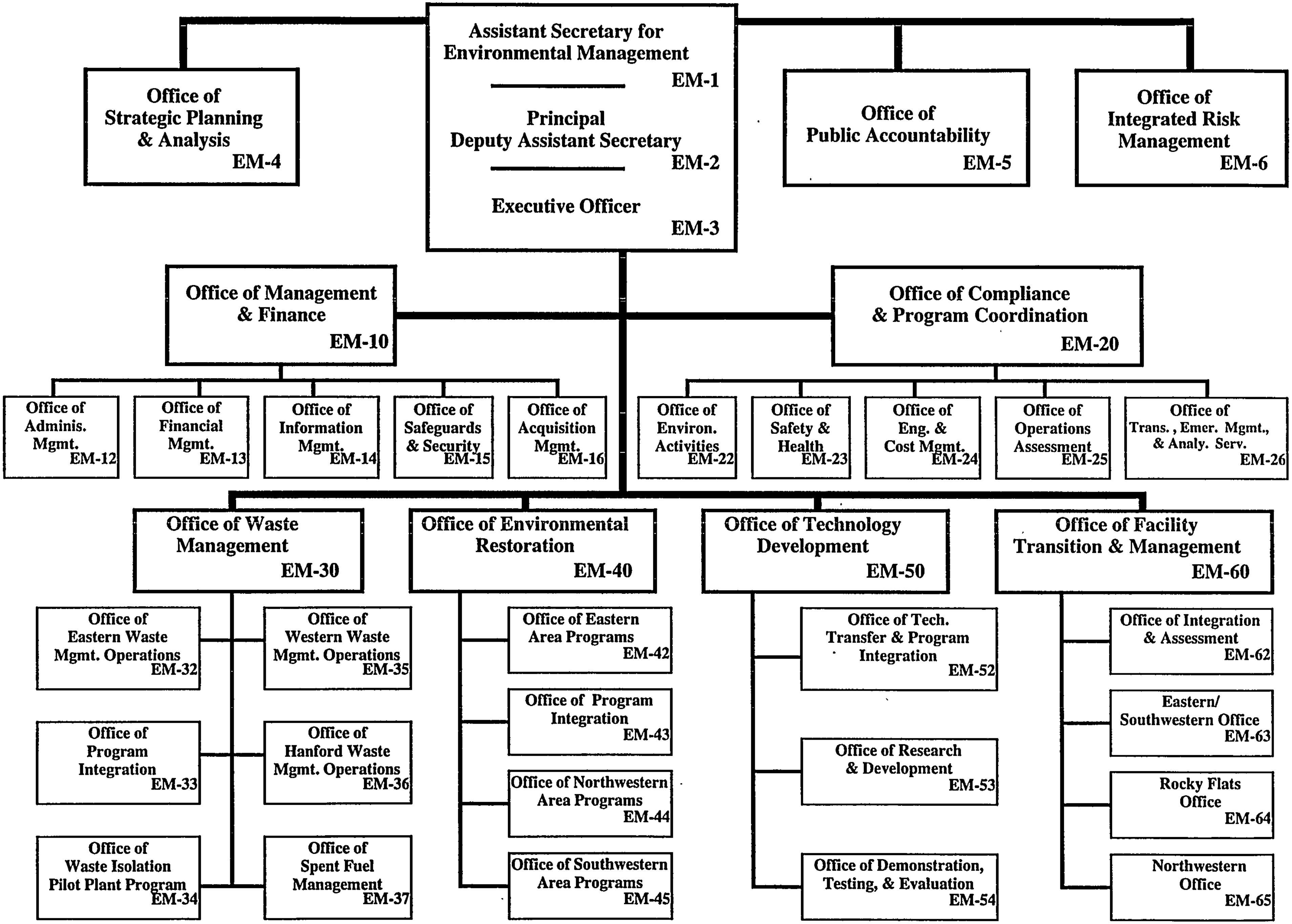

FIGURE 1. EM Organizational Chart (FY 1994)

The ISR IP is part of EM-53, the Environmental Restoration Research and Development Division.

This report summarizes project work conducted in FY 1994 under the ISR IP in three major areas: treatment (bioremediation), treatment (physical/chemical), and containment technologies. Buried waste, contaminated soils and groundwater, and containerized waste are all candidates for in situ remediation. Contaminants include radioactive waste, volatile and nonvolatile organics, heavy metals, nitrates, and explosive materials. Additional information about the ISR IP can be obtained from:

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ACRONYMS

AC	alternating current
ANL	Argonne National Laboratory
API	American Petroleum Institute
BNL	Brookhaven National Laboratory
BRADTEC	BRADTEC - U.S., Inc.
BRS	Biomass Remediation System
BTSG	Bioremediation Technical Support Group
BWNT	Babcock and Wilcox Nuclear Technologies
c-DCE	cis-1,2-dichloroethylene
CDIF	Component Development and Integration Facility
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act of 1980
CF	chloroform
COC	contaminant of concern
CRADA	cooperative research and development agreement
CS	colloidal silica
CT	carbon tetrachloride
DNAPL	dense nonaqueous phase liquids
DOE	U.S. Department of Energy
EM	Office of Environmental Management
EMS	electromagnetic separator
EM-50	Office of Technology Development
EPA	U.S. Environmental Protection Agency
FST	fractionation separation technology
FY	fiscal year
GE	General Electric
GPR	ground-penetrating radar
GRI	Gas Research Institute

HDC	halogenated hydrocarbon degradation catalyst
ID	integrated demonstration
IGT	Institute of Gas Technology
IIT	Illinois Institute of Technology
INEL	Idaho National Engineering Laboratory
IP	integrated program
ISR IP	In Situ Remediation Integrated Program
ISV	in situ vitrification
LBL	Lawrence Berkeley Laboratory
LLNL	Lawrence Livermore National Laboratory
LNAPL	light nonaqueous phase liquids
LPM	low permeability media
MMO	methane monooxygenase
Monticello	Monticello Mill Site
MOU	Memorandum of Understanding
MWLID	Mixed Wasted Landfill Integrated Demonstration
NAPL	nonaqueous phase liquids
NASA	National Aeronautics and Space Administration
OCA	oil core aphron
OGMS	open gradient magnetic separation
ORNL	Oak Ridge National Laboratory
PAH	polyaromatic hydrocarbons
PB	polybutene
PCB	polychlorinated biphenyl
PCE	tetrachloroethylene or perchloroethylene
PLFA	phospholipid fatty acid
PNL	Pacific Northwest Laboratory
PRDA	program R&D announcements
PSX	polysiloxane
RCRA	Resource Conservation and Recovery Act

R&D	research and development
RD&D	Research Development and Demonstration
ROA	research opportunity announcements
SB-TIP	Small Business Technology Integration Program
SEG	Scientific Ecology Group
sMMO	soluble methane monooxygenase
SRTC	Savannah River Technology Center
SNL	Sandia National Laboratories
SRS	Savannah River Site
SVOC	semi-volatile organic compounds
TCA	trichloroethane
TCE	trichloroethylene
UST	underground storage tank
UT	United Technologies Corp.
UTK	University of Tennessee, Knoxville
VC	vinyl chloride
VOC	volatile organic compound
WDOE	Washington State Department of Ecology
WETO	Western Environmental Technology Office
WHC	Westinghouse Hanford Company

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SECTION 1.0

TREATMENT (BIOREMEDIATION)

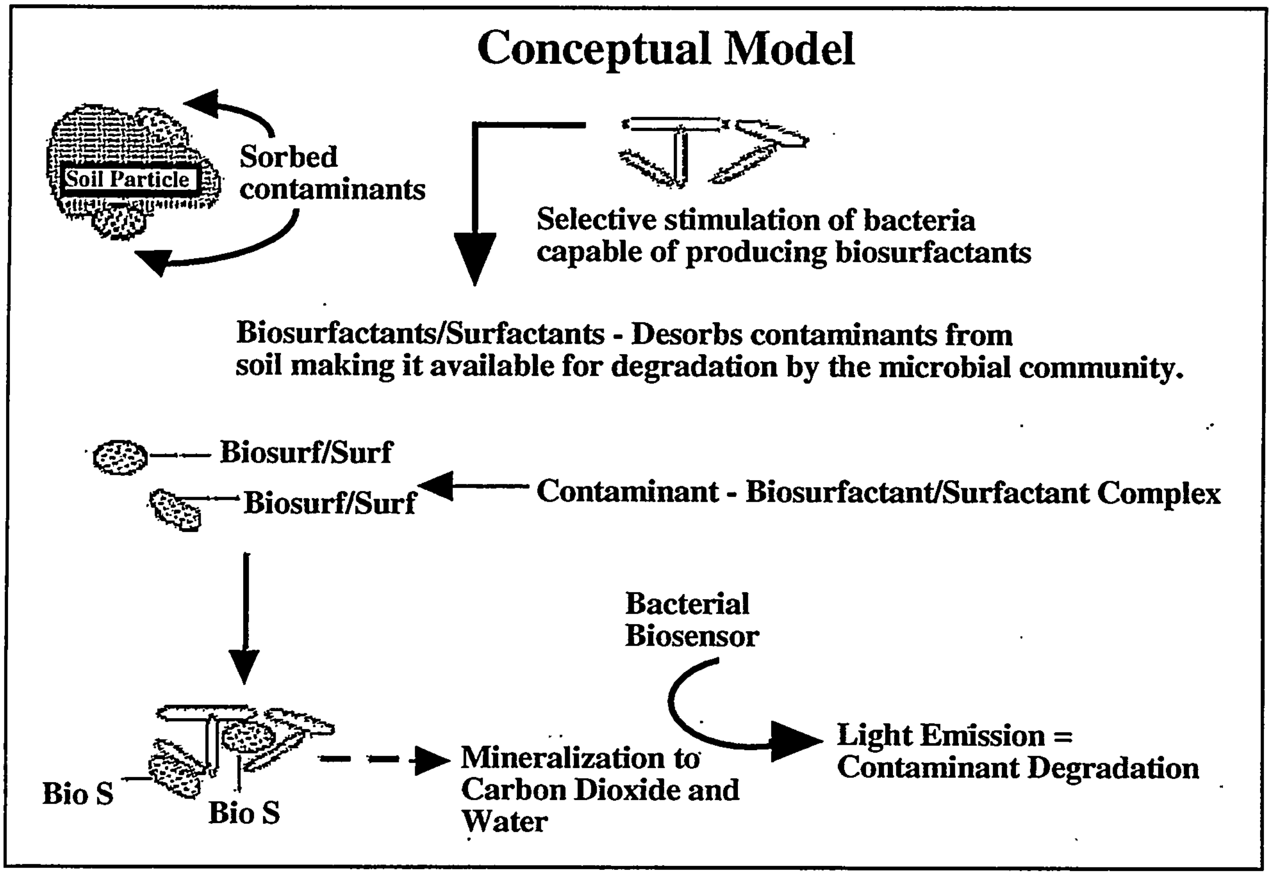
- *Bioremediation* refers to the use of biological systems or organisms that degrade or transform, mobilize, or immobilize contaminants in soil and groundwater.
- Bioremediation takes advantage of the natural abilities of microorganisms and plants to metabolize, sorb, oxidize, or reduce organic and inorganic compounds.
- The areas of emphasis include treatment of chlorinated solvents; treatment of mixed contaminants, including inorganics and radionuclides; process enhancement, including nutrient delivery methods; monitoring technologies for assessing process performance and degradation products; treatment of nonaqueous phase liquids; biostimulation for treating mixtures of chlorinated solvents; and development of standard protocols for assessing the feasibility of bioremediation.

ADSORPTION/DESORPTION RELATIVE TO APPLYING BIOREMEDIATION TO ORGANICS

TASK DESCRIPTION

This task is developing the technology necessary to accelerate the rates of in situ biological remediation of sorbed contaminants. The laboratory work has involved two related approaches that enhance the bioavailability of the contaminants (i.e., increase the biodegradation rates by desorbing the contaminants from the soil matrix): 1) surfactant (including biosurfactant) addition for enhanced contaminant bioavailability, and 2) isolation of adhesion-deficient bacteria as a biocatalyst for trichloroethylene (TCE) degradation.

Advances in these areas have implications for most bioremediation activities because the delivery of nutrients and bacteria to the contaminated zones/areas is a common problem with in situ bioremediation.



Conceptual Model

Biosurfactants/Surfactants - Desorbs contaminants from soil making it available for degradation by the microbial community.

TECHNOLOGY NEEDS

The U.S. Department of Energy (DOE) manages numerous sites contaminated with complex organic/inorganic mixtures. Restoring these sites using current technologies is often not cost effective. However, the benefits of in situ remediation technologies for site restoration include lower costs because of less excavation and storage and complete mineralization of the contaminant. Results from this work show the potential to greatly increase the efficiency of bioremediation at hazardous waste sites 1) through selectively stimulating indigenous microorganisms, 2) by introducing highly active and mobile bacteria, and 3) by desorption of contaminants, which leads to enhanced rates of degradation.

Because the proposed in situ method adds more control by virtue of the specialized biocatalyst (adhesion-deficient TCE-degrading bacteria) and mobility/desorption enhancement, this process is expected to be more efficient for contaminant degradation than are other in situ approaches. This technology should be capable of restoring small source areas in less than 1 year, thus producing significant savings in cleanup operation, maintenance, and monitoring costs.

ACCOMPLISHMENTS

Laboratory proof-of-principle experiments were conducted during FY 1994. Experiments were designed to use biosensors to detect changes in the bioavailability of a contaminant in response to the addition of biosurfactants, surfactants, and other degradation enhancers. These organisms enable us to directly monitor the physiological activity of the contaminant-degrading bacteria as well as the contaminant's bioavailability. Specifically, these biosensors are a recombinant microorganism containing the genes responsible for light generation coupled to degradative genes. This combination is controlled by the promoter, resulting in expression of the degradative genes. When the bacteria contact (degrade) the contaminant, the *lux* genes are expressed and the bacteria produce visible light (see picture). This light is detected and quantified using sensitive photomultiplier equipment. The amount of light corresponds to the amount of substrate/contaminant being metabolized.

Experiments with these organisms have shown that contaminant bioavailability can be increased by adding surfactant compounds at low levels, below the critical micelle concentration. Laboratory experiments have measured a decreased light emission with increased surfactant concentration, suggesting a toxicity effect or reduced bioavailability. Batch experiments have also shown that the addition of surfactants to soil slurries before contaminant addition reduces contaminant sorption, maintaining a higher bioavailability. Furthermore, analytical analyses (gas chromatograph) showed that surfactants decreased headspace partitioning, keeping the volatile compounds in the aqueous phase where they are available for degradation.

Surfactant use in soil-washing technologies has been proposed by many investigators. However, surfactants may play another role in pump-and-treat regimes. It may be important to introduce surfactants into an uncontaminated region in front of the contaminant plume. Then, as the contaminants are pumped to the surface for remediation, the surfactants have the potential to reduce the contaminants' subsequent adsorption to the soil matrix.

A second area of focus involved a bacterial selection procedure performed by Envirogen, Inc. (Lawrenceville, New Jersey). This task focused on the isolation of natural bacteria that have the ability to penetrate the aquifer solids because of an adhesion-deficient characteristic. Laboratory experiments show that these bacteria do not strongly adhere to a soil column and, therefore, it is expected they will move/transport through the subsurface to sources of contamination. The bacteria are capable of degrading organic contaminants such as TCE and may be capable of degrading sorbed compounds. Remediation activities that use adhesion-deficient bacteria would not only remove dissolved compounds from the aquifer solids, but could also enhance the region of contaminant degradation as the bacteria migrate/transport away from the injection source. Thus, this treatment could impose a "time-release" source of degradation deeper into the contaminated regions.

SCHEDULE OF DEVELOPMENT

The project was designed in two phases. The first phase (FY 1994) was laboratory proof-of-principle technology development. In addition to laboratory experiments, initial contacts were made with various DOE sites for the proposed field demonstration (FY 1995 and FY 1996). The milestones for the first year included a test plan for the laboratory experiments, completion of a site selection document, and completion of a report on increasing TCE degradation and enhanced transport of six adhesion-deficient bacterial strains through soil columns.

An additional project development item included completing laboratory experiments demonstrating the effectiveness of a new, innovative colloidal tracer. The field testing of this tracer is planned for FY 1995.

The second phase (FY 1995) will focus on technology demonstration at a DOE site. The planned in situ demonstration of this enhanced remediation technology will employ growth conditions to induce high levels of degradative enzymes in the adhesion-deficient, TCE-degrading bacteria prior to injection. The general operating system will consist of storage tanks, pumps, and associated instrumentation. This system will be configured to permit the addition of bioenhancing compounds (nutrients with surfactant-like properties) that increase contaminant bioavailability. Application of the system will require drilling multiple delivery wells, and may include horizontal wells or multipoint injection technology, one or more of which will be tested in FY 1995. Once the system is operating, all contaminant degradation will occur below land surface and no secondary treatments, adsorbent regeneration, or landfill disposal will be required. The cost of this remediation design is expected to be lower than that for pump-and-treat methods currently in use.

COLLABORATION/TECHNOLOGY TRANSFER

The isolation of adhesion-deficient, TCE-degrading organisms was performed under a subcontract with Envirogen, Inc. Organisms isolated by Envirogen, Inc., as well as other strains developed by DOE, can be used in this enhanced remediation process. Joint participation with an industry subcontractor will facilitate technology transfer as well as future cooperative research and development agreements. Both participants can benefit from the joint technology, capabilities, and experience brought to the project.

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BIOMASS REMEDIATION SYSTEM

TASK DESCRIPTION

The goal of this task is to demonstrate the economic and technical feasibility of commercializing a biotechnology that uses plants to remediate soils, sediments, surface waters, and groundwaters contaminated by heavy metals and radionuclides. The work has included an evaluation of a Ukrainian fractionation separation technology (FST) for processing heavy metals-contaminated leaf and stalk biomass plus algal biomass, obtained largely from CERCLA sites in southwestern Montana. The FST process uses mechanical and electrochemical methods to separate and concentrate the contaminants of concern (COC) from bulk leaf and stalk biomass. This technology had been applied in the Ukraine as an emergency measure for remediating soils and livestock forage contaminated by radiocesium and radiostrontium emitted during the Chernobyl power station accident.

Harvesting alfalfa grown in soils containing elevated levels of heavy metals. The alfalfa was used in fractionation tests to evaluate the Ukrainian fractionation separation technology.

TECHNOLOGY NEEDS

Widespread heavy metal and radionuclide contamination exists in soils and groundwater across the U.S. Department of Energy (DOE) complex, and much of this contamination is present in low concentrations or at low activity levels. For such low levels of contamination in relatively large quantities of soil and water, removal and storage or remote treatment (such as incineration for soil) becomes extremely expensive. The bioremediation technology proposed could be less expensive than soil removal and treatment given the areal extent and topography of the sites under consideration, the problems associated with process-generated fugitive dust emissions, and the investment of energy and money in the soil-moving or water-pumping and treatment processes. Moreover, in situ technology may receive regulatory acceptance more easily than ex situ treatments. Taking advantage of the natural ability of plants to take up stable or radioactive metals is an inexpensive and publicly appealing method for remediating low-level contamination.

ACCOMPLISHMENTS

Ukrainian engineers and scientists, working with MSE, Inc., completed the first phase of proof-of-process testing at the DOE's Western Environmental Technology Office (WETO) at Butte, Montana. This phase involved FST processing of alfalfa grown in heavy metals-contaminated soils, forbs and conifer needles associated with base metal and uranium mine waste rock dumps, and green algae collected from acidic mine water near the Berkeley Pit. In general, the COCs (e.g., arsenic, cadmium, lead, and uranium) were not sufficiently partitioned by FST into waste concentrate and clean leaf and stalk biomass, nor were COC levels sufficiently great in leaf and stalk biomass to support effective phytoremediation of these environmental media. However, follow-on studies of stable cesium and strontium uptake by garden peas grown in hydroponic solution at WETO lends support to the original claims of FST cleanup utility at Chernobyl. The cesium (a potassium analog) largely partitioned to the cell juice fraction, while most of the strontium (a calcium analog) was incorporated into the cell pulp fraction. It is conceivable that gross radioactivity could be sufficiently reduced by FST to allow emergency consumption of the treated pulp by livestock after such a disaster as occurred at Chernobyl. A comprehensive report documenting these FST investigations is nearing completion.

A peer review meeting was held in February 1994 to assess the experimental results. The peer review committee, composed of experts from academia and industry, reviewed the test results and recommended termination of further FST evaluations. The project was redirected to address the larger issues associated with phytoremediation. The new set of objectives for the second half of FY 1994 included 1) developing and implementing methods for evaluating COC mass transfer from soils to leaf and stalk biomass and 2) evaluating potential technologies for biomass volume reduction, resulting in further concentration of the extracted COCs, prior to reuse (e.g., smelting) or ultimate disposal (e.g., vitrification) of the contaminants. The activities completed during the second half of FY 1994 are described below.

- Literature reviews were conducted which 1) document the existence of metals-hyperaccumulating terrestrial and aquatic plants that are needed for timely phytoremediation of soils and water, 2) support the likely cost-effectiveness of this in situ technology versus ex situ alternatives (e.g., soil washing), and 3) document the existence and likely availability of thermal treatment processes for biomass volume reduction/contaminant concentration in ash.

- Field-related protocols were developed and applied for evaluating uranium uptake by plants grown in contaminated soils at Fernald, Ohio; at an abandoned uranium mine near Clancy, Montana; and at a heavy metals-contaminated soil site near Anaconda, Montana.

- Heavy metal uptake by select aquatic plants (ranging from pond weed-macrophytes to microalgae) was evaluated by Harbor Branch Oceanographic Institute, Inc., Ft. Pierce, Florida.

- In July, a group of world class researchers (soil and plant scientists, molecular biologists, etc.) convened in Santa Rosa, California, to evaluate basic and applied research issues required to expedite development of phytoremediation technology.

- MSE, Inc., planned and implemented an initial search for naturally occurring, but presently unidentified, heavy metal hyperaccumulation species in the Rocky Mountain West. Essentially, this effort involved plant and soil sampling at abandoned hardrock mine-mill (tailings) sites in southwestern Montana, northern Idaho, and near Leadville, Colorado.

COLLABORATION/TECHNOLOGY TRANSFER

MT International, Inc., a United States corporation, has established a joint venture agreement, American-Ukrainian Biotech IV(AUB), with the Central Scientific Research Laboratory of Comprehensive Processing of Plant Raw Materials of the Ukrainian Academy of Agrarian Sciences. The Ukrainian Academy of Agrarian Sciences and Berevetnik Scientific Research Institute have conducted large-scale soil remediation, implementing a biomass processing system near the radioactive Chernobyl site. American Ukraine Biotech IV provided the laboratory-scale FST system design and personnel necessary for operation. MSE, Inc., established a contract with MT International, Inc., to provide access to the Ukrainian technology. A contract was also established with Harbor Branch Oceanographic Institute, Inc., and Microbial Products, Inc., to assist in selecting algae species for study and to produce sufficient quantities of selected species to perform bioremediation evaluations and assess the applicability of FST to algae.

The Uranium in Soils Integrated Demonstration Program participated in the project and worked with MSE, Inc., to perform field demonstrations at Fernald, Ohio.

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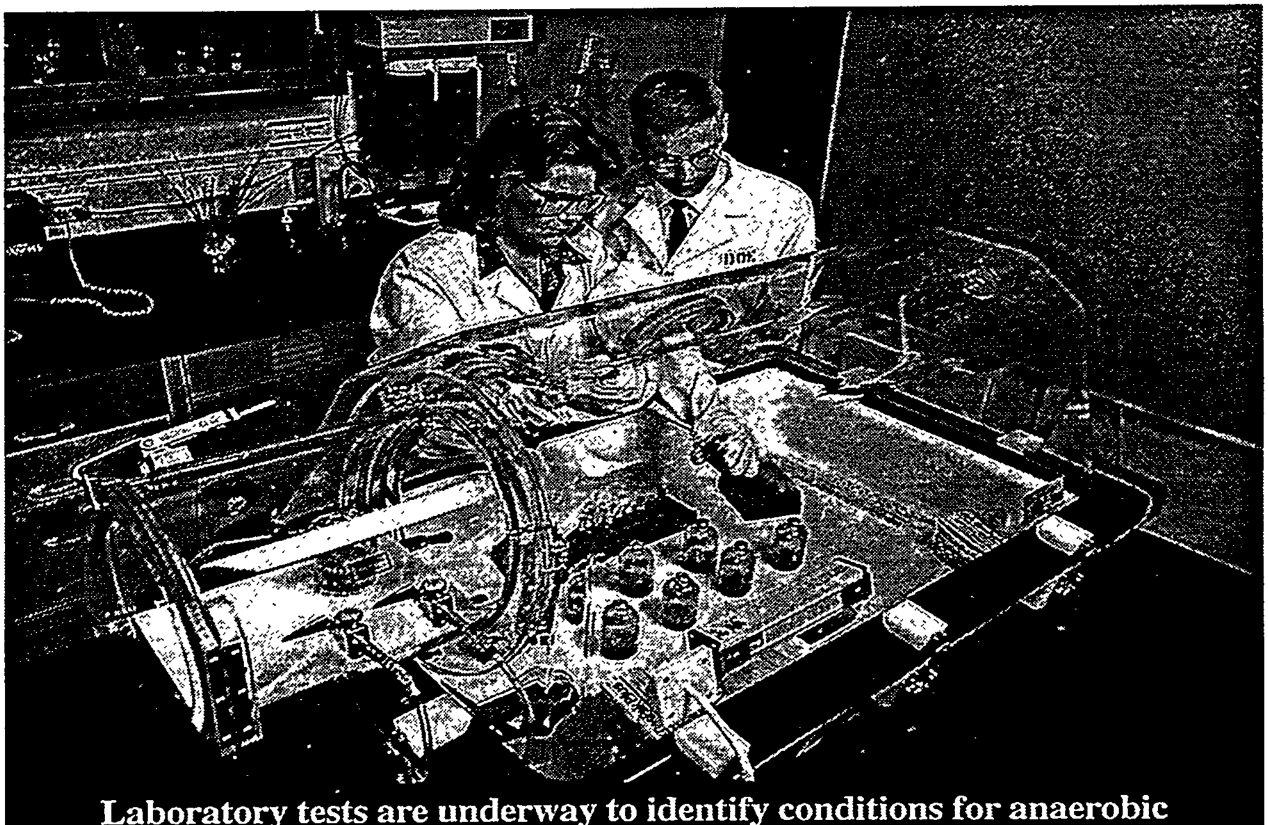
BIOREMEDIATION OF PCB CONTAMINATION

TASK DESCRIPTION

This task is focused on developing and demonstrating a bioremediation technology for polychlorinated biphenyl (PCB)-contaminated soils and sludges. Bench-scale experimental studies are underway to identify favorable conditions for anaerobic dechlorination of PCBs. Microbial inocula have been provided by the General Electric Company (GE), who is our partner under the auspices of a cooperative research and development agreement (CRADA). The microbial cultures from GE were obtained in the form of PCB-contaminated sediments from the Hudson River. GE staff have shown that these sediments are capable of biodegrading PCBs. Project staff at the Oak Ridge National Laboratory (ORNL) are inoculating PCB-contaminated soils with these sediments to develop and test conditions to stimulate degradation of the PCBs in the soils. The goal is to achieve a sufficient amount of anaerobic (reductive) dechlorination to enhance the susceptibility of the contaminants to further aerobic (oxidative) degradation and ideally complete mineralization.



Laboratory tests are underway to identify conditions for anaerobic dechlorination of PCB-contaminated soils and sludges.

TECHNOLOGY NEEDS

The U.S. Department of Energy (DOE) has significant quantities of PCB-contaminated soils in storage at several locations, notably ORNL. These soils have been excavated from spill sites and also contain radionuclides; hence, they are mixed wastes. Bioremediation offers a potentially simple means to destroy the PCBs at relatively ambient conditions. The treated soils could then be disposed as radioactive waste at existing facilities.

ACCOMPLISHMENTS

Work to date has demonstrated that organisms in Hudson River sediments, provided by GE, can be used to inoculate soil slurry bioreactors. Tests with various nutrient amendments have led to the selection of specific conditions that favor anaerobic dechlorination of the meta position on the biphenyl rings. Removal of chlorines from the meta position is known to increase the susceptibility to microbial aerobic oxidation to break the rings. Further tests are under way to study the aerobic ring breakage and anaerobic dechlorination in radioactive soils. Human PCB exposure data have been incorporated into evaluations of results to determine half-life expectancy of the PCBs in humans before and after bioremediation.

SCHEDULE OF DEVELOPMENT

Work during FY 1994 focused on validating and refining the conditions to promote meta dechlorination in small (100 mL) or large (1 L) scales. The phenomenon appears to depend on nutrient conditions. However, the details of the biochemistry are not yet known. In FY 1995 the 1-L scale radioactive and nonradioactive soils will be completed, including a microbial aerobic oxidation of the products remaining after anaerobic dechlorination. Over 70% reduction of the original PCBs is anticipated in sequential anaerobic-aerobic biotreatment. The results will be evaluated to see if an approach using a soil slurry reactor should be considered for a technology demonstration. The presence of radioactive constituents is problematic. The use of radioactive material enhances the realism of the demonstration (and such materials are readily available), but adds cost.

COLLABORATION/TECHNOLOGY TRANSFER

The project is being carried out under the auspices of a CRADA with GE. ORNL is benefiting from the GE expertise in the field and their sediments obtained from the Hudson River. In turn, GE is benefiting from the ORNL work to extend their knowledge based on sediments into degradation of PCBs in soils, which is a significantly different matrix at the physicochemical and biological levels. Results from studies at ORNL and GE have been presented widely at technical symposia and DOE meetings.

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BIOSORPTION OF URANIUM

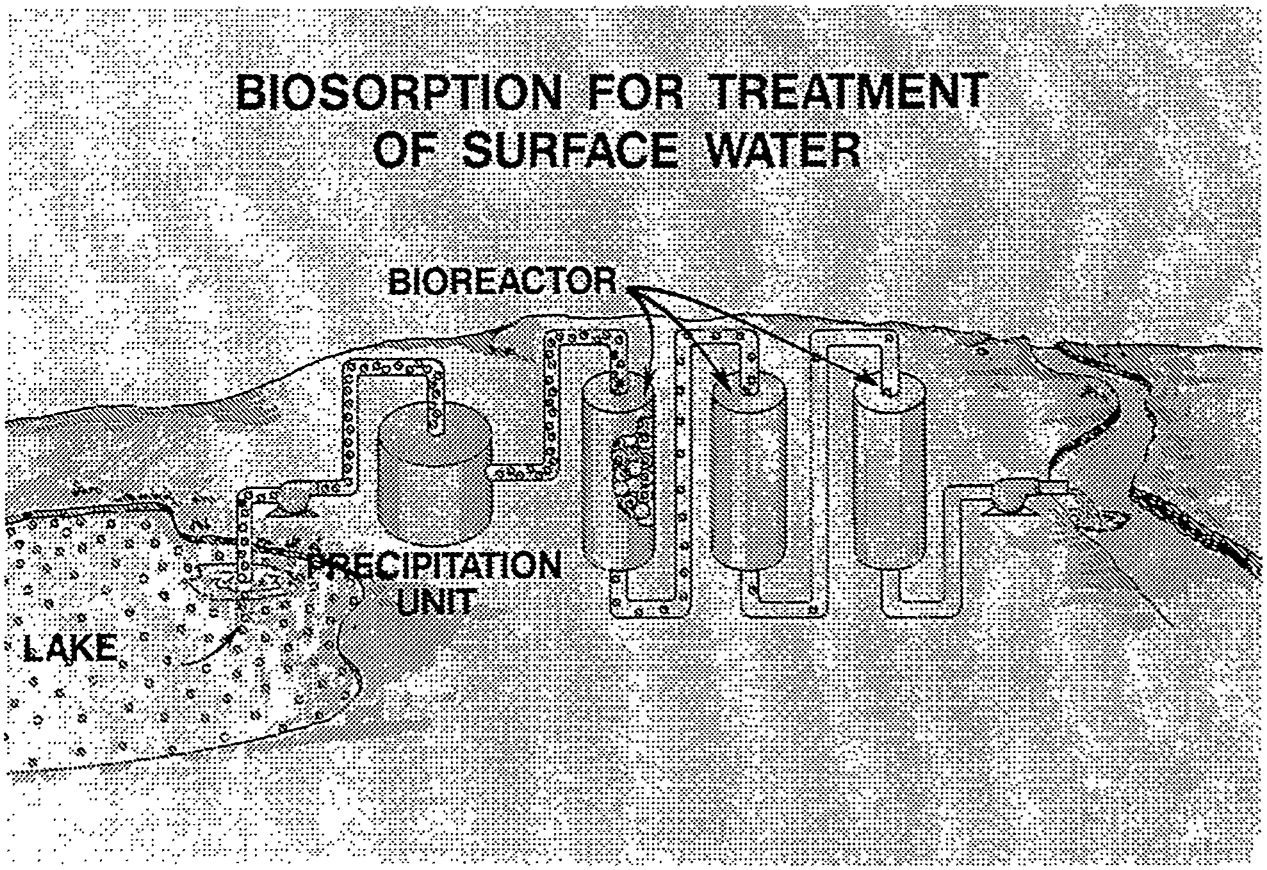
TASK DESCRIPTION

The goal of this task is to develop a biosorbent technology that can selectively remove uranium or other designated metals present at low concentrations in surface or groundwater. This work will lead to a demonstration of biosorption remediation of uranium contamination in groundwater and surface water.

The proposed process uses biosorbents (sorptive biomass or biological material) immobilized in permeable beads in turn contained within flow-through bioreactor systems. Systems will be operated in a continuous or semi-continuous mode, and will be operated onsite as a pump-and-treat methodology. The system will achieve waste fixation and volume reduction. Uranium concentrations will be reduced from parts per million to parts per billion levels.

TECHNOLOGY NEEDS

Technologies are needed to treat waste water contaminated with low



concentrations of uranium. Current technologies for uranium removal include precipitation with alkali, adsorption onto activated carbon or other inorganic resins, reverse osmosis, and extraction with tributyl phosphate or other materials. These technologies may generate unacceptable secondary wastes, e.g., large amounts of sludge and/or mixed waste. None of these technologies is suitable for treatment of dilute waste streams, and processes based on these technologies are expensive.

ACCOMPLISHMENTS

Various strains of bacteria, yeast, fungi, and algae have been screened for their ability to extract uranium from contaminated water containing low concentrations of this heavy metal. Certain species of *Pseudomonas* have been identified as the optimal biological material for binding uranium from acidic water (i.e., pH less than 3). *Pseudomonas aeruginosa*, the lead candidate, has been shown to bind over 30% of its dry weight as uranium. Methods for improving these binding characteristics, e.g., pretreatment with polar organic solvents, have been developed. Bound hexavalent uranium is converted by living cells to insoluble tetravalent uranium, which precipitates intracellularly. Binding by killed biomass has also been demonstrated. Certain cellular components have also been shown to bind uranium in cell-free systems.

In previous work, *Pseudomonas aeruginosa* immobilized within a matrix of calcium alginate reduced uranium levels in a simulated waste water from 10 ppm to 6.8 ppb. Over 350 column volumes were successfully treated before breakthrough occurred and bound uranium was quantitatively removed from the column by treatment with five column volumes of 0.15 M nitric acid.

In more recent work, improved stable immobilization matrices have been developed. Tests of *Pseudomonas aeruginosa* immobilized within polyacrylamide have been carried out using an authentic domestic waste water. The test biosorbent was shown to be superior to several commercial nonbiological sorbents, including chelating resins, weak cation-exchange resins, and activated carbon. Preliminary tests indicate that the enhanced specificity of the biosorbent for uranium will allow the biosorbent to be competitive with strongly acidic cation-exchange resins for treating multi-component solutions. A new, less-costly polyurethane-based immobilization matrix has been developed and successfully tested.

SCHEDULE OF DEVELOPMENT

The major focus for FY 1994 includes completion of bench-scale optimization tests, including a comparison of the immobilized biosorbent to other commercially available biological and nonbiological sorbents; preparation of a technology development progress report, including a cost and market analysis; initiation of pilot-scale tests; and design of a site-specific process for use at the Ronneburg mine in eastern Germany.

COLLABORATION/TECHNOLOGY TRANSFER

This technology development work is being carried out in cooperation with an industrial partner, Ogden Environmental and Energy Services, Inc. (a United States-based company), via a cooperative research and development agreement with the U.S. Department of Energy. The technology will be demonstrated by Ogden at Ronneburg, a German uranium mine site with a large surface impoundment, an underground mine subject to groundwater encroachment, and various small drainage streams. There have been no previous efforts at site remediation. The targeted waste site was identified by Ogden in cooperation with DFA (formerly Wismut), the German enterprise responsible for activities analogous to those covered by the Uranium Mine Tailings Remedial Action Program.

Oak Ridge National Laboratory (ORNL) and Ogden, Inc., are the principal participants in this task. ORNL will be mainly responsible for biotechnology development, including a field demonstration in Germany. Technology development activities will be based in part on data provided by DFA. Technology development will be carried out in the United States in collaboration with a researcher at Florida International University. This technology will be evaluated in tandem with biosorption under development at the U.S. Geological Survey and Los Alamos National Laboratory in the United States, at McGill University in Canada, and at the University of Birmingham in the United Kingdom.

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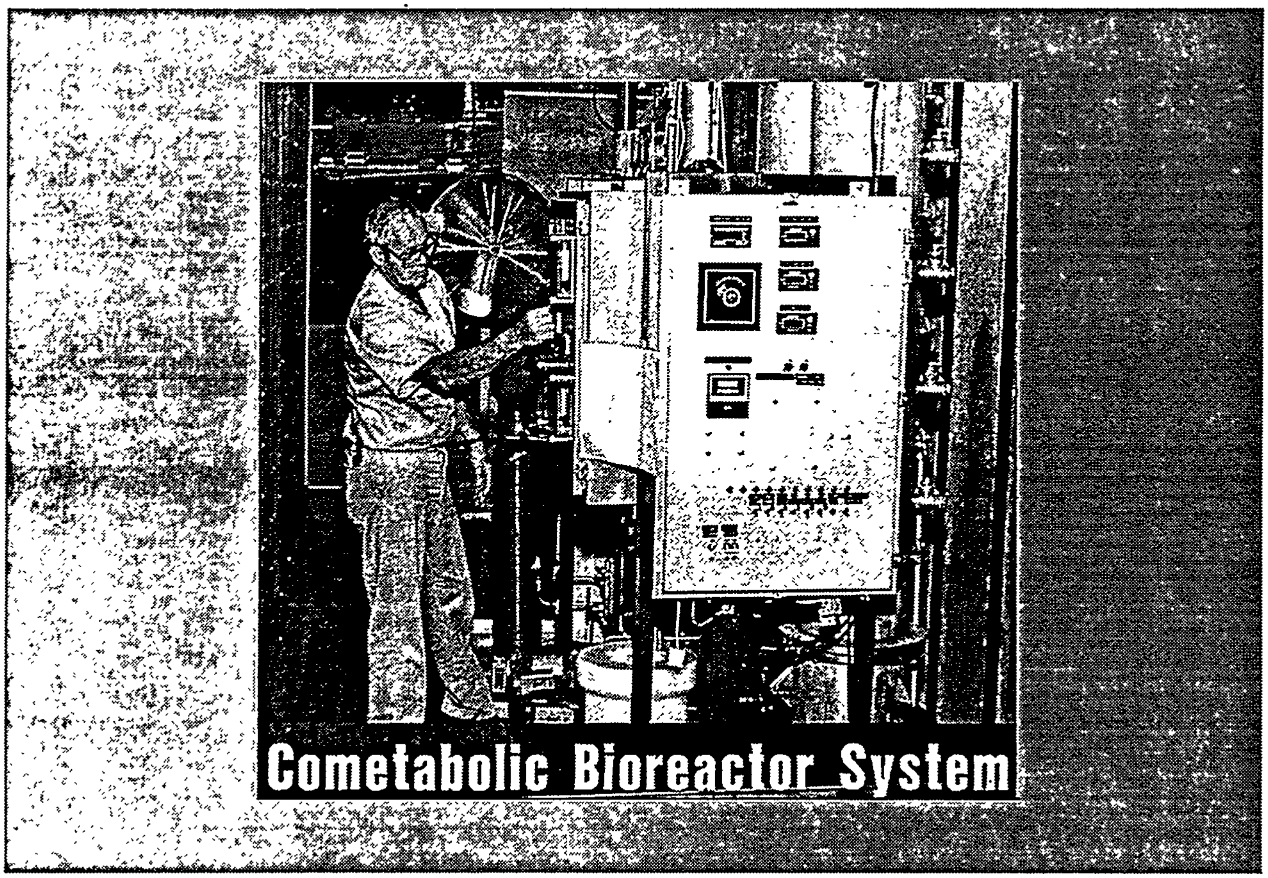
DEMONSTRATION OF COMETABOLIC TECHNIQUES

TASK DESCRIPTION

This task is a field demonstration of two cometabolic techniques for biodegradation of chlorinated solvents in groundwaters and leachates. The site of the field demonstration is a groundwater seep discharging in the vicinity of the K-1070-C/D Classified Burial Ground at the Oak Ridge K-25 Site.

The primary technology being demonstrated involves the use of methanotrophic (methane-consuming) microorganisms in a packed-bed bioreactor. Contaminated water applied to the top of the packed bed trickles down over the packing surfaces which are covered with biofilms. Methane and oxygen are provided to the vapor phase to support the microbial culture. Some of the chlorinated solvents (including trichloroethylene [TCE]) are oxidized by the enzyme methane monoxygenase produced by the methanotrophs.

This technology is being demonstrated using a pilot-scale bioreactor system loaned to the Oak Ridge National Laboratory (ORNL) by the Air Force Civil



Engineering Support Agency, Tyndall Air Force Base. Steam stripping is used in conjunction with the bioreactors to remove the volatile organic compounds (VOCs) from the water and to prevent exposure of the aerobic bioreactor environment to iron. Exposure to iron would cause serious scale deposition. The VOCs removed in the steam stripper are treated in the bioreactor. The feed stream to the process is a leachate from a burial ground at the Oak Ridge K-25 Site containing TCE and other chlorinated and nonchlorinated organics at sub-ppm levels.

The second cometabolic system is based on pseudomonas organisms that use aromatics such as toluene as a primary carbon source. Tests using a bench-scale bioreactor were carried out by Envirogen, Inc., under the auspices of a cooperative research and development agreement (CRADA) with ORNL. The work was done at the field site using the same leachate stream.

TECHNOLOGY NEEDS

Cometabolic biotreatment technologies such as these offer destruction of chlorinated VOCs in groundwater and leachates. The U.S. Department of Energy (DOE) has various sites with groundwater and leachates contaminated with chlorinated solvents. The bioreactor technologies demonstrated in this project are primarily applicable for pump-and-treat applications or for situations where leachates are available above ground. In situ variations of this and related technologies are also being developed and tested by other investigators at DOE and elsewhere.

ACCOMPLISHMENTS

The methanotrophic system has been operated for several brief campaigns. Long-term continuous operation has been hampered by waste generation and disposal considerations. Destruction of chlorinated solvents was demonstrated, as evidenced by loss of target compounds and generation of comparable quantities of chloride ion. The final technical report was reviewed by the DOE program manager prior to its publication and release.

Tests were conducted jointly by Envirogen, Inc., and ORNL staff using the bench-scale pseudomonas system over a period of several months. The leachate appears to be somewhat inhibitory to the microbial culture in suspended growth; the affects were shown to be concentration dependent. Some evidence was obtained for degradation of TCE. Further work would be needed to determine a suitable operating mode for this reactor system with this feed stream.

SCHEDULE OF DEVELOPMENT

Experimental tests at the K-25 Site in Oak Ridge, Tennessee, are complete and the equipment has been removed from the site. The final technical report, including the results of the joint work with Envirogen, Inc., under the CRADA, will be available in the spring of 1995.

COLLABORATION/TECHNOLOGY TRANSFER

The project has benefitted from substantive collaborations with the U.S. Air Force and Envirogen, Inc., both of whom are potential users of this technology. In a separate but complementary program, ORNL has collaborated with the University of Tennessee in a project to develop a multi-stage bioreactor system for cometabolic degradation of chlorinated solvents by methanotrophs, funded by the U.S. Air Force. The progress and results of the field demonstration have been presented at various technical symposia and DOE technology transfer meetings.

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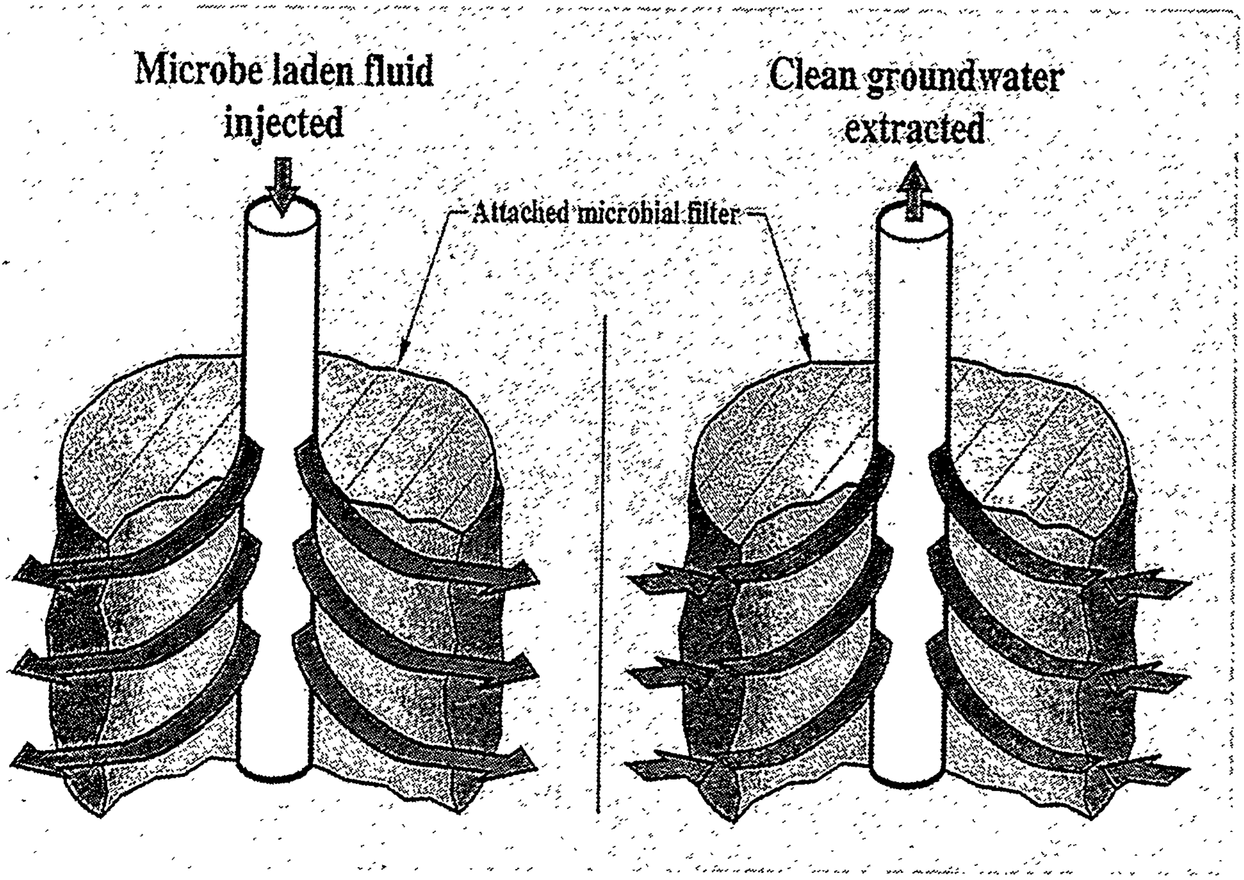
IN SITU MICROBIAL FILTERS

TASK DESCRIPTION

Groundwater contaminated with volatile organic compounds such as trichloroethylene (TCE) is costly and time consuming to remediate using pump-and-treat technology. In addition, bioremediation methods have been difficult to implement because of problems that accompany nutrient injections: fouling, inhibition of the biodegradation reaction, and difficulty in achieving contact between the stimulated microbe population and the contaminants.

This task is adapting the bioremediation concept by developing in situ microbial filters. With this approach, microbes that degrade TCE are injected into the subsurface, instead of nutrients, to form a fixed-bed biofilter. Since nutrients are not used in the subsurface, the microbes are considered to be in the resting state. As TCE-contaminated groundwater flows through the biofilter, the microbes degrade the TCE to harmless compounds.

A key element of the concept is implementation of the subsurface filter. A portion of the injected microbes attaches to



the soil and forms a fixed-bed biofilter. The actual geometry of the biofilter depends on the injection pattern but, generally, a thin region forms across the expanding contaminant plume. The attached microbes degrade the TCE to harmless compounds as it is transported through the biofilter region by the flowing groundwater.

TECHNOLOGY NEEDS

The expense of pump-and-treat technologies for remediating contaminated groundwater, and the complexities associated with injecting nutrients to stimulate contaminant-degrading organisms in a contaminated region, point to the need for a much simpler, less expensive technique for field applications of in situ bioremediation. The concept of a microbial filter in which microbes, not nutrients, are injected into the subsurface to form a filter may be an inexpensive technique for implementing bioremediation capabilities in the field.

ACCOMPLISHMENTS

The filter design depends on three sets of parameters that are being addressed by this task: 1) filter residence time - the time required for the contaminant to remain in the filter so it can be degraded to levels within regulatory limits; 2) filter degradation capacity - the amount of TCE that can be degraded by the biofilter before the filter must be replenished through re-inoculation; and 3) enzyme longevity - the amount of time the microbial population can remain catalytically active in the resting state.

Work conducted in previous years measured these key engineering design parameters. Scaled laboratory experiments were also completed. In FY 1994, a field treatability study at Wilson Corners, Kennedy Space Center, demonstrated the principle of biodegradation using resting-state microbes, but ultimately was limited to about 2-ppm total contaminant degradation by the significant contaminant concentrations (~10 ppm) relative to dissolved oxygen content of the groundwaters (~0.5 ppm). In addition, analysis of samples confirmed the presence of additional, undifferentiated volatile compounds. Because of these problems, alternative locations are being investigated for follow-up work.

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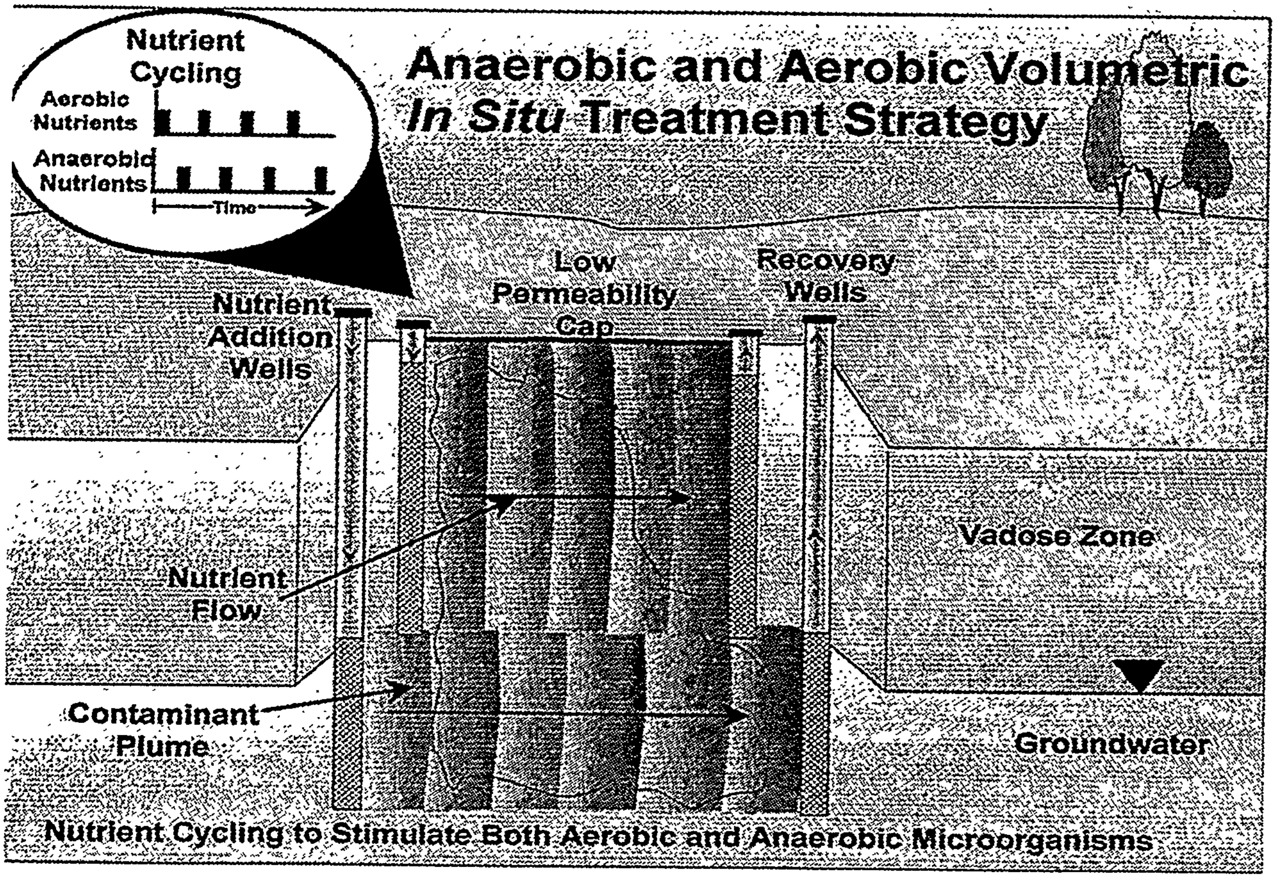
MIXED CHLORINATED SOLVENT IN SITU BIOREMEDIATION IN THE VADOSE ZONE

TASK DESCRIPTION

This task will develop and evaluate viable concepts for in situ bioremediation of mixtures of chlorinated solvents in groundwater. This objective will be achieved by evaluating the effectiveness of various classes of microorganisms to destroy chlorinated ethylenes and by testing methods to control the metabolic activity of multiple populations of microorganisms in the subsurface. Experiments will also be conducted to test the effects of oxygen on anaerobic activity to support developing combined aerobic-anaerobic technologies. Understanding this interaction is important to developing anaerobic-aerobic processing systems since oxygen is a known toxin to many anaerobic organisms.

TECHNOLOGY NEEDS

Chlorinated solvent contamination in soils and groundwater is a widespread problem at both government and industrial sites.



Pump-and-treat is the primary remediation technology used for groundwater, while soil vapor extraction is employed for the vadose zone. In both technologies, volatile organics are typically transferred to an air phase and then adsorbed to granular activated carbon for later thermal destruction. One major disadvantage of these techniques is the inability to extract all the contaminants since the materials can adsorb to the soil or be retained in small, tortuous pores. Another undesired characteristic of the current technologies is the increased risk of exposing workers to the hazardous material. In addition, above-ground handling of large volumes of contaminated media is expensive. In situ bioremediation can avoid these problems since contaminants are not extracted. However, implementing in situ bioremediation to treat the U.S. Department of Energy's (DOE) chlorinated solvent contamination requires developing techniques to remediate both single contaminants and mixtures of contaminants in saturated and unsaturated soils. This situation is complicated since many of the different classes of microorganisms required for degradation need very different chemical conditions for active metabolism. Also, the conditions that support activity by one class of organisms may inhibit another class. The goal of this work is to develop processes to treat contaminant mixtures by applying basic engineering principles to process design and evaluation.

ACCOMPLISHMENTS

- Studies were conducted on the kinetics of growth, methane production, and chlorinated ethylene dechlorination by an anaerobic microbial consortium enriched from contaminant-free river sediment. The purpose of these experiments was to provide a conservative representation of dechlorination by examining anaerobic tetrachloroethylene (PCE) degradation by an environmental isolate that had not been exposed previously to chlorinated solvents. This work is being contrasted to published studies where organisms have had long durations (typically years) to adapt to the presence of the contaminant.

- Microcosms have been established using aquifer materials from several private, DOE, and U.S. Department of Defense waste sites with PCE contamination. This material is being used to evaluate natural methods to increase the efficiency of anaerobic dehalogenation activity.

- Biologically reactive flow-and-transport computational tools have been developed to simulate both aerobic and anaerobic microbial activity in the saturated subsurface. These computer tools are being used to rapidly evaluate the effectiveness of potential bioremediation system designs and nutrient feeding strategies for aquifer restoration.

SCHEDULE OF DEVELOPMENT

To facilitate field application of the results from this research, an in situ treatability protocol is being developed in FY 1995. This test will use computational tools to analyze field tracer data and nutrient injection data to evaluate the potential for anaerobic and/or aerobic bioremediation at a given waste site. In addition, the test will provide the microbial characterization information that is needed for remediation system design. Currently, the cost of developing this information is extremely high since a combination of both laboratory and field analysis is required. It is anticipated that using a single in situ test will greatly reduce these costs. The usefulness of the in situ treatability test will be demonstrated at several field sites in FY 1996.

COLLABORATION/TECHNOLOGY TRANSFER

This project involves a collaboration between the DOE's Pacific Northwest Laboratory, Washington State University, and Montana State University

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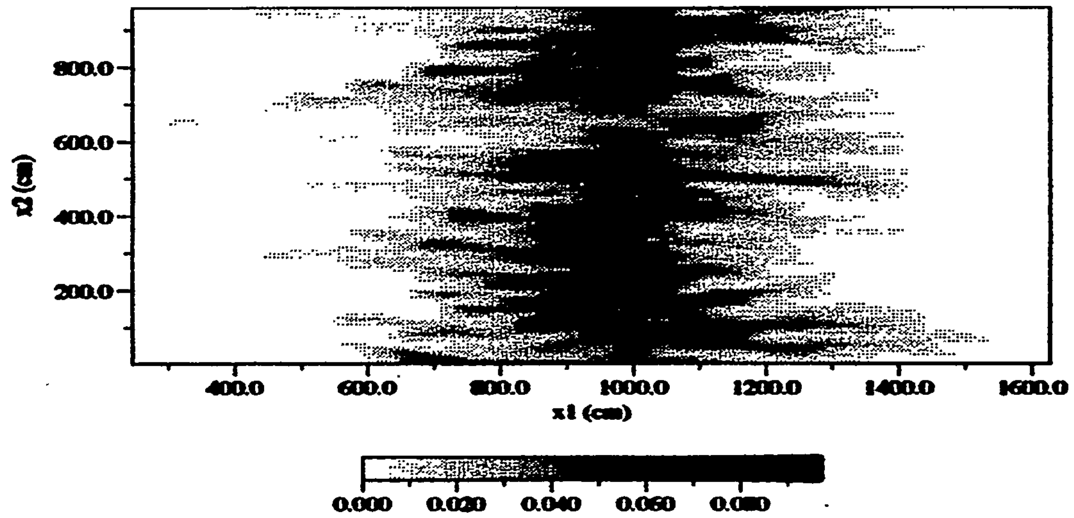
MODELING STRATEGIES FOR OPTIMIZING IN SITU BIOREMEDIATION

TASK DESCRIPTION

This task will conduct laboratory experiments, evaluate field data, and investigate processes (physical, chemical, and biological) of solute transport and fate to improve our understanding of processes associated with in situ bioremediation. Primary objectives are to improve the ability to predict in situ mixing and the cometabolic transformation of halogenated aliphatic compounds. The overall goal of this work is to recommend effective designs of chemical delivery, mixing schemes, and strategies for improving in situ bioremediation.

In FY 1994, this project was combined with a VOC Arid Soils Integrated Demonstration project. A recirculation unit is being designed for the delivery and mixing of chemicals at a site at Hanford, and experiments are being conducted to evaluate schemes for the complete degradation of carbon tetrachloride (CT). The in situ anaerobic transformation of CT may leave some chloroform (CF) as a transformation product. This study will



A successful in situ bioremediation scheme must enhance the mixing of contaminants with other reagents. In the simulation, TCE concentration (in ppm) is highly variable because of heterogeneity in aquifer properties. The simulation indicates that the compound is concentrated at certain hotspots.

also evaluate the ability of indigenous microcosms from the Hanford subsurface to aerobically cometabolically degrade CF. If successful, an aerobic process may be used as a final polishing step for remediation at the site.

TECHNOLOGY NEEDS

Efficient biodegradation requires good mixing of reagents (microorganisms, nutrients, and contaminants) and methods for introducing chemicals into the soil and controlling their concentrations. Other in situ remediation methods, such as in situ chemical treatment, redox manipulation, or sparging, also require a good grasp of dilution and mixing processes. Practical methods to evaluate rates of dilution and mixing under field conditions are not available and must be developed. Mathematical modeling, in combination with laboratory and field experiments, is essential to understanding the complex interaction of factors affecting in situ mixing in order to improve bioremediation and other in situ remediation methods. Also, it will be useful to designers of effective systems for delivery and mixing of chemicals in the subsurface. Among the crucial questions that need to be addressed is aquifer plugging caused by biomass growth and ways to repress this development.

Microbial systems that are effective in degrading CF, which is a byproduct of the anaerobic degradation of CT, are needed for the Hanford Site as well as other facilities. It is also essential to develop methods for evaluating the potential for in situ bioremediation at a certain site. This evaluation capability can best be achieved through laboratory studies and the development of mathematical models that represent biotransformation processes.

ACCOMPLISHMENTS

A methodology for quantifying the rate of dilution and mixing has been developed. Reports under preparation will describe the mechanisms that control mixing in the subsurface. Research is continuing by evaluating how geologic heterogeneity affects rates of dilution and mixing of solute plumes in flowing groundwater. The research is unique in that it focuses on mixing under realistic conditions encountered under in situ remediation conditions. The research is producing graphs for evaluating rates of mixing that can be of great practical importance in designing in situ bioremediation schemes. Furthermore, a computational procedure has been developed to determine the flow around a recirculation unit. The method has been extended to account for heterogeneity in hydraulic conductivity and changes in conductivity due to biomass growth. Continuing studies illuminate the factors controlling plugging of the formation and suggest procedures for its control.

A practical computational procedure has been developed for the hydrodynamics of air sparging. The methodology is applied in two steps: 1) locating the interface between the volume that contains air bubbles and the surrounding water, and 2) determining the pressure distribution and rates of flow. The method fills an important gap in the technology for designing sparging systems.

To study the anaerobic biotransformation of CT and the aerobic transformation of CF, a recirculating bioreactor was fabricated and packed with aquifer material from the site of the VOC-Arid Bioremediation Demonstration project. The anaerobic transformation of CT was studied under representative subsurface flow conditions of the in situ bioremediation project. Benzoate and acetate were tested as growth substrates. Denitrification was more effectively promoted with acetate and 20% to 30% of the CT was transformed within a 2-day fluid residence time in the bioreactor. More effective CT transformation was observed in the absence of nitrate. CF represented 20% to 30% of the CT transformed. During batch operation of the bioreactor, 94% of the CT was transformed in 12 days, with 40% converted to CF, following first-order kinetics with respect to CT concentration. The results indicate that it may be possible to achieve complete removal of CT in the Hanford subsurface over weeks or months by injecting the anaerobic substrate in excess of that required for complete denitrification. Research continues and studies of the sequential anaerobic/aerobic transformation of tetrachloroethylene and trichloroethylene (TCE) are also planned.

A soil microcosm method was developed to screen for the aerobic cometabolic degradation of CF by Hanford subsurface microorganisms. Cometabolic substrates evaluated include phenol, methane, ammonia, propane, butane, propene, and octane. Isoprene, propane, and butane were discovered to be the most effective substrates. These are believed to be the first observations of butane as an effective aerobic cometabolic substrate, and butane-using microorganisms appear to be the most promising cometabolic system for CF cometabolism studied to date. However, the system needs to be studied further. Pure cultures are being isolated from the microcosm enrichments. Microcosm and pure culture studies with 14-C radiolabeled CF will confirm whether complete degradation of CF to carbon dioxide is achieved.

SCHEDULE OF DEVELOPMENT

The VOC-Arid Site Bioremediation Demonstration of anaerobic transformation of CT was scheduled to start in early FY 1994. The studies on mixing and the observations from the anaerobic bioreactor study guide the demonstration study. The research on in situ mixing will continue in FY 1995 with the development of practical procedures for evaluating rates of dilution and mixing. Evaluation of the aerobic cometabolism of CF also continues. Isolation of pure cultures, radiolabeled transformation studies, and microcosm and bioreactor studies will continue throughout FY 1995.

COLLABORATION/TECHNOLOGY TRANSFER

The technology is applied to the VOC Arid Soils Integrated Demonstration site at Hanford. There is considerable interest from industry in technologies developed in this project, particularly in situ mixing technologies and procedures for CT and CF degradation. Work is being carried out at Stanford University and at Oregon State University.

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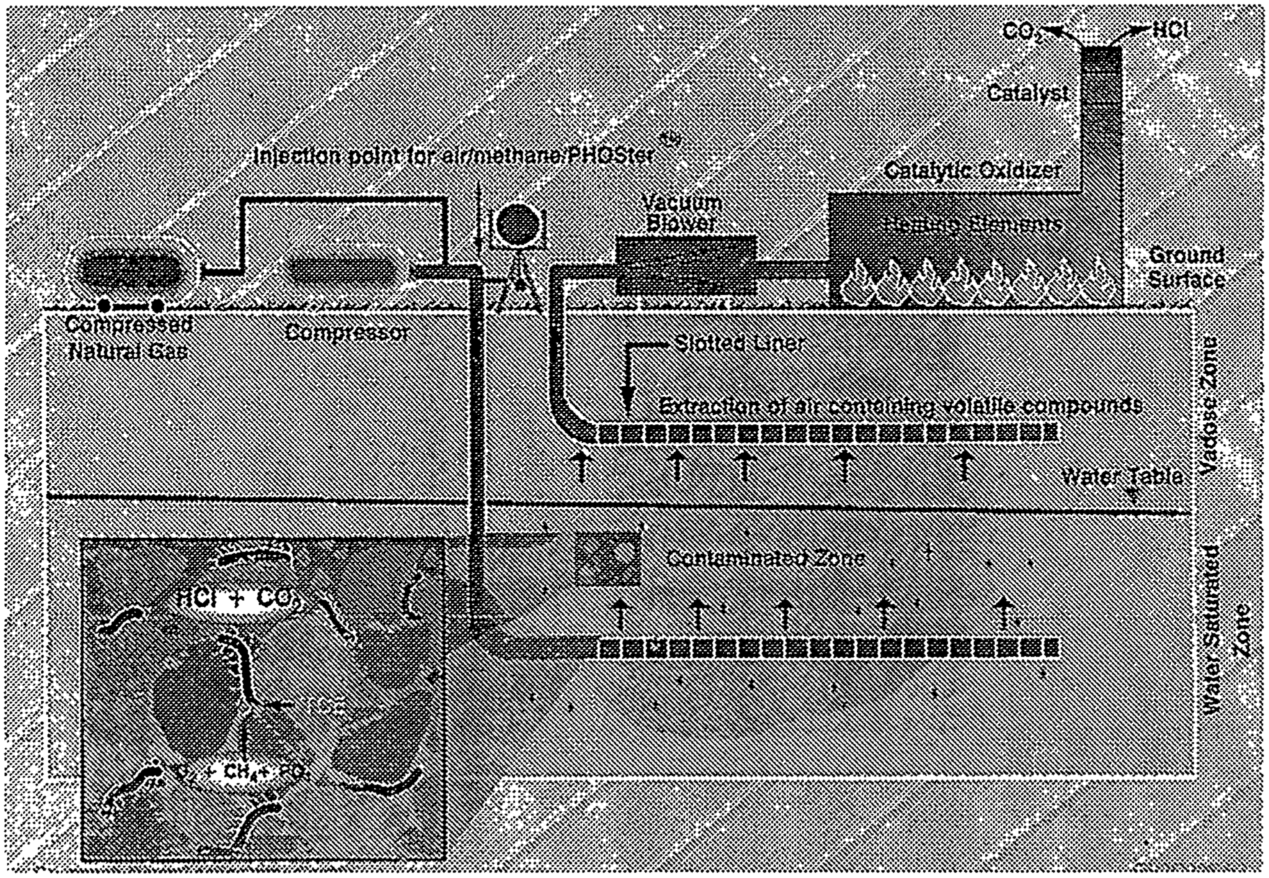
VALIDATION AND PUBLICATION OF SR BIOREMEDIATION FIELD EXPERIMENTS

TASK DESCRIPTION

Subsurface soils and water adjacent to an abandoned process sewer line at the Savannah River Site (SRS) have been contaminated with chlorinated solvents. In conjunction with the volatile organic compounds (VOCs) in Nonarid Soils Integrated Demonstration, this task is demonstrating in situ bioremediation of the contaminated area by stimulating indigenous microorganisms to degrade trichloroethylene (TCE), tetrachloroethylene (PCE), and their daughter products. The degradation occurs in situ by adding nutrients to the contaminated aquifer and adjacent vadose zone. The principal carbon/energy source used in this work is methane (natural gas). The horizontal wells that form the basis for this integrated demonstration are expected to be superior to conventional in situ bioremediation in which vertical wells or infiltration galleries are used. The increased surface area will improve the delivery of nutrients and ease the recovery of gas and water, plus minimize problems with clogging and plugging.



TECHNOLOGY NEEDS

The U.S. Department of Energy (DOE) manages numerous sites contaminated with organic solvents. Restoring these sites using current technologies (e.g., pump-and-treat or excavation) is not cost effective. The benefits of in situ remediation technologies for site restoration include lower costs and reduced risk to workers and the public. In situ bioremediation is a promising technology for the in-place destruction of organic contaminants.

ACCOMPLISHMENTS

A 14-month demonstration of this bioremediation strategy concluded this fiscal year. The demonstration was conducted at the SRS within an area contaminated with chlorinated solvents (TCE/PCE) leaking out of a process sewer line. The demonstration consisted of injecting methane mixed with air into the contaminated aquifer using a horizontal well installed below the water table and extracting the mixture from the vadose zone using a horizontal well installed in the vadose zone above the water table. Groundwater was monitored biweekly from 13 wells for a variety of chemical and microbiological parameters. The following sections highlight the results of this demonstration.

Biostimulation/Biodegradation

The evidence for biostimulation and biodegradation of TCE/PCE was significant. A minimum of 26 separate measurements of sediment and groundwater done by 6 different laboratories indirectly demonstrated biostimulation and biodegradation in situ by the processes tested. Densities of methanotrophs, the functional group the process was trying to stimulate, increased in the groundwater by as much as 7 orders of magnitude. This stimulation occurred first in the wells closest to the injection point and later moved farther and farther away. Densities of methanotrophs in the sediment closest to the injection well increased from rarely detectable to over a million cells/groundwater. The methanotroph enumerations were done by three different laboratories (University of Tennessee, Pacific Northwest Laboratory [PNL], and Savannah River Technology Center [SRTC]) using three different methods and all obtained nearly identical results. Increases in methanotroph densities were observed only after methane injection started. Phospholipid fatty acid (PLFA) analyses done by the University of Tennessee and Oak Ridge National Laboratory (ORNL) also indicated biostimulation of methanotrophs, and that methanotrophs were being stimulated to become the dominant population in the total microbial community. Studies by SRTC and the University of Tennessee using soil columns and mineralization assays demonstrated that PCE was being biodegraded even under bulk aerobic conditions. This later observation is particularly significant since PCE can only be degraded anaerobically. Their data suggests that enough anaerobic pockets are created by the increased biomass to allow a significant amount of anaerobic reductive dechlorination of PCE to TCE, which can then be oxidized by the methanotrophs.

Nucleic acid probe analyses by five different laboratories, PNL, Washington State University, University of Minnesota, SRTC, and the University of Tennessee, showed very specifically that methanotrophs were being stimulated in the sediment. Biostimulation was also indirectly shown by the depletion of nitrate (a limiting nutrient) in the groundwater as stimulation continued. Biostimulation was indirectly indicated by the increase in carbon dioxide observed in the extraction air after injection was started and by the consumption of methane (50%), calculated via measurements of methane and helium tracer in the injection well and extraction well. It is important to note that community changes caused by a biostimulation process were reversible as demonstrated for nitrogen-transforming bacteria as measured by SRTC using fluorescent antibody probes. In general, pulsing and multiple nutrient injection were found to give the greatest biostimulation. The continuous 4% methane injection was not as stimulatory as continuous 1% methane injection or pulsing of 4% methane.

The evidence for biodegradation is also convincing. Increased biodegradation was demonstrated by increases seen by three different labs (ORNL, the University of Tennessee, and PNL) measuring TCE and PCE mineralization potential and by measurements of nucleic acid probes. The nucleic acid probe analyses demonstrated that the methanotrophs being stimulated were those possessing soluble methane monooxygenase (sMMO), the form of MMO most active in TCE oxidation. Methanotroph isolates from the water that were positive for sMMO were tested for their ability to oxidize both TCE and naphthalene by the University of Tennessee. Those isolates from wells most affected by the injection process were shown to have rates of TCE oxidation over three times greater than the rates for *Methylosinus trichosporium* OB3b, the type of culture for methanotrophs and reputed best TCE oxidizer. Studies by the University of North Carolina using MICROTOX and MUTATOX assays demonstrated that both sediment and water samples were not significantly toxic before, during, or after the stimulation processes tested. Detectable toxicity differences were seen only temporarily in two wells during the period of greatest biostimulation. Water analyses by SRTC also indicated a strong inverse correlation between TCE concentration and chloride concentration. Thus, as TCE concentration declined in the groundwater, the chloride concentration increased. The only mechanism known that could result in this correlation is the biodegradation of TCE to carbon dioxide and chloride.

Bioremediation

Though a mass balance was difficult to determine, several measurements provide both direct and indirect evidence that very significant amounts of bioremediation occurred in situ. The evidence for bioremediation is linked by necessity to changes in TCE/PCE inventories in the soil gas, sediment, and groundwater and the evidence for biodegradation and biostimulation discussed above. TCE/PCE concentrations declined in all media examined; however, the amount degraded and original amount present were difficult to determine. The problem with inventories at the site was a lack of source control, i.e., more contaminated material (soil gas and water) was constantly moving from outside the treatment zone used for inventories to the inside. Water with greater levels of contamination could move into the saturated zone treatment area from below, because of water flow created by the injection, the sides, and from above. Soil gas with greater levels of contamination was constantly moving into the treatment area because of the much larger area influenced by the extraction well. Even given these limitations, concentrations of TCE and PCE declined in all well samples coincident with the onset of injection. Water concentrations of TCE/PCE decreased by as much as 95%, reaching concentrations below detectable limits, i.e., < 2 ppb in some wells, well below drinking water standards of 5 ppb. Those wells closest to the injection well showed the greatest decline, although as the test progressed even wells that showed no effect during the previous in situ air stripping demonstration showed significant decline. Soil gas TCE/PCE declined by more than 99%, with the piezometers closest to the injection well having consistently undetectable concentrations by the end of the demonstration. Sediment concentrations were significantly lower after only 3 months of 1% methane injection. Total sediment concentrations of TCE/PCE declined from 100 ppb to nondetectable concentrations in most areas. Densities of methanotrophs also were inversely correlated with the concentration of TCE in groundwater, i.e., as densities of methanotrophs increased, the concentration of TCE decreased. Soil gas, groundwater, and sediment were constantly monitored for vinyl chloride and dichloroethylene, toxic daughter products of anaerobic biodegradation. Neither of these compounds was detected except transiently at concentrations below drinking water concentrations (< 5 ppb). Thus, unlike anaerobic processes, the methanotrophic process did not generate toxic daughter products. This further suggests that the disappearance of VOC in situ was due primarily to aerobic processes. Studies by Idaho National Engineering Laboratory using sediment/groundwater chambers with material from the SRS demonstration site showed that high rates of biodegradation of TCE could be stimulated by the injection strategies used and that the amount of TCE biodegraded was directly proportional to the amount of chloride being produced. During the field demonstration, chloride, the end product of TCE/PCE biodegradation, was measured directly in the groundwater. Chloride concentration in the water was inversely correlated to TCE concentration in the same sample. This observation provides direct chemical evidence that bioremediation was occurring during the demonstration.

Cost Effectiveness

Analyses completed by Los Alamos National Laboratory (LANL) have shown that in situ air stripping is more cost effective than the baseline technology of soil vapor extraction and groundwater pump-and-treat. The in situ bioremediation process tested was 8% less expensive than the baseline technology, even if no TCE/PCE was biodegraded. LANL history matching models suggest that 41% more TCE/PCE is biodegraded/removed as compared to in situ air stripping alone. The in situ bioremediation process employed in this demonstration has only the cost of the natural gas, trace nutrients, and methane monitoring equipment as an additional cost. As little as 1570 lb of TCE/PCE needs to be biodegraded to offset the additional costs of the in situ air stripping system. In addition, the LANL analyses indicate that it would take over 10 years using in situ air stripping to achieve 95% removal of the contaminants, while the in situ bioremediation process would take < 4 years. This difference alone would result in a $1.6M cost savings over the conventional system for just this one site.

Ease of Use and Operation

The system was almost completely automated and extremely trouble free, once the initial shakedown period (2 weeks) was complete. It was so easy to use that one full-time technician, also responsible for monitoring analytical performance, could operate at least six of these systems simultaneously. Excluding down time because of weather, experiments, and scheduled power outages, the system was operational 95% of the time. The electrical repairs all occurred during the first week of operation and after a lightning strike disabled a microprocessor board. All repairs were completed within 72 hours.

This demonstration represents the first time ever that multiple nutrients (carbon, nitrogen, phosphorus) have all been injected as gases. The horizontal wells that form the basis for the SRS integrated demonstration provided significant advantages over conventional bioremediation nutrient delivery techniques. The increased surface area allowed better delivery of nutrients and easier recovery of gas, as well as minimizing formation clogging and plugging phenomena. There was never any indication of reduced flow or plugging during any of the six operational conditions employed. Indeed, the zone of effect was far greater than that ever reported for liquid nutrient injection systems.

Conclusions

This demonstration has shown that 1) bacteria capable of degrading TCE/PCE can be stimulated in situ using relatively simple nutrients, 2) biostimulation and biodegradation occurred in situ without producing toxic daughter products, 3) the process is easy to use and can be automated, 4) the cost for adding the methane injection capability is relatively low and easily recovered, 5) gaseous nutrient injection represents a significant new delivery technique for in situ bioremediation, and 6) combined with in situ air stripping, this technology represents a significant improvement in terms of cost and efficiency over conventional baseline technologies used for remediation of chlorinated solvents.

COLLABORATION/TECHNOLOGY TRANSFER

This work was performed as part of the VOCs in Nonarid Soils Integrated Demonstration. The work was conducted cooperatively by various DOE laboratories, industries, universities, the U.S. Department of Defense, the U.S. Environmental Protection Agency (EPA), and others. The host site was the SRS in South Carolina. The field work was performed at SRS as well as at other sites across the country. Primary regulatory surveillance was provided by the South Carolina Department of Health and Environmental Control and the EPA (Region IV).

The criteria for success, test planning and design, data analysis and evaluations, and final conclusions were a consensus of the Bioremediation Technical Support Group (Expert Panel). This group of experts from DOE, EPA, the U.S. Geological Survey, industry, and academia met regularly for the last 3 years and provided valuable perspectives for conducting this demonstration. This group is responsible for the great success of this demonstration, which was the largest and most technically comprehensive full-scale in situ bioremediation demonstration ever conducted.

Industrial partnerships have been formed and licenses for the technology are being granted. The industrial partners include Gas Research Institute, Chicago, Illinois; Radian Corporation, Austin, Texas; and ECOVA Corporation (WastTech), Redmond, Washington. Eight companies currently hold a license for this technology: Barr Engineering/Asanti Trust; Groundwater Technology Inc.; Pollution Equipment Company, Inc.; AWD Technologies; IT Corporation; Heritage Remediation and Engineering, Inc.; Burlington Environmental, Inc.; and Catlin Associates, Inc. Several other companies are pursuing licenses for this technology, and efforts to sell additional licenses are continuing.

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SECTION 2.0

TREATMENT (PHYSICAL/CHEMICAL)

- Contamination of soil and groundwater with organic contaminants, inorganic contaminants, and radionuclides is prevalent at U.S. Department of Energy sites. To restore the sites, the contaminants can either be treated in place or transferred to the surface for subsequent treatment.

- *In situ physical/chemical treatment* involves additions to or alterations of the subsurface to change the chemical and/or physical properties of the subsurface environment, thereby destroying, immobilizing, or removing the contaminants.

- The technology gaps for in situ treatment technologies include inadequate technical data, particularly at the field-scale; lack of performance verification; implementation constraints; limitations to applicability; and cost. These gaps are being addressed by the In Situ Remediation Integrated Program.

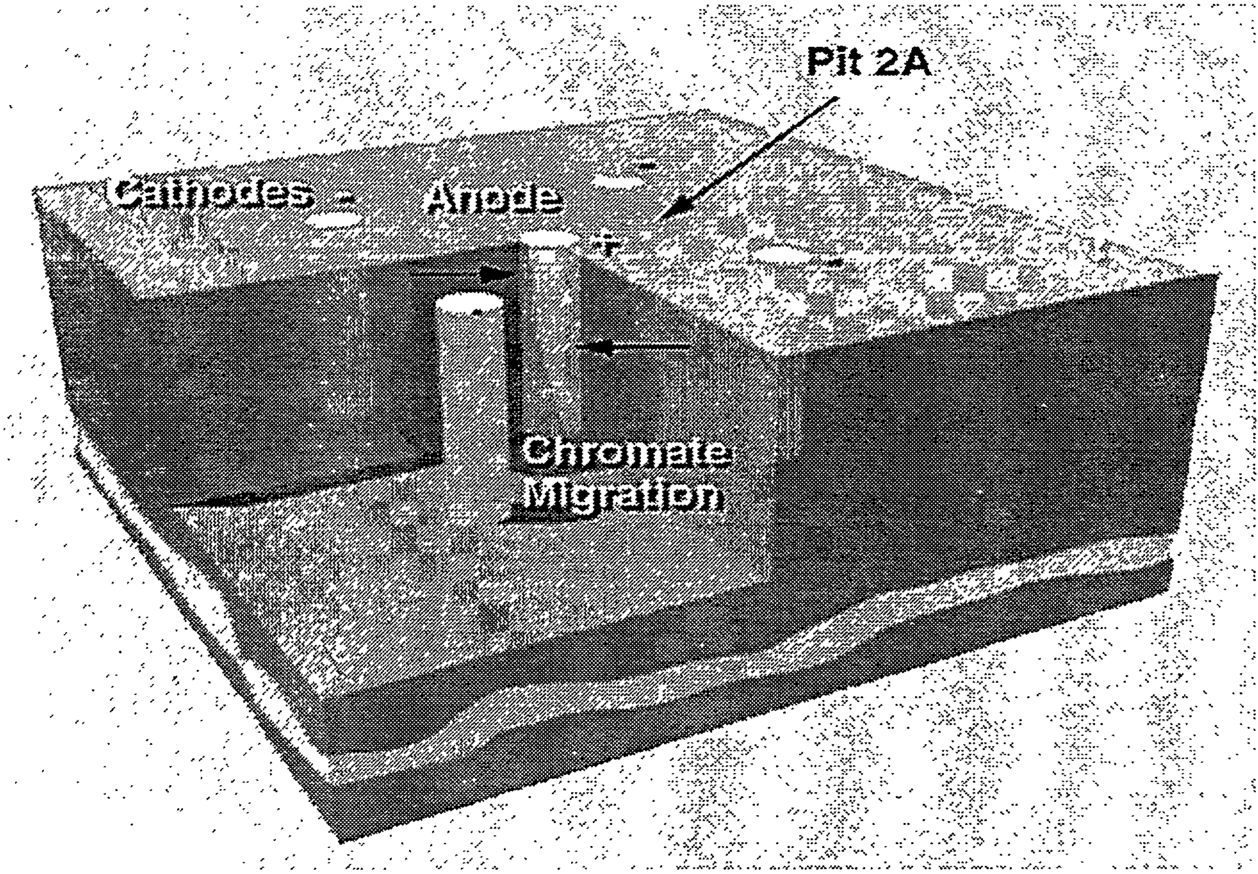
ELECTROKINETIC REMEDIATION OF HEAVY METAL CONTAMINATED UNSATURATED SOIL

TASK DESCRIPTION

The goal of this task is to develop an in situ electrokinetic process for removing chromate contamination from unsaturated soil. The technology was developed and tested at the bench- and pilot-scale in FY 1993 and field tested in clean soil in FY 1994 to characterize the process and demonstrate in situ water control in unsaturated soil. Demonstration of the process in chromate-contaminated soil at the Sandia Chemical Waste Landfill is scheduled for FY 1996 as part of the Plume Focus Area.

TECHNOLOGY NEEDS

A large portion of the U.S. Department of Energy's (DOE) contaminated soil is unsaturated, containing small amounts of water. This is typical of the western states. In regions where contaminated saturated soils are more common, there also exists a zone of contaminated unsaturated soil lying above the saturated zone. Currently, viable in situ methods for remediating heavy metal contamination from these unsaturated soils do not exist. Excavation and processing, or disposal at a



licensed landfill (the baseline technology), will not always be feasible and will always be expensive.

This research is directed at remediating chromate (CrO_4^{2-}) contamination in unsaturated soil in Sandia's Chemical Waste Landfill, where chromium contamination has been detected to a depth of 75 ft. This technology should be applicable for treating other DOE sites contaminated with mobile anions (e.g., MoO_4^{2-}, SeO_4^{2-}, $HAsO_4^{2-}$, $UO_2(CO_3)_3^{4-}$, TcO_4^-). Anions are highly mobile in soil because they typically do not adsorb strongly on the soil surface.

ACCOMPLISHMENTS

Experiments at Sandia National Laboratories demonstrated that electrokinetic processes can move large organic dye anions, as well as chromate anions, through unsaturated sands having moisture contents typical of subsurface soils found in arid regions (the minimum moisture content for observable migration to occur in the soils tested was 3.5 wt%). An electrode system has also been developed for extracting anionic contaminants from unsaturated soil without significantly changing the moisture content of the soil. Control of water introduction and removal of 95% of the chromate contamination have been demonstrated in bench-scale testing. This electrode system has been reviewed by the Sandia patent office and a patent application has been filed.

Prototype electrode systems were fabricated and used in the FY 1994 clean soil field test. A preliminary analysis of the test has been completed and means to improve process efficiency have been identified. A preliminary test plan and application for a Resource Conservation and Recovery Act (RCRA) Research Development and Demonstration (RD&D) permit have been prepared for the FY 1996 chromate removal demonstration.

COLLABORATION/TECHNOLOGY TRANSFER

All potential additions to the subsurface will be identified and discussed with the New Mexico Environmental Department to ensure compliance with all applicable regulations. A RCRA RD&D permit will be obtained. An industrial partner having prior field experience with electrokinetics, ElectroPetroleum, Inc., has assisted with the design and review of the field demonstration at Sandia. A possible cooperative research and development agreement with United Technologies Corp. (UT) is being considered. UT is interested in further developing the technology to better suit their needs and will test the technology at their site.

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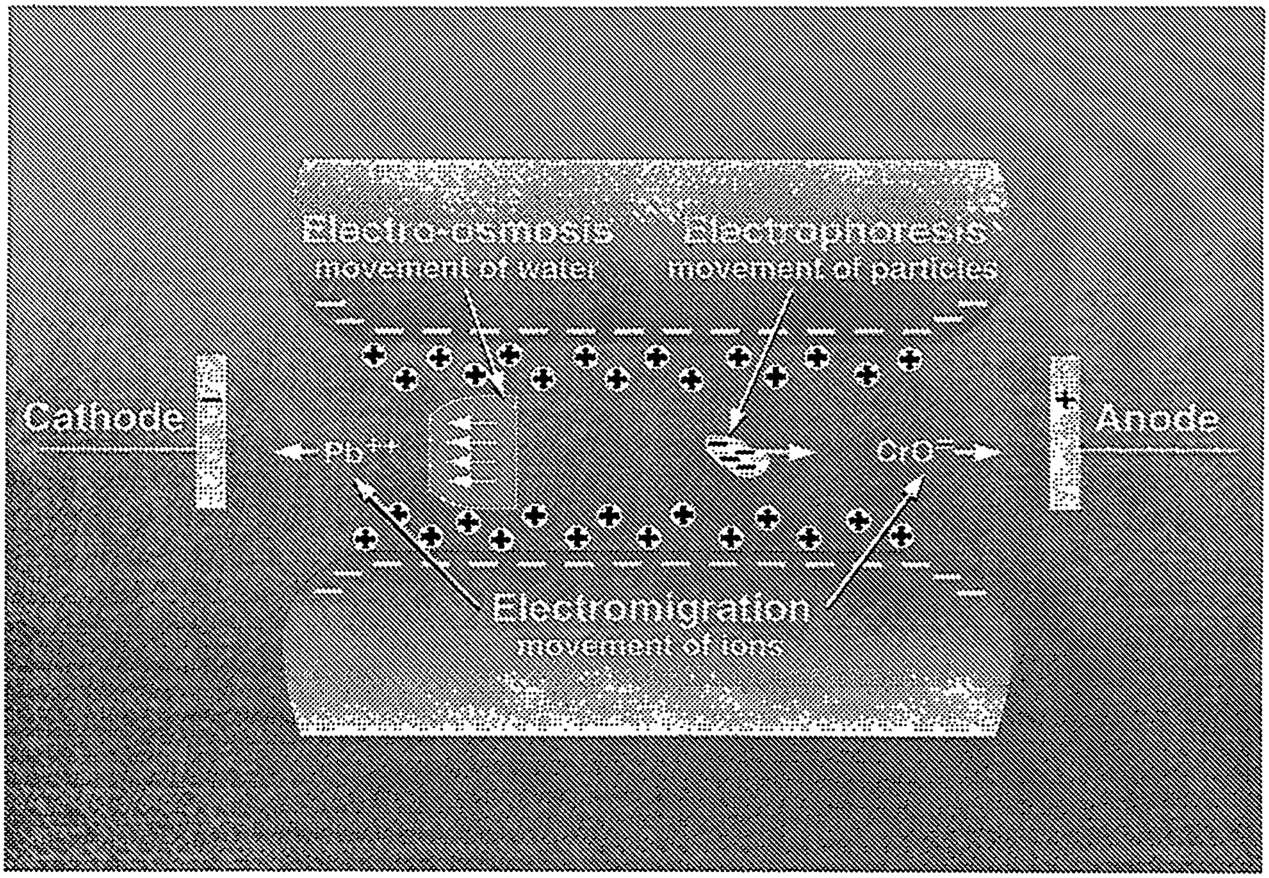
ELECTROKINETIC REMOVAL OF METALS FROM SOILS

TASK DESCRIPTION

The objective of this task is to develop a mathematical model that can be used to determine the optimum operating conditions for electrokinetic decontamination at specific waste sites. A theoretical and experimental investigation is being conducted to provide the information required to refine a numerical model of the electrokinetic remediation process by incorporating equilibrium chemical and electrochemical reactions. Under study are the process responses to many changes that can occur during remediation, including changing pH, together with the effects of various naturally occurring matter and co-disposed wastes, all of which can affect the speciation and solubility of the heavy metals and, hence, their mobility. Variations in soil permeability and water content will also be investigated, and tests will be conducted in a three-dimensional apparatus to verify the model with respect to its applicability to soils contaminated with a mix of metals and/or organic wastes.



TECHNOLOGY NEEDS

Electrokinetic remediation is not completely understood because of the numerous parameters affecting the process and because of the complex interactions that occur when a direct current is applied between buried electrodes in complex waste-geochemical mixtures. Although laboratory experiments have demonstrated that certain pollutants dissolved in an aqueous phase can be removed from contaminated soils by electroosmosis and electromigration, the reproduction of site conditions in the laboratory has proven difficult and can account for anomalous results in the field.

Some field trials, together with more detailed laboratory investigations, have revealed several pitfalls that can reduce the practical effectiveness of the electrokinetic remediation process. These range from the presence of artifacts in the soil to immobilization of the metals by undesirable chemical reactions with naturally occurring and co-disposed chemicals, and even pH and reduction-oxidation changes induced by the process electrode reactions. The physical site characteristics, including permeability and degree of water saturation, can also alter the process effectiveness.

A mathematical model of all these effects operating simultaneously will necessarily be complicated, but will be needed as a guide, because it can be expected that the effects of parameters measured in isolation will not be the same as when changes occur together.

ACCOMPLISHMENTS

A number of parameters important to the success of electroremediation have been analyzed. Experiments in one-dimensional cells have demonstrated that electromigration may be the principal removal mechanism for metal wastes and that electroosmosis may make a negligible contribution. Moreover, in the removal process, the metals may accumulate in a narrow band in the soil where there is a jump in pH instead of being purged, a phenomena akin to isoelectric focusing.

A model that accounts for transport and chemical reactions, including complex formation, adsorption, and precipitation, gives results in excellent agreement with experimental results for the removal of zinc from soil containing excess sodium ions. The model shows that the electric field is very large at the location of the pH jump and very small elsewhere. It also shows that rinsing the cathode to wash away the sodium ions, together with the hydroxyl ions generated by electrolysis, will prevent a high pH front from entering the soil and result in successful metal removal. This behavior was confirmed experimentally. It has also been found that equilibrium models can be used to determine the speciation of metals in complex geochemical mixtures and, if presented as Pourbaix diagrams, are particularly useful for rapidly identifying conditions that might enhance mobility.

It has been concluded that the excellent removal efficiencies obtained in the laboratory can be achieved in the field, provided mobilization problems are adequately addressed. In this respect, it is expected that the model developed will provide an important guide to laboratory- and pilot-scale treatability studies.

COLLABORATION/TECHNOLOGY TRANSFER

Close cooperation between this investigator and others at the U.S. Department of Energy's sites who are attempting practical application of electrokinetic remediation is being maintained. General understanding of the process fundamentals will be key to applying the technology in an efficient and cost-effective manner.

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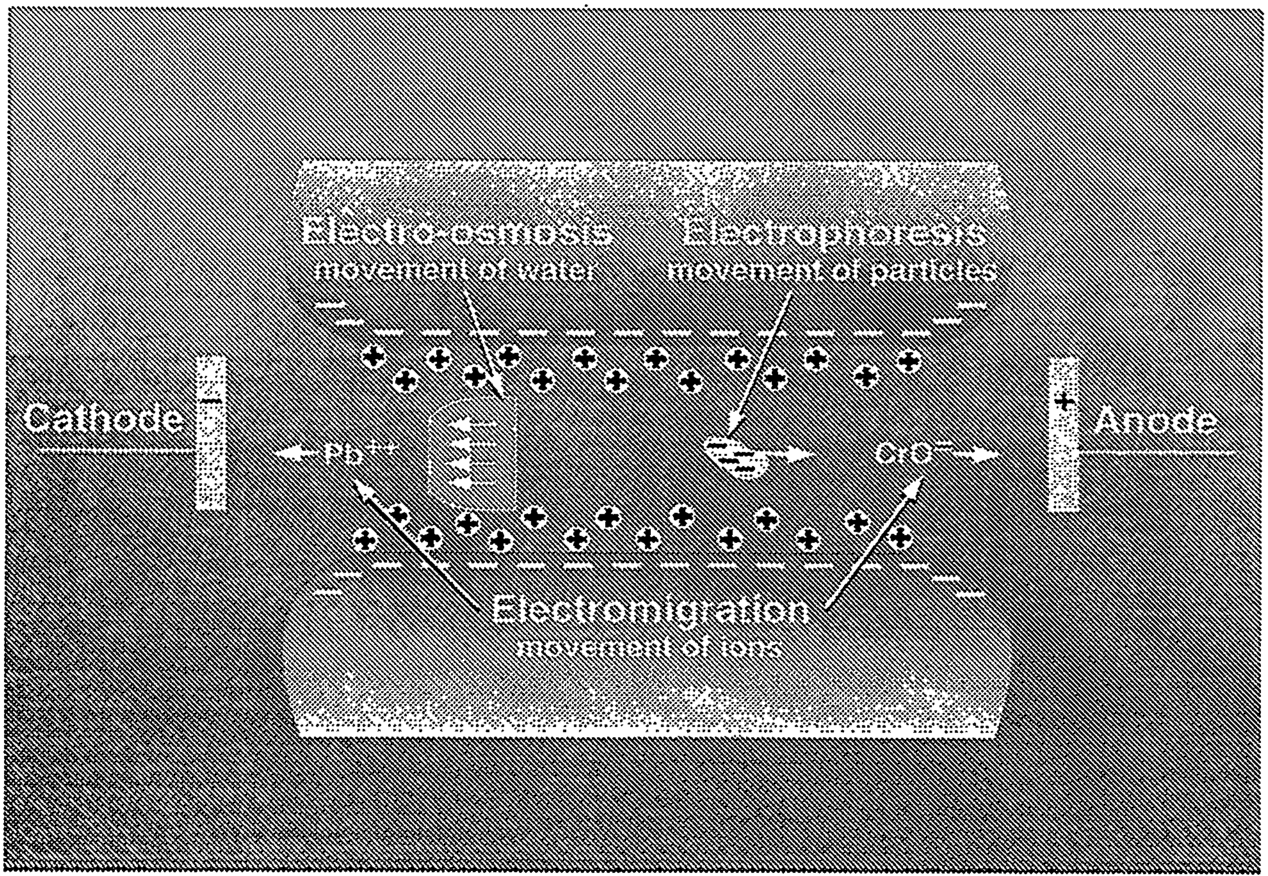
ELECTROKINETICS IN URANIUM CONTAMINATED SOILS

TASK DESCRIPTION

This task will demonstrate pilot-scale electrokinetic removal of uranium from contaminated soil. Site selection and treatability studies will precede the pilot-scale test, with a full-scale field test at a site to be determined following evaluation of the pilot-scale test results. Removal efficiency, control of added fluids, contaminant recovery and disposal, power consumption, mass balance, and control of soil pH all must be evaluated to ensure this process is viable. Technology advances made by Russian scientists in this area of environmental remediation will be used as much as possible. The selected site should allow easy permitting for testing, be representative of the uranium problems throughout the U.S. Department of Energy (DOE), and be accessible to industry, regulatory agencies, and academia.

TECHNOLOGY NEEDS

Remediation of uranium-contaminated soil is a major cleanup task facing DOE, and in situ remediation methods are needed



that can remove enough uranium to reduce contaminant concentrations to acceptable levels and return the soil to productive use. Electrokinetic methods are being evaluated for this purpose. The applicability of electrokinetic methods for uranium removal from saturated and partially saturated soils will be documented as part of the evaluation.

ACCOMPLISHMENTS

Treatability studies were performed for electrokinetic removal of uranium from the K-25 site in Oak Ridge, Tennessee. The studies were conducted by Isotron Corporation with participation from Russian scientists. These studies showed the feasibility for in situ removal of uranium by the electrokinetic process. Observed characteristics of the process include

- formation of uranyl anionic complexes with carbonate/citrate ligands (by electrode delivery); these complexes can be effectively transported in situ through soils by the electrokinetic process

- effective in situ capture and concentration of the uranyl anionic complexes by a cylinder impregnated with ion exchange media (powder form) that surrounds the anode

- post-treatment soil analyses showing insignificant amounts of soil degradation

- cost data for the process of <$200/cubic yard.

Characterization studies conducted at the K-25 site by Oak Ridge National Laboratory have shown the uranium to be soluble, at an average concentration in the range of 1000-2000 pCi/g, and existing at a depth of approximately 2 ft. A contract has been placed with Isotron Corporation for a pilot-scale demonstration of the electrokinetic process at the contractor's facility. Preliminary activities, such as electrode design, optimum electrode configuration analysis, and undisturbed sampling of K-25 soils, have been initiated.

COLLABORATION/TECHNOLOGY TRANSFER

HAZWRAP personnel have visited sites in Russia where electrokinetics have been used to remediate uranium contamination in soil. This information will be useful in developing the technical specifications for a demonstration at a DOE site.

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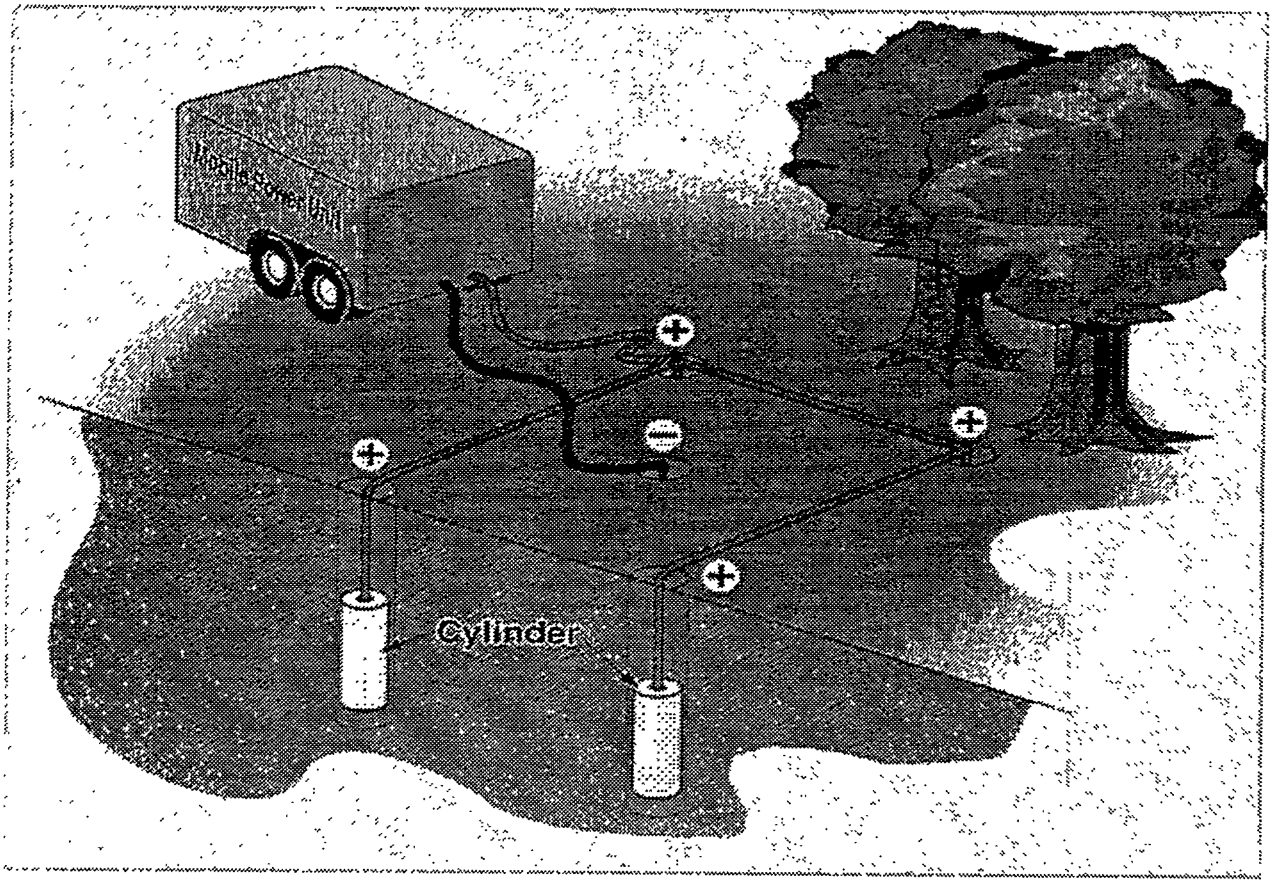
FIELD DEMO OF ELECTROKINETIC MIGRATION TECHNOLOGY AT OLD TNX BASIN

TASK DESCRIPTION

The primary goal of this task is to demonstrate the ability of Isotron Corporation's proprietary ELECTROSORB™ electrokinetic migration technology to remove mercury contamination from an unsaturated soil in the Old TNX Seepage Basin at the Savannah River Site. The ELECTROSORB technology uses cylindrical electrode assemblies, with the electrode coated with Isotron Corporation's ISOLOCK™ polymer material. The polymer will be impregnated with pH-regulating chemicals to prevent pH excursions during the demonstration. The electrodes are placed in boreholes in the soil and a direct current is applied. Under the influence of the current, ions migrate through the pore water to an electrode, where they are trapped in the polymer matrix. If desired, the polymer can also contain ion exchange resins or other sorbants that can trap and hold ions before they reach the electrode.



TECHNOLOGY NEEDS

The Old TNX Basin at the Savannah River Site, one of the DOE sites that will require remediation, was used in the past as a seepage basin and is now contaminated with various heavy metals, including mercuric nitrate. Elevated levels of mercury have been detected in groundwater samples collected from wells near the basin. The mercury is presumed to have leached from the basin soil. Removing the mercury source from the basin soil is expected to eliminate the mercury in the groundwater. Electrokinetic migration technology is being studied as an in situ means of removing the mercury contamination.

ACCOMPLISHMENTS

Laboratory studies were conducted in one-dimensional cells designed to produce data that will move the technology to the field. Soil from the Old TNX Seepage Basin was used in the studies. Operating parameters, such as current density, time, pH regulators, polymer construction, and electrode construction, were determined and have been translated into the electrode array design and operating plans for the demonstration. Another parameter studied was the effectiveness of complexing agents, introduced from the polymer at an electrode so they can migrate through the soil and interact with the metal ions, in the mobilization and removal of mercury.

The electrode array was operated initially for 3 months at the Old TNX Basin. Chloride ion was distributed to the soil from the cathodes to achieve complexation of the mercury to the tetrachloromercury anion, which was expected to be captured at the anode. Voltages, current, temperatures, and pH were recorded regularly. Buffers were periodically replenished in the electrode polymer wells. At the end of the run, soil samples were taken at designated positions in the basin and analyzed for metals content. The data collected indicated that very little of the current had actually been transferred to the soil; most of the current was lost to the anode. Furthermore, chemical analyses of the polymers, buffers, and soil showed that the electrode polymers and buffer solutions did not trap any mercury. Comparison of the analyses of soil samples, taken at the same distances from each electrode before and after the demonstration, indicated migration of mercury into the region of the array from the contaminated soil outside of the array.

The test was extended to allow data to be collected with more powerful electrodes in a slightly different array. Instead of cathodes at each corner of the array and a single electrode in the center, two cathodes were placed at two corners opposite two anodes. When the new array was dismantled, electrodes, polymers, and buffers were removed for analysis. Soil sampling is underway.

During the demonstration, several smaller tests were conducted to test improved concepts using complexants that have shown promise for mobilizing the mercury in the soil. The first of these tests was performed at the Isotron Corporation facility in New Orleans. A prepared bed, similar to the electrode array used in the first part of the demonstration, was used to measure the transport of a radioactively labeled complexing agent. The complexant was traced in the soil and at the electrodes to determine its fate. The complexant was not as effective as had been expected from data collected in lab-scale one-dimensional tests. As expected, the complexing agent was dispersed through the soil from the cathode to the anode, but a large quantity of the agent was lost to either chemical or microbial degradation during the transport. Enhancement to mercury mobilization was not achieved. Therefore, the complexing agent was not used in the demonstration.

A second concept involved substituting iodide for the chloride used in the first run. This was tested in the laboratory at the Savannah River Technology Center (SRTC) in one-dimensional tests using TNX soil. Results from this study did not indicate improved mobilization of the mercury in the soil and, therefore, the extended tests at the TNX Basin were continued using chloride ion.

More data is needed on how to scale from the laboratory tests to the field. This information may be best derived by modeling studies or from testing in large soil beds.

A particularly important issue that had to be addressed was the need for a reliable procedure to analyze the soil for mercury, in particular, and other ions, in general. The Analytical Development Section at SRTC has developed two methods for soil analysis and has purchased analytical instruments to quantify total mercury in the soil and electrode components. Although it is known that the mercury was introduced into the soil as the mercuric ion, the effects of time, chemistry, and the electric field on mercury speciation in the soil may be very hard to determine.

COLLABORATION/TECHNOLOGY TRANSFER

Isotron Corporation has applied for patents on the design of the electrode assemblies and for several aspects related to the operation of the electrode array. Modeling of the ELECTROSORB process has been initiated by Dr. Ralph White of the University of South Carolina under a South Carolina University Research and Education Foundation contract, funded from Interim Waste Technology funds at SRTC.

This effort is directly applicable to remediation of contaminated soils both within and outside the U.S. Department of Energy's complex.

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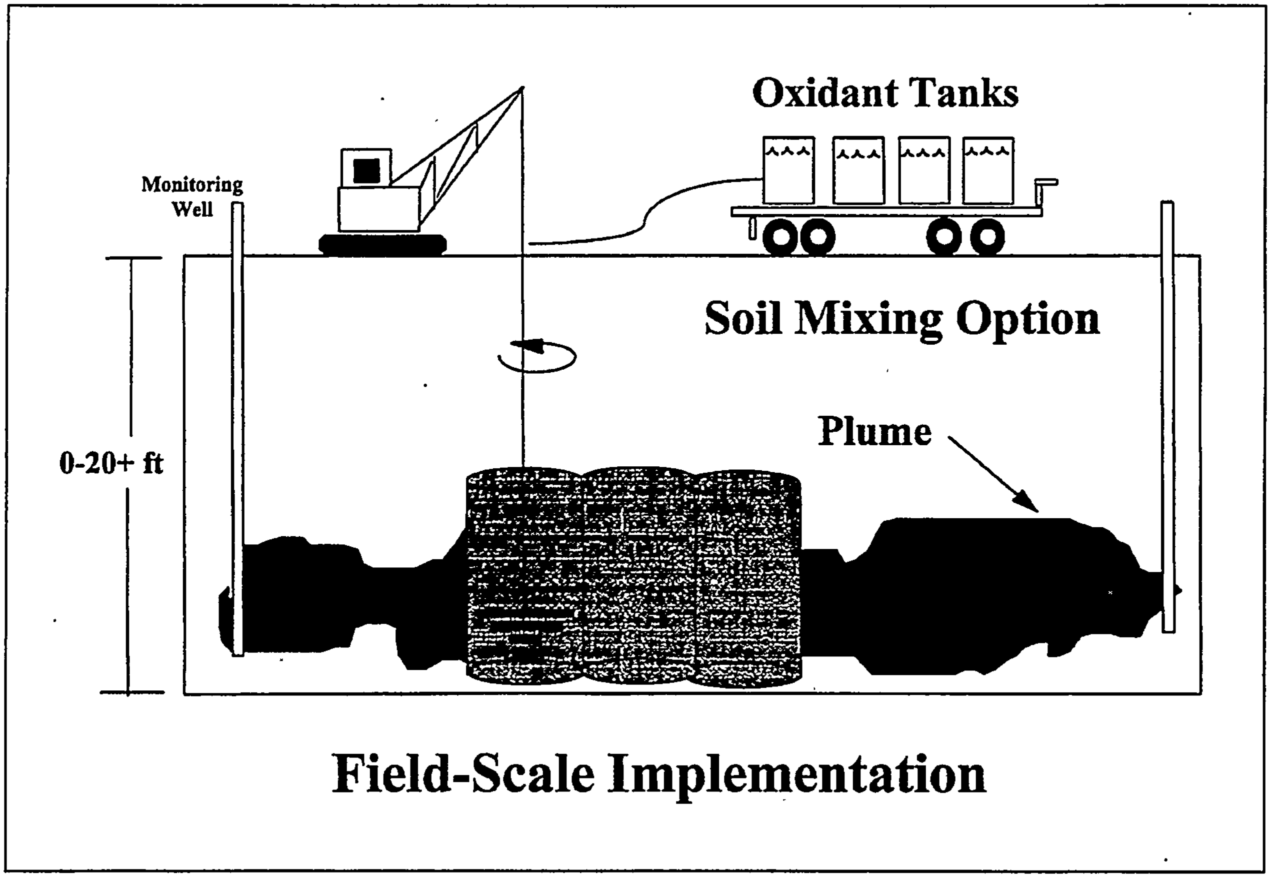
IN SITU CHEMICAL OXIDATION OF SOILS

TASK DESCRIPTION

The goal of this task is to determine the conditions under which chemical oxidation can be effectively used as an in situ treatment process for soil contaminated with a variety of hydrocarbons and/or metals. The initial phase of this work included bench-scale experiments using artificially contaminated clean soil. Current work includes intermediate-scale batch and continuous mode experiments using both clean and field-contaminated soils. A field demonstration of this technology is also being planned.

With in situ physical/chemical treatment processes, the treatment goal is to manipulate the chemistry of the subsurface environment so the contaminants of interest are destroyed and/or rendered non-toxic. Chemical properties that can be altered include pH, ionic strength, oxidation/reduction potential, and chemical equilibria. In situ contaminant destruction processes, such as chemical oxidation, alter or destroy contaminants in place and are typically applied to compounds that can be either converted to innocuous species such as CO_2 and water, or



degraded to species that are non-toxic or amenable to other in situ processes (i.e., bioremediation).

In situ chemical oxidation uses the hydroxyl radicals (OH•) formed by hydrogen peroxide (H_2O_2) and potassium permanganate ($KMnO_4$) to oxidatively degrade the contaminants of interest. Hydroxyl radicals are known to be very powerful, non-specific oxidizers that react very rapidly with many compounds, including volatile and semi-volatile contaminants of interest to the U.S. Department of Energy (DOE). With this technology, organic compounds are oxidized with low-strength chemical oxidants to form simple inorganic compounds (i.e., HCl), water, carbon dioxide (with H_2O_2), or manganese oxide (with $KMnO_4$).

TECHNOLOGY NEEDS

Soil and sediment contamination has been identified and documented throughout the complex of DOE facilities. The DOE's Subsurface Science Program (DOE, 1992) reviewed, identified, and evaluated the types of chemicals disposed of at DOE facilities. Fuel hydrocarbons were the most commonly reported class of contaminants at the facilities included in the report. The fuel hydrocarbons most frequently reported include aromatic and polyaromatic compounds such as phenanthrene, pyrene, and naphthalene. The primary sources of these semi-volatile organic compounds (SVOCs) are coal and coal waste from coal-fired electric power plants, used at many of these facilities in the past, and gasoline spills and leaks. Mixtures of chlorinated hydrocarbons and metals were reported as the primary contaminants at 16 DOE sites and 9 DOE facilities responding to Subsurface Science Program inquiries. The most commonly reported chlorinated hydrocarbons (occurring at 50% or more of the facilities) were trichloroethylene (TCE), tetrachloroethylene (PCE), and 1,1,1,-trichloroethane (TCA) with concentrations in the range of 0.2 to 12,000,000 μg/kg. These three volatile organic compounds (VOCs) are all known or suspected carcinogens, which have been found to be amenable to oxidative processes that do not produce any end products (Gates and Siegrist, 1993).

In situ chemical oxidation may be an option for the rapid and cost effective treatment of contaminated soils and sediments. The treatment offers several advantages over other in situ and ex situ remediation technologies. In addition to the benefits associated with most in situ treatment processes (less worker exposure to hazardous compounds, reduced cost, and applicability to inaccessible sites), in situ chemical oxidation uses inexpensive, readily available reagents, is easily controlled, and is applicable to a wide variety of volatile and non-volatile contaminants. Also, in situ chemical oxidation may enhance in situ biological processes.

ACCOMPLISHMENTS

A statistically designed screening study to evaluate the effect of several factors, including oxidant type, oxidant concentration, soil type, reaction time, dosing regime, and surfactant addition, on in situ chemical oxidation process efficiency was completed in FY 1994. Both H_2O_2 and $KMnO_4$ were evaluated as potential in situ chemical oxidants. These studies were designed to evaluate the applicability of the proposed technology to several soil types (low permeability clayey and high permeability sandy soils) that are representative of the soils found at contaminated DOE sites. The model contaminants for the screening studies included TCE, PCE, TCA, naphthalene, phenanthrene, and pyrene.

The screening studies completed during FY 1994 revealed that oxidant type, oxidant concentration, and soil type are the primary factors determining in situ chemical oxidation treatment efficiency. Reaction time was found to be significant to a lesser extent. Oxidant dosing regime (single vs. multiple doses) and surfactant addition were not found to have a significant effect on treatment efficiency. Iron supplementation and pH adjustment were evaluated as means of improving the H_2O_2 treatment efficiency and were found to improve treatment somewhat. However, regardless of soil type, the greatest removal of both groups of model contaminants was always achieved with the $KMnO_4$.

With 5% $KMnO_4$ solutions, greater than 95% removal of TCE, PCE, naphthalene, pyrene, and phenanthrene was observed in both the clay and sandy soils. The greatest removals of TCE and PCE, observed with 8.5% H_2O_2 in the clay soils, were 86% and 68% respectively. Lower TCE and PCE removals (61% and 32%) were observed in the sandy soil treated with H_2O_2. In the clay soil H_2O_2 was able to remove over 95% of the three SVOCs, while in the sandy soil considerably lower SVOC removals (avg = 24%) were observed.

SCHEDULE OF DEVELOPMENT

Bench-scale experiments have been completed and intermediate-scale experiments should be completed during FY 1995. In two previous demonstrations (Portsmouth 1992, 1994), chemical oxidants have been injected into the subsurface. In 1993, H_2O_2 was injected through the hollow shaft of a deep soil mixing apparatus into a VOC-contaminated site. In 1994, H_2O_2 and $KMnO_4$ were injected into uncontaminated test cells using a subsurface injection and fracturing system. Planning is in progress for a FY 1996 demonstration of chemical oxidation with H_2O_2 and/or $KMnO_4$ at a contaminated site. A demonstration site should be selected by the end of the second quarter of FY 1995.

COLLABORATION/TECHNOLOGY TRANSFER

Research in support of this activity is being conducted at the University of Tennessee, Knoxville (UTK). Researchers at UTK, led by Dr. Kevin Robinson, are evaluating the effect of in situ chemical oxidation on the mobility of metals in soil.

During FY 1995, a commercialization plan for this technology will be developed. Efforts have been initiated to identify suitable industrial partners for commercialization.

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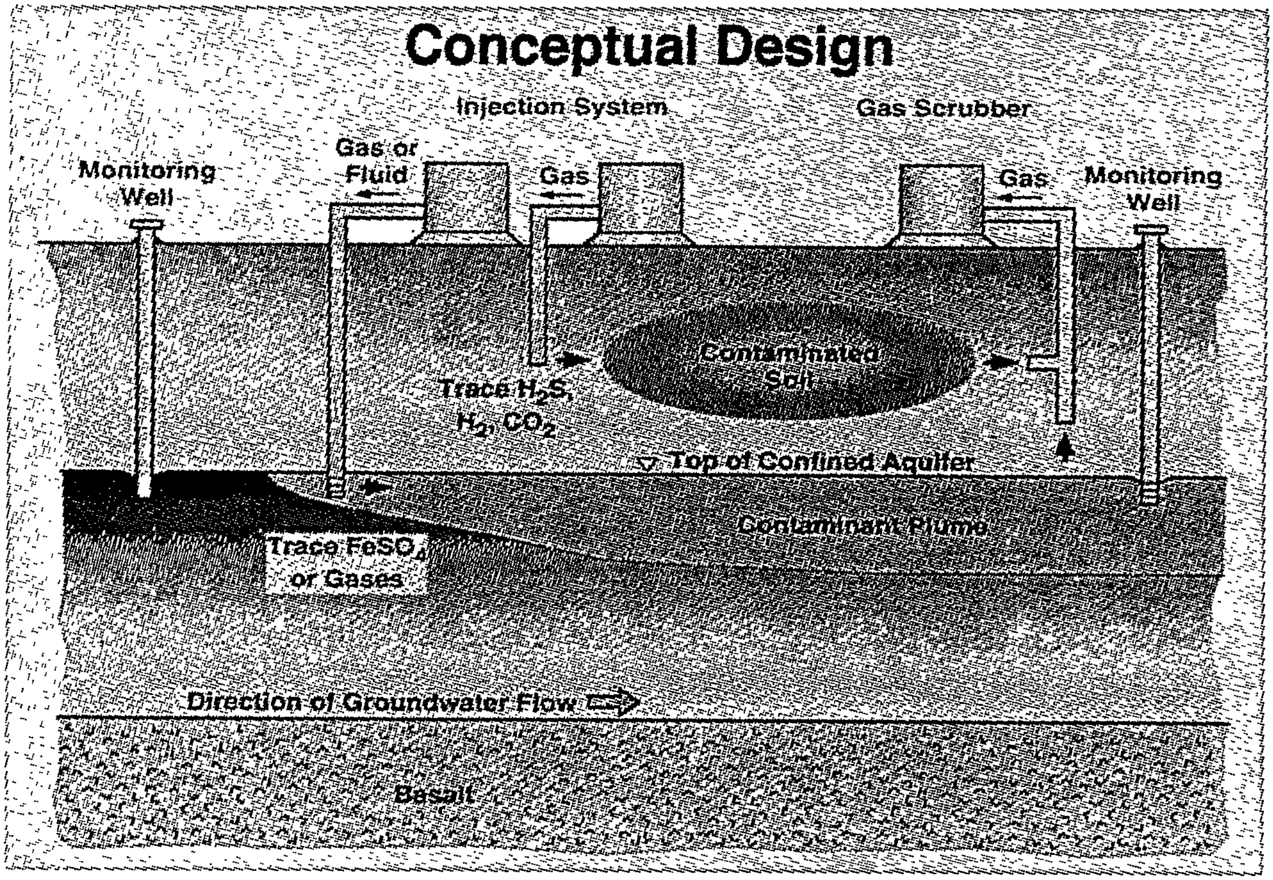
IN SITU CHEMICAL TREATMENT: EVALUATION OF THE IN SITU CHEMICAL TREATMENT APPROACH FOR REMEDIATION OF SOILS AND GROUNDWATER

TASK DESCRIPTION

This task is evaluating the feasibility of treating unsaturated soils by injecting reactive gases into the soil. It is proposed that dilute mixtures of hydrogen sulfide in air or nitrogen can be used to treat soils contaminated with heavy metals, such as chromate, uranium, lead, mercury, or cadmium.

Although the chemical principles of in situ chemical treatment are well established, limited data are available to assess the treatment's practical potential. In particular, the interaction of potential treatment agents with soil or groundwater has not been sufficiently evaluated. Thus, initial experiments were performed to better establish the viability of the approach. This testing, directed towards the treatment of solutions containing hexavalent chromium and soils spiked with hexavalent chromium or uranium, indicated that significant immobilization is possible. Tests recently conducted with



actual chromate-contaminated soil from a U.S. Department of Energy (DOE) site have further confirmed that gas treatment of soil is viable. Further testing is currently being conducted with actual contaminated soil and groundwater samples from DOE facilities to quantify the amount and concentrations of treatment agents required and to evaluate the potential for treatment and immobilization of a variety of metals and radionuclides.

A field demonstration will be conducted at a waste site containing contaminated soils as part of the development of this technology. Work associated with this demonstration will serve to optimize treatment procedures, determine treatment costs, and develop approaches for ensuring the control of the reactive gases and homogeneous treatment of significant masses of contaminated soil.

TECHNOLOGY NEEDS

Conventional approaches to environmental remediation have relied primarily on physical isolation or removal technologies. It has been observed, for example, that in most instances the pump-and-treat approach has not succeeded in restoring contaminated aquifers to regulatory standards. This may be attributed to desorption of contaminant constituents from the soil particles in aquifers and to channeling effects associated with variations in hydraulic conductivity.

Introduction of chemical treatment agents into contaminated aquifers should serve to strongly bind the residual contaminants to aquifer sediments and, via diffusion, also treat regions of the aquifer that are bypassed during active pumping of groundwater. This approach should be especially effective for metals and radionuclides, whose solubilities or sorption characteristics are strongly dependent on concentrations of associated ligands or the redox and pH characteristics of the environment.

ACCOMPLISHMENTS

Bench-scale tests were completed in FY 1993 using soils from three DOE sites that were artificially contaminated with hexavalent chromium, uranium, and nitrate. Test results indicated greater than 90% immobilization of chromate and approximately 50% immobilization of uranium subsequent to reaction with gas mixtures containing as little as 100-ppm hydrogen sulfide in nitrogen. Gas treatment studies conducted in FY 1994 involved treatment of chromate-contaminated soil samples obtained from a waste site located at Sandia National Laboratories (SNL). These tests confirmed that the gas treatment method greatly immobilizes chromium associated with the soils. Based on these results, system design and scale-up activities have been initiated in support of a potential field demonstration at the waste site.

COLLABORATION/TECHNOLOGY TRANSFER

Potential DOE sites for demonstration, testing, and evaluation of this technology include Hanford, Fernald, and SNL. In addition, a number of chromate-contaminated waste sites exist in the private sector, and uranium-contaminated sites associated with mining and ore milling activities have been identified.

An effort is currently underway involving staff associated with the Westinghouse Hanford Company (WHC) and SNL to undertake a field demonstration of gas treatment of chromate-contaminated soil at SNL. Laboratory testing activities have been conducted which confirm that significant immobilization of chromium in the waste soil site at SNL can be achieved by gas treatment. A permit is currently being prepared for a potential field demonstration at the site in FY 1996.

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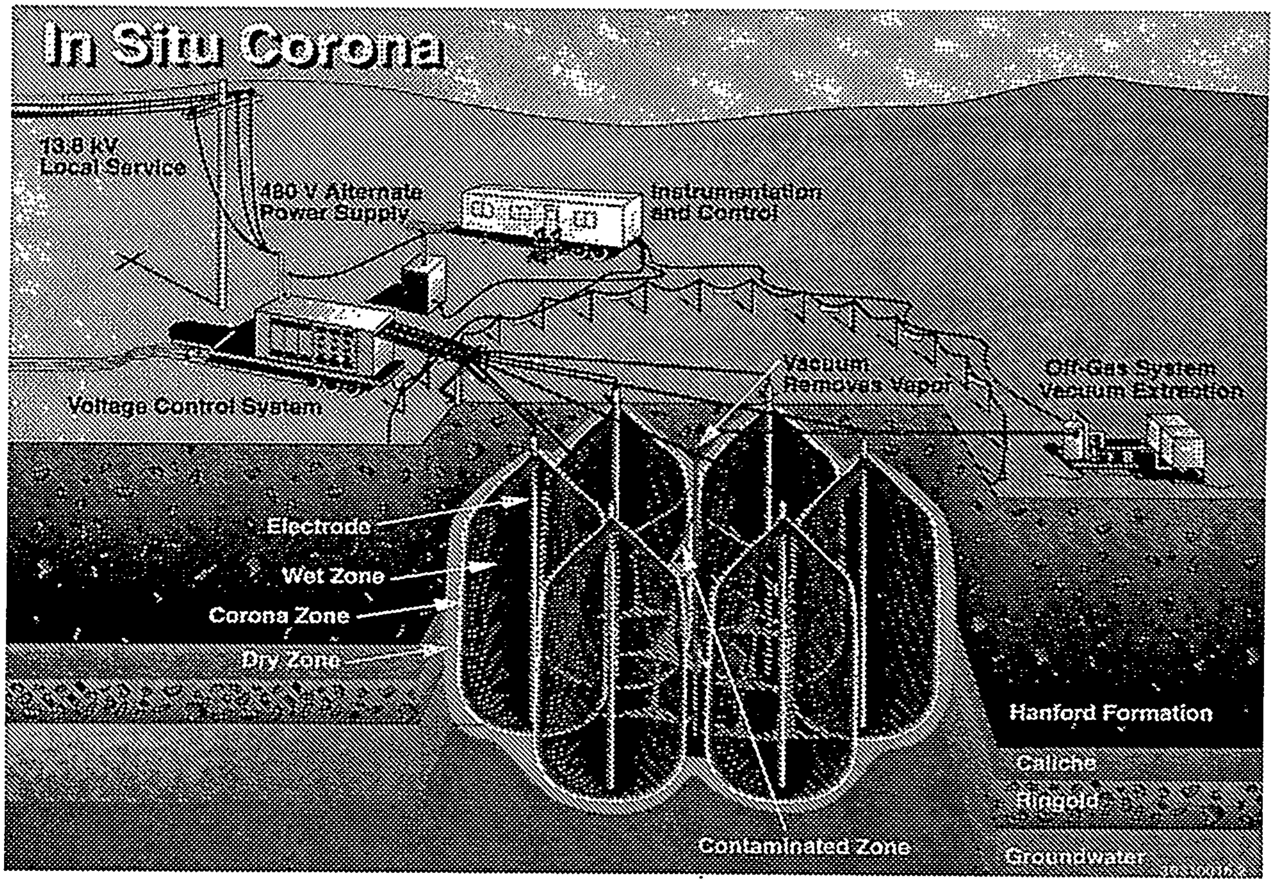
IN SITU CORONA FOR IN SITU TREATMENT OF NONVOLATILE ORGANIC CONTAMINANTS

TASK DESCRIPTION

The objective of this task is to develop and demonstrate a new technology that uses electric fields to oxidize organic compounds in situ. This work is developing a practical technique for decomposing nonvolatile and bound organic contaminants using gas-phase oxidants produced in situ. These gas-phase oxidants are created by electrical corona made to occur on soil particles by alternating current (AC) electrical power delivered through an array of electrodes installed in the soil. The expected result is clean soil, without resorting to excavation, high temperatures, or injected chemicals. Corona soil treatment is expected to treat difficult-to-treat refractory compounds, such as polychlorinated biphenyls (PCBs), and to be very effective in low permeability soils.

The task consists of research and development over a 3-year period to sufficiently understand the physics and chemistry of in situ corona in terms of its potential for field applications, and to



provide baseline laboratory data on treatment efficiency, reaction byproducts, energy requirements, and site applicability.

TECHNOLOGY NEEDS

The successful field application of some in situ technologies can be made very difficult by complex physical conditions at the treatment site or the presence of contaminants that are always difficult to remediate. Problems may include sites with complex stratigraphies that include low-permeability soils contaminated with nonvolatile or bound contaminants, or contaminants such as polyaromatic hydrocarbons and polychlorinated biphenyls (PCBs). One in situ technology being developed to accommodate these problems is the in situ corona technology.

ACCOMPLISHMENTS

Based on the results of tests performed to date, it appears that in situ corona is feasible, at least at the bench scale, and is capable of removing a nonvolatile contaminant (naphthalene) to levels well below regulatory limits. The technology also appears to be fairly robust in that 99% of methylene-blue dyed sand was completely blanched to a snow-white appearance, even outside the electrode area, in another bench-scale experiment. This same methylene-blue sand was heated for 150 hr at various temperatures, including 100°C, with very little change in color, further suggesting destruction by corona rather than by heating. Exposure of naphthalene and benzene to a simulated corona sheath in a high-energy corona reactor, developed for treating organic contaminants in soil offgases, demonstrated their rapid destruction and the simultaneous formation of carbon dioxide as detected using an on-line Fourier transform infrared gas analyzer.

Laboratory tests have shown that corona can dechlorinate PCBs, a high-priority contaminant difficult to treat by other methods.

Based on electric field measurement tests, a set of equations was developed to permit an estimation of voltage and power requirements associated with treating large volumes of soil. To treat a cylindrical soil volume 10-m wide by 10-m deep would require a power system rated at 1.2 MW and 5 kV. Calculations, based on present data, predict that soil could be treated with in situ corona at the relative low overall cost of \$100-\$120/yd^3. Ex situ treatment has been estimated at \$200-\$1000+/yd^3.

SCHEDULE OF DEVELOPMENT

FY 1995 efforts will complete work on PCBs, including product identification. Bench-scale testing will refine our predictions regarding scale-up and establish procedures for a reliable field operation. Parallel efforts will continue toward selecting a site for field testing.

COLLABORATION/TECHNOLOGY TRANSFER

Potential sites for demonstration, testing, and evaluation of this technology include the Oak Ridge National Laboratory, Kansas City Plant, and the Twin City Ammunition Plant (nongovernment). Collaboration has been initiated with these sites. Opportunities for a joint demonstration of in situ corona with six-phase soil heating are also being pursued.

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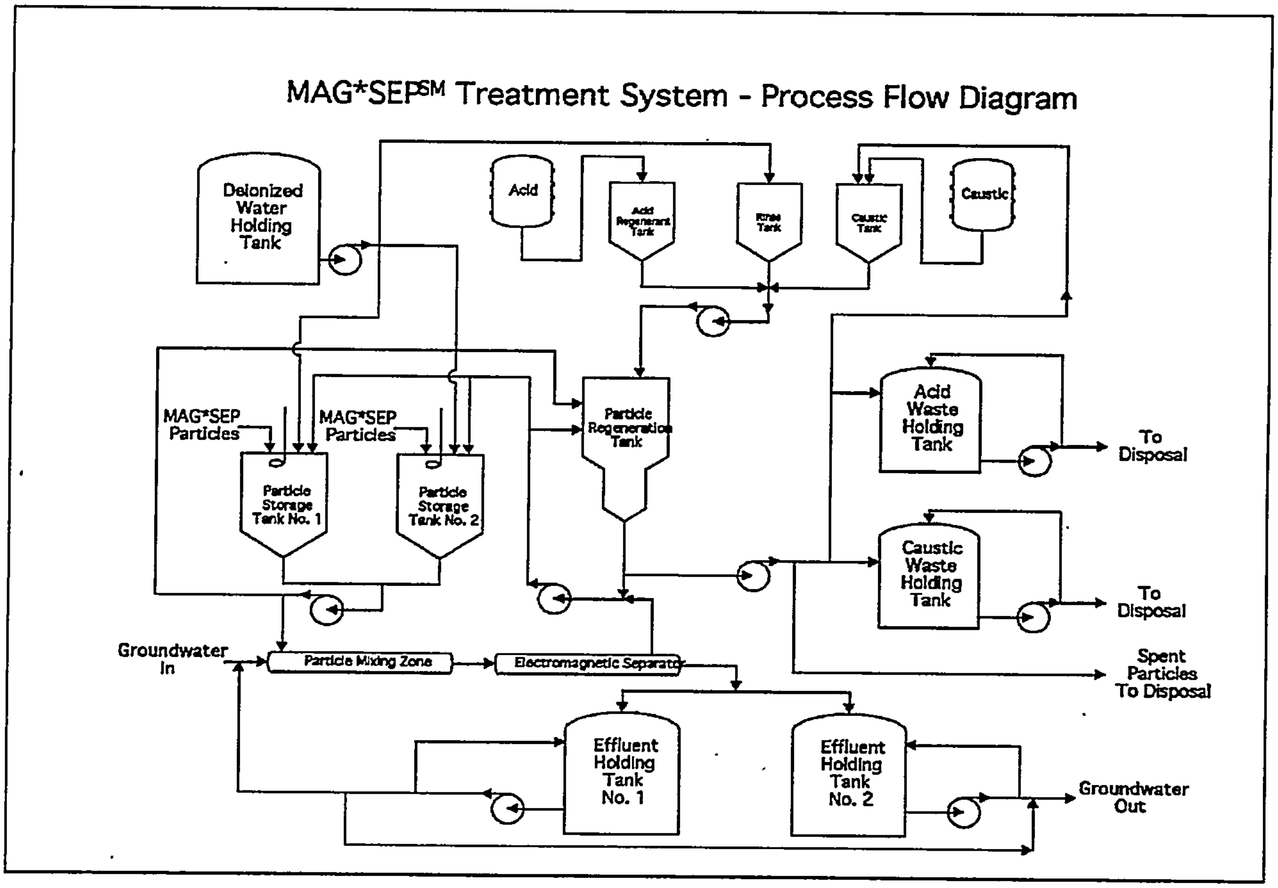
IN SITU GROUNDWATER TREATMENT USING MAGNETIC SEPARATION

TASK DESCRIPTION

This task will demonstrate and evaluate the MAG*SEP^{SM} technology of BRADTEC U.S., Inc. (BRADTEC) for in situ groundwater treatment. The MAG*SEP technology uses specially designed particles to selectively adsorb contaminants from effluent water or groundwater. The technology can recover low levels of radioactive and/or inorganic hazardous contamination (in the ppb range).

The selective adsorption particles are composites that can range in size from 2 to 500 microns. The particles have a magnetic core and either a functionalized resin coating or selective seed materials embedded in the coating. To treat contaminated water, the particles are injected into the water where they adsorb the contamination. Because the particles are small and adsorption is a surface phenomenon only, the adsorption kinetics are very rapid (typically less than 2 minutes). The particles are then recovered from the water using a magnetic


MAG*SEP^{SM} Treatment System - Process Flow Diagram

filter. The magnetic core gives the particle a high magnetic susceptibility. Because the contamination is chemically bound to the particles, a high percentage of adsorbed nonmagnetic contaminants can also be removed from the water. Once the particles have been recovered by a magnetic filter, they are discharged in a separate stream and regenerated (much as ion exchange resin is regenerated), the contaminants are recovered for recycle or treatment, and the particles can be reused.

Some key tasks within this task include:

- developing the optimized process chemistry for contaminated water from the Savannah River Site (SRS)
- developing an electromagnetic separator (EMS)
- designing, fabricating, and testing the integrated MAG*SEP process components
- conducting an above-ground field demonstration of the MAG*SEP treatment system integrated with an innovative barrier containment system at the D Area Coal Pile Runoff site at SRS

Longer term tasks (field demonstrations at other SRS sites and Berkeley Pit) will be conducted if performance goals are met during the initial field demonstration.

TECHNOLOGY NEEDS

Groundwater contamination consisting of heavy metals, radionuclides, nitrates, and organics exists across the U.S. Department of Energy's complex, as well as within private industry. Restoring contaminated groundwater is a significant cleanup challenge. Technologies capable of removing these contaminants, which typically appear in very low concentrations over a large area, and that will minimize the generation of secondary wastes, are needed.

The D Area Coal Pile Runoff Site at SRS has produced a contaminated groundwater plume that has been identified for a treatment demonstration using the MAG*SEP process, along with the EnviroWall™ barrier technology. A field demonstration of these combined technologies will be conducted to determine the viability of each. For this demonstration, a subterranean barrier will be installed to contain and isolate contaminated groundwater. The contaminated groundwater will then be channeled through a pass-through pipe and pumped to the surface to a transportable trailer containing the MAG*SEP treatment system.

ACCOMPLISHMENTS

This work has identified a candidate adsorber material (the amino form of iminodicarboxylic acid) for selective removal of contaminants found in SRS groundwater. In laboratory testing, contaminants were removed to achieve the following results:

Contaminant	% Removal
Pb	91.3
Cd	88.5
Ni	98.7
Cr	77.8

The initial phase of barrier installation was completed by installing a 30-ft-deep pass-through section at the D Area site of SRS. This part of the barrier includes the groundwater collection system, main valve, high-density polyethylene membrane, and the required piping to pump groundwater to the surface.

The MAG*SEP system design is complete. The design includes the EMS, particle injection/mixing zone, electrical wiring and piping layout, and overall process operation.

Process chemistry testing is complete. The tests indicated that the MAG*SEP particles could effectively remove Cd, Ni, Pb, and Cr from groundwater to achieve concentrations meeting drinking-water standards. This work also showed that the particles could be regenerated to almost 90% of the original particle adsorption capacity. Additionally, it was learned that several follow-up tests are required to resolve other technical issues. These follow-up tests are currently underway.

BRADTEC has constructed a lab-scale particle manufacturing facility at its Atlanta, Georgia, site. This facility has enabled production of small-batch quantities of MAG*SEP particles using one of several adsorbers designed for particular applications.

SCHEDULE OF DEVELOPMENT

The construction, installation, and integration of EnviroWall's barrier containment system with BRADTEC's MAG*SEP technology and Babcock and Wilcox Nuclear Technologies' (BWNT) magnetic separator is scheduled to be completed in late FY 1995. The actual demonstration of this integrated system will begin immediately after installation. Subsequent activities, including data analysis and report preparation, are scheduled to take place in early FY 1996.

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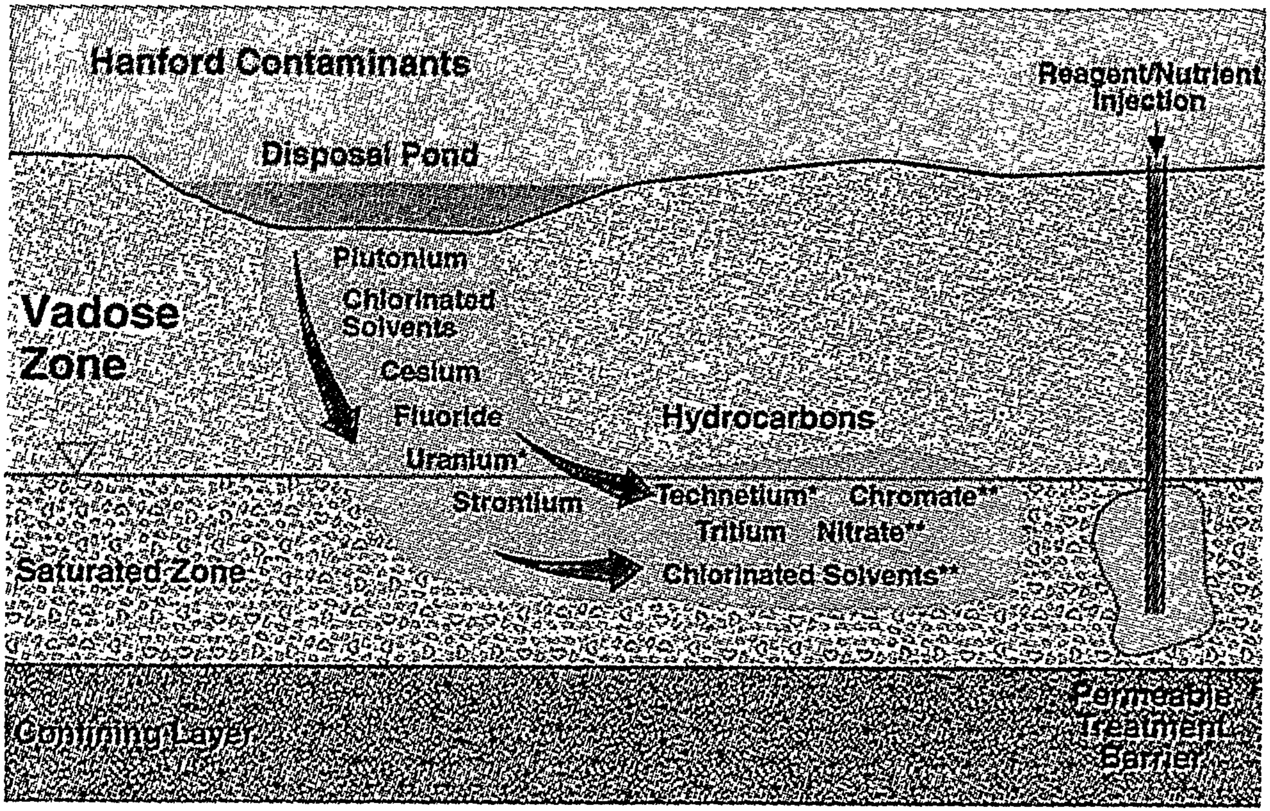
IN SITU REDOX MANIPULATION

TASK DESCRIPTION

This task is developing an in situ, permeable subsurface treatment barrier to immobilize or destroy target contaminants. The treatment barrier is a zone of favorable redox potential created by the addition of chemical and/or microbiological reducing agents. The goal is to design a barrier emplacement scheme that will effectively transform metals, ions, and radionuclides to less soluble forms and promote the destruction of organics, especially chlorinated hydrocarbons. A series of experiments is being performed to test different reagents, or microbial nutrients, for their efficiency in manipulating the redox conditions of an unconfined aquifer.

An unconfined aquifer is usually an oxidizing environment; therefore, most of the contaminants that are mobile in the aquifer are those that are mobile under oxidizing conditions. If the redox potential of the aquifer can be made reducing, then a variety of contaminants could be treated. Chromate could be immobilized by reduction to highly insoluble chromium hydroxide or iron



* Potential Candidate for Redox Treatment
** Favorable Candidate for Redox Treatment

chromium hydroxide solid solution. This case is particularly favorable, because chromium is not easily reoxidized under ambient environmental conditions. In addition, uranium and technetium could be reduced to less soluble forms, and nitrate could be degraded. Laboratory studies have also shown that carbon tetrachloride and other chlorinated solvents can be degraded by microbes if the redox potential is reduced to the point where nitrate or iron acts as an electron acceptor in place of oxygen.

Because the great majority of the chemically reactive mass in the subsurface system resides in the solid phases, it is necessary to involve the solid phases in order to substantially influence the chemistry of the system. If changes are made only to the aqueous component, equilibrium with the solid phases will be quickly re-established.

TECHNOLOGY NEEDS

Subsurface contaminants at U.S. Department of Energy (DOE) sites occur in both the vadose and groundwater saturated zones. Many of the groundwater plumes are already dispersed over large areas (square miles) and are located hundreds of feet below the ground. This type of dispersed, inaccessible contamination, which is more difficult than other types of contamination to treat using excavation or pump-and-treat methods, may only be treated successfully by the in situ manipulation of natural processes to change the mobility or form of the contaminants. Presently, the complex interactions of natural subsurface physical, chemical, and microbial processes limit the predictability of system-wide impacts from such manipulation.

In situ methods for immobilizing inorganic contaminants (metals, inorganic ions, and radionuclides) and destroying nitrates and organic contaminants (primarily chlorinated hydrocarbons) may be created by controlling the oxidation-reduction (redox) potential of the unconfined aquifer. The concept is to create a permeable treatment barrier in the subsurface by injecting reagents and/or microbial nutrients into the subsurface. The types of reagents and nutrients injected will be selected to make the aquifer reducing, thereby destroying or immobilizing specific contaminants.

ACCOMPLISHMENTS

During FY 1994 bench-scale testing was conducted to determine the nature of the reactions that occur and the efficiency with which the reactions are induced by the reagent, or nutrient. This includes the kinetics of reduction and subsequent re-equilibration of the reduced phases. Based on the bench-scale information, field experiments will be performed in FY 1995 to test the feasibility of in situ redox manipulation. The initial field experiment will involve reduction through introduction of a chemical reagent.

Results of the FY 1994 work conducted under this task are summarized here.

Chemical Reduction

A series of batch experiments was conducted under controlled atmospheric conditions to determine the factors affecting the aqueous stability of dithionite and its efficacy as a reductant of structural iron in clay-sized layer silicate minerals and in a sediment from the Hanford formation. These experiments showed that stability was enhanced in solutions that were buffered by $CaCO_3$ (s) near pH 8 and contained higher concentrations of dithionite. The decomposition/oxidation of dithionite by the sediment sample could be described by a pseudo-first-order rate equation and yielded rate constants inversely proportional to the dithionite concentration. At the highest concentration of dithionite, all the dithionite decomposed within a week at 30°C. During this same period, about 50% of the structural ferric iron present was reduced. Similar experiments with hydroxylamine as a reductant yielded essentially no reduction of structural iron.

To determine the longevity of the reduced structural iron after dithionite treatment, a flow-through column experiment using the Hanford formation sediment was conducted in which the reduced sediment was reacted with a fresh stream of oxygenated simulated Hanford groundwater. Changes in the pH and oxygen content of the effluent stream showed that a subsurface barrier created in this manner could maintain a reducing environment for approximately 45 pore volumes before being reoxidized by the groundwater.

A set of dithionite-stability and soil Fe-reduction studies designed to quantify the effects of soil:solution ratio and prior Fe oxidation state on the efficiency of the dithionite treatments was completed. As a result of this effort, a kinetic expression for the decomposition of dithionite that explicitly incorporates the mass of soil present was developed.

The results of these laboratory experiments suggest that dithionite has excellent promise for use as a reductant in oxidizing aquifers containing iron-bearing clay minerals. Even at Hanford, where the clay-sized mineral concentrations are typically on the order of 10-50 g kg^{-1}, enough ferric iron can be reduced to make in situ remediation by abiotic reduction a realistic alternative.

Microbiological Reduction

Dissimilatory metal-reducing bacteria couple the reduction of a wide range of multivalent metals (including iron, chromium, and uranium) to the oxidation of reduced organic matter or hydrogen. This enzymatic process can directly and indirectly affect the environmental fate and persistence of both organic and inorganic contaminants. Metal-reducing bacteria are difficult to isolate, but scientific evidence strongly suggests they dominate many anoxic aqueous, sedimentary, and subsurface environments. Technologies for stimulating indigenous populations of metal-reducing bacteria or for introducing specific metal-reducing bacteria to the subsurface are currently being investigated.

Metal-reducing bacteria were tested for their potential to remediate subsurface environments contaminated with carbon tetrachloride and chromium. Cells of the environmental bacterium strain BrY were added to sealed, anoxic flasks containing Hanford groundwater, porous subsurface materials, and either carbon tetrachloride or oxidized chromium, Cr(VI), in environmentally relevant concentrations. With lactate or hydrogen as the electron donor, BrY dechlorinated carbon tetrachloride and reduced soluble, toxic Cr(VI) to insoluble, less toxic Cr(III). Dechlorination proceeded through an indirect mechanism involving Fe(III) that was reduced and made chemically reactive by BrY. Cr(VI) was reduced by direct enzymatic activity in the presence or absence of Fe(III)-bearing porous media.

Intermediate-Scale Experiments

Intermediate-scale experiments will be conducted in FY 1995 to provide information on the efficiency of iron reduction by sodium dithionite in a flowing system at a similar scale and under similar conditions planned for the redox manipulation field experiment. In FY 1994, the design of this experiment was completed. A wedge-shaped flow cell was chosen for the intermediate-scale experiments to simulate the radial velocity profile that will occur during the injection stage of the field experiment. The 7-m radial length of the intermediate-scale experiment is close to the 9-m radial length of the field experiment. In addition to the wedge-shaped flow cell, existing 2-m by 4-m flow cells will also be used. The intermediate-scale experiments will be conducted by Dr. Jonathan D. Istok at Oregon State University in Corvallis, Oregon, under subcontract to the Pacific Northwest Laboratory (PNL). These experiments will provide data for determining injection strategies (i.e., concentration and duration) and placement of monitoring wells and boreholes for the field experiment.

Site Selection and Characterization

A test site at the Hanford 100H Area has been selected. Initial site characterization activities using existing monitoring wells have been initiated.

Information from laboratory studies and the preliminary field characterization has been incorporated into numerical models of the field site. Output from these models is being used to design the field experiment, accounting for uncertainty in field conditions. Factors that will be determined through the design analysis include well placement, reagent concentration, injection and withdrawal rates, and durations of various phases of the experiment (injection, reaction, and withdrawal).

Meetings with Regulatory Agencies

Members of the PNL In Situ Redox Team met with the Operable Unit Managers for the Hanford 100HR-3 Operable Unit. The site chosen for the In Situ Redox Field Test at the 100H Area is contained within this Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (CERCLA) Operable Unit. Present were representatives from the Washington State Department of Ecology (WDOE), the U.S. Environmental Protection Agency, and DOE's Richland Operations Office. All three representatives were briefed on the project concept and the specifics of the proposed field test. Copies of the CERCLA Treatability Test Plan and the Description of Work were provided to all three representatives. Approval to initiate drilling of the injection well and 14 monitoring wells was obtained from WDOE.

SCHEDULE OF DEVELOPMENT

The basic approach in the field experiment, planned for FY 1995, involves a forced gradient, single-well, reactive tracer test. The reagent is injected into the aquifer, creating a 60- to 100-ft diameter zone, and allowed to react for 5 to 30 days. Then, water containing the reaction byproducts and any remaining reagent is pumped out. In this manner, a permeable treatment barrier will be formed in advance of a contaminant plume.

A key issue is the scale-up of redox manipulation from the carefully controlled conditions of the bench-scale tests to the less certain conditions found in the field. The design methodology developed in this project includes tools to systematically analyze reagent and site chemistry in the context of field-scale transport. The analysis tools and framework being developed will be applicable to designing and evaluating other in situ chemical treatment technologies as well.

COLLABORATION/TECHNOLOGY TRANSFER

A potential site to demonstrate, test, and evaluate this technology is the 100 Area at Hanford. The field demonstration will be conducted to support the VOC Arid Soils Integrated Demonstration. Collaboration has been initiated with the managers of the site. The In Situ Redox Manipulation Project is also collaborating with Water Development Corporation to test sonic drilling techniques at the field test site, and with Schlumberger to test the applicability of geophysical techniques to characterize in situ remediation sites.

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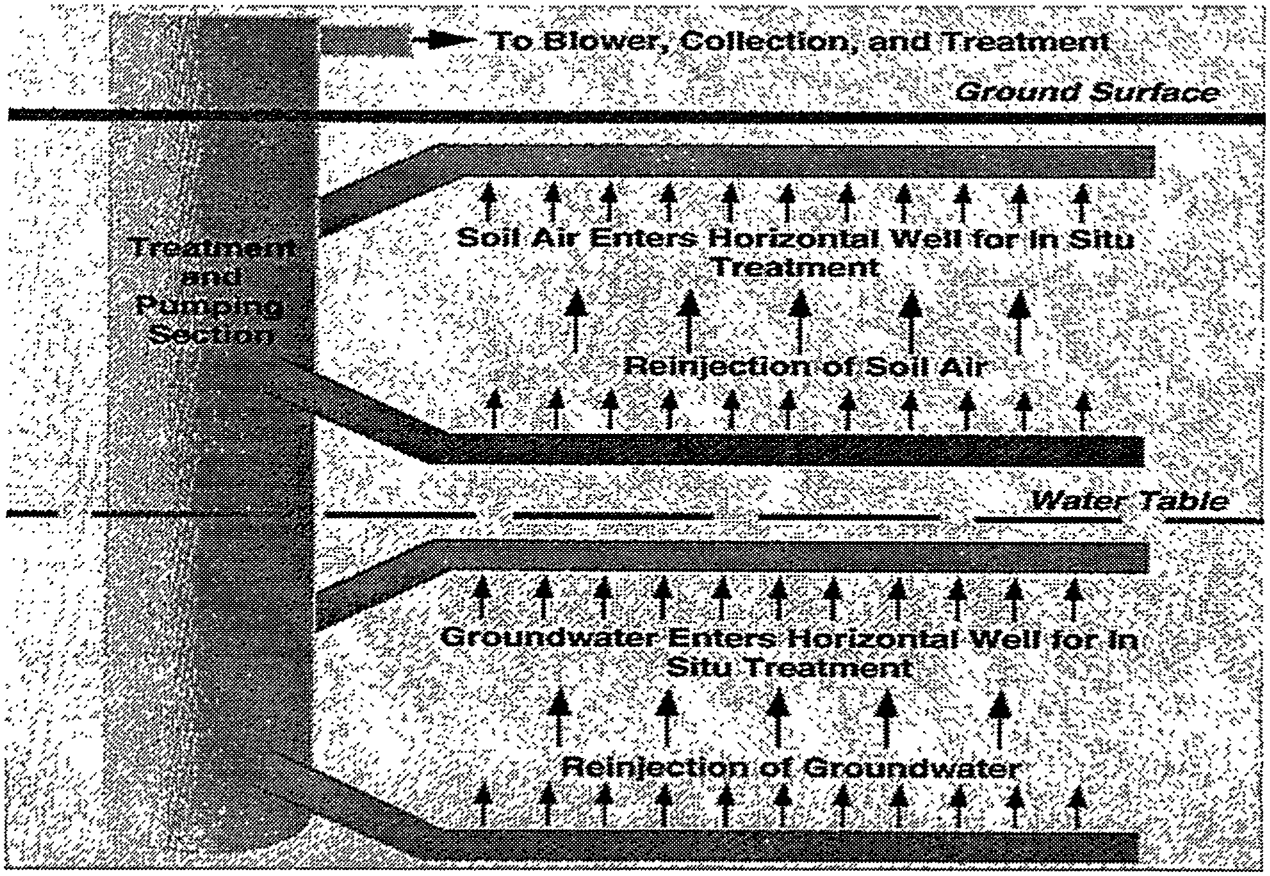
IN SITU TREATMENT OF MIXED CONTAMINANTS IN GROUNDWATER

TASK DESCRIPTION

The goal of this task is to package one or more unit processes for in situ treatment of volatile organic compounds (VOCs) and radionuclides (e.g., trichloroethylene [TCE] and Tc-99) in groundwater as modular components in vertical and/or horizontal recirculation wells. Task objectives include 1) evaluation of horizontal wells for inducing groundwater recirculation, 2) development of below-ground treatment modules for simultaneous removal of VOCs and radionuclides, and 3) demonstration of a coupled module-recirculation system at a U.S. Department of Energy (DOE) field site where both VOCs and radionuclides are present in the groundwater.

Recirculation wells are emerging technologies for treating subsurface fluids (groundwater and soil air). These specially designed wells pull water or soil air through a screened interval and transfers it back into the aquifer through a separate interval. Treatment occurs below ground within the well casing, thereby



reducing expenses from utility, maintenance, and regulatory costs. In addition, recirculation provides better control of groundwater flow through hydrodynamically connected wells. Presently, practitioners use only VOC stripping as a treatment strategy.

TECHNOLOGY NEEDS

Groundwater contaminated with mixed contaminants (e.g., VOCs and radionuclides) presents complex problems regarding treatment at many DOE sites. Although VOCs are often the most abundant contaminants, the radionuclides require specific treatment methods to protect workers and the environment from exposure. In addition, the radionuclides may yield mixed solid wastes if the VOCs are treated conventionally (e.g., pump-and-treat with above-ground carbon adsorption). Methods to treat mixed contaminants in situ would both expedite treatment and make the treatment more cost effective.

Recirculation-well networks coupled with in situ treatment modules may provide an efficient method for simultaneously heating mixed contaminants.

ACCOMPLISHMENTS

Accomplishments include the publication of a project description and a report describing the extensive technology screening effort used to select a treatment approach. These reports were used as a basis for selecting computer codes for modeling the expected benefit of the horizontal recirculation system, and are source material for developing the clean test site at Portsmouth for the pilot test. The Portsmouth test area has been well characterized and is suitable for a number of additional tests, such as evaluating contaminant recovery using horizontal recirculation, comparing recirculation efficiency of various fluids, and comparing groundwater tracers. After the clean test site was characterized, a pair of horizontal wells was installed using a porous flexible filter pipe instead of conventional well casing. This is the first time such material has been installed in the United States. The porous filter pipe is made of high-density polymer with essentially no microporosity. Thus, there is little potential for biofouling or for contaminant sorption.

Installation of flexible pipe was directed by Oak Ridge National Laboratory (ORNL) in collaboration with FloTex and Schumacher, two German companies. Scientists from Germany assisted with the installation and also conducted, at no cost to the project, laboratory tests for selecting the appropriate filter material. Based on the success of the installation at the clean test site, a contaminated site has been selected for a full-scale demonstration. This site has a well-characterized Tc-99 and TCE plume and provides an excellent location for the field test required by this project.

SCHEDULE OF DEVELOPMENT

This task consists of five phases to be accomplished over a 3-year period.

Phase 1 activities included selection of site characteristics, target contaminants, and appropriate unit operations. Portsmouth, Paducah, ORNL, and Hanford were considered as project sites. Portsmouth was selected based on the site's interest in implementing the technology as part of ongoing environmental restoration activities. The target contaminants are TCE and Tc-99. Phase 2 activities included the collection of hydrogeologic data, modeling, and bench- and pilot-scale experiments. The bench experiments consisted of two parts. Various configurations were evaluated for performing air stripping of TCE within the well and various materials were evaluated for sorbing the Tc-99. The pilot-scale tests consisted of the installation of horizontal porous filter pipe at a clean test site at Portsmouth. The porous filter pipe was used instead of conventional well screen and represents the first test of this material in this country. Pumping tests and tracer tests are also being performed as part of the pilot scale program. The final integration of the treatment modules and the recirculation well system, including final scale-up, occurs during Phase 3. Initial testing of the wells and all ancillary equipment occurs during Phase 4, while Phase 5 includes the field demonstration at a contaminated site and preparation of a final report.

COLLABORATION/TECHNOLOGY TRANSFER

Previous work included collaboration with J. Parker from Virginia Technological University, and that collaboration will continue. Collaboration with other DOE facilities, both at the laboratory and field level, will also continue. For example, prior experience in horizontal well design at the Savannah River Site will be considered. Research with vertical recirculation and in situ treatment of radionuclides is of interest at Hanford. Research on the ability of zero valence metals to dechlorinate TCE and sorb Tc-99 being conducted at Portsmouth, Paducah, and ORNL is also being evaluated. Finally, the host site will include this research as part of its ongoing Resource Conservation and Recovery Act (RCRA) or Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (CERCLA) program. Hence, future interactions will include both the prime contractor and the various environmental and construction subcontractors that are present. The results of the research will be published in open scientific literature and in various conference proceedings. Any patentable developments will be licensed with private industry using the appropriate DOE procedures.

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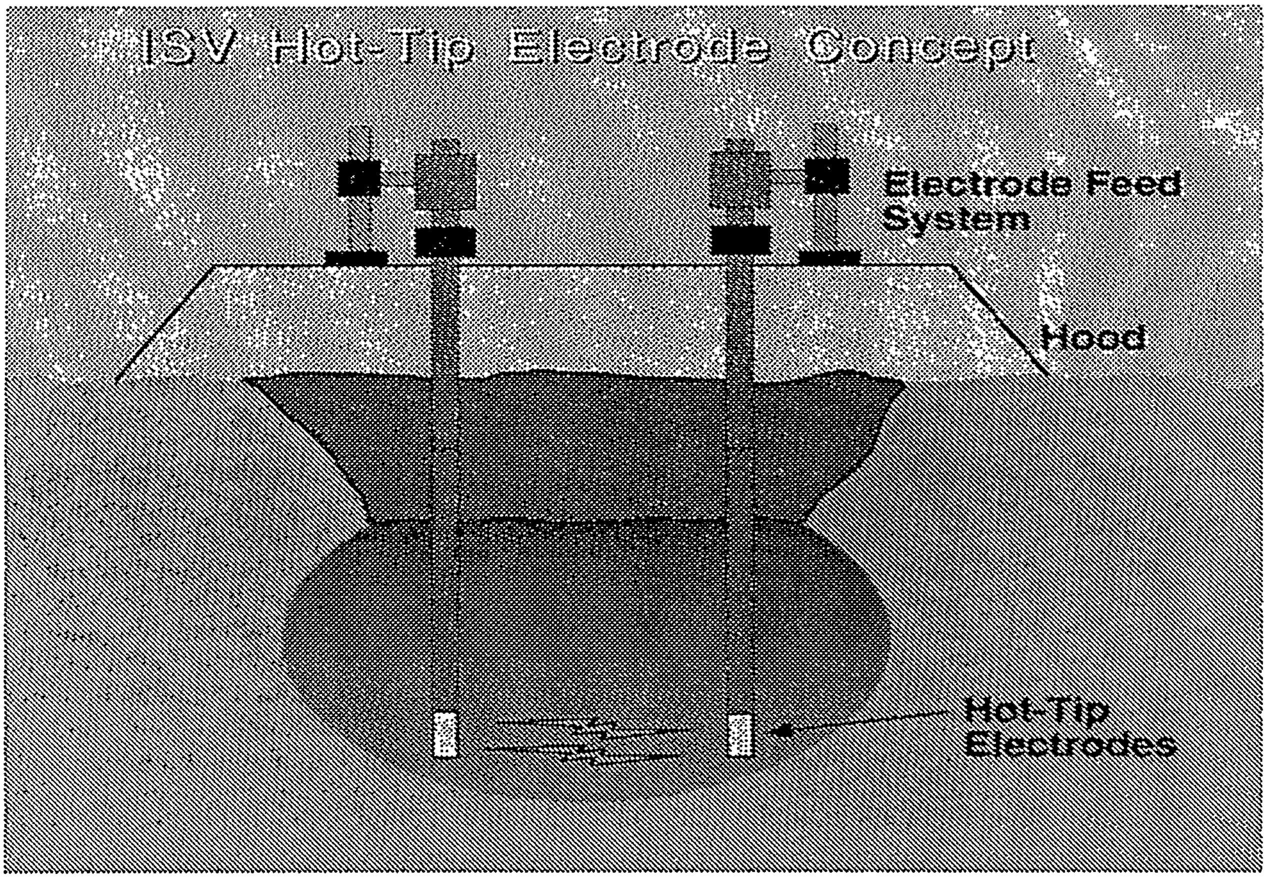
IN SITU VITRIFICATION (ISV)

TASK DESCRIPTION

One technology that has been successfully developed and is now commercially available for soil remediation is in situ vitrification (ISV). With this technology, electrical energy is supplied to a soil/waste matrix. The resulting Joule heat raises the temperature of the soil and waste, producing a pool of molten soil. Once the energy source is removed, the molten soil hardens, producing a solid, glass-like form that retains the contaminated soil. The technology is especially applicable to sites with a variety of different contaminants (i.e., radionuclides, heavy metals, organics, etc.).

This task is structured to address key issues associated with three near-term technology needs of ISV:

- melting low-alkali soils
- increasing ISV treatment depth
- quantifying the behavior of organic and inorganic volatile compounds in and around the ISV melt.



Low-alkali soils have proven difficult to melt using ISV because of their low alkali content. Bench-scale ISV tests conducted on uncontaminated, low-alkali soils from the Savannah River Site (SRS) showed that the SRS soils could be melted if fluxants were mixed with the soil to increase its alkali concentration. While effective, this approach is undesirable for processing the target SRS sites because it defeats the in situ treatment advantages offered by ISV. The first element of this task will evaluate and demonstrate, at the engineering-scale, methods to implement ISV on SRS soils without intrusively mixing fluxants directly into the target contaminated region.

A treatment depth of 5 m has been successfully demonstrated in the field with the ISV technology. The technology will have greater applicability at U.S. Department of Energy (DOE) sites if the depth capability can be increased to 10 m or more. Computational models of the ISV melt process indicate that the majority of the Joule heat energy dissipated in the soil is concentrated in the upper regions of the melt. By redirecting a greater proportion of this energy so it is dissipated in the lower portion of the melt (in the proximity of the advancing melt front), greater melt depths should be achieved. One concept appearing to hold great promise for depth enhancement, while simultaneously requiring virtually no modifications to the existing ISV system or its operation, is the modified or "hot-tip" electrode. The second element of this task will investigate several hot-tip electrode modifications to assess the electrode's capability to increase ISV treatment depth.

TECHNOLOGY NEEDS

ISV has been shown to be successful at sites in which 1) the contaminants are distributed in the soil in an unconfined manner, 2) the contaminants are amenable to thermal treatment, and 3) the contamination depth is less than 5 m. Extending the technology's capability beyond this established operating envelope will greatly increase the number of sites suitable for ISV treatment. The unresolved issues to be addressed include transport of certain volatile contaminants in and around an ISV melt, application at sites with inadequate concentrations of alkali and alkali-earth materials, and greater treatment depth.

Once these issues have been addressed, ISV can be considered for remediation of numerous contaminated sites at the SRS and contaminated low-alkali soils along the Eastern Seaboard of North America. There are many DOE, U.S. Department of Defense, and private-sector contaminated sites in this region. The technology will also be applicable to a much greater number of sites with contaminated regions extending below 5 m.

ACCOMPLISHMENTS

Increasing Treatment Depth

Two approaches for extending ISV treatment depth were tested. The first involved computational investigations and engineering-scale experiments of electrodes that were modified to concentrate the Joule heat energy delivered to the soil/waste matrix in the lower region of the target melt zone. The electrodes used to accomplish this are called "hot-tip" electrodes. The second approach involved a series of engineering-scale experiments in which the melt was initiated at depth and propagated in either vertical direction (i.e., downward, upward, or both) to treat the waste zone.

Two engineering-scale tests were conducted using the hot-tip electrode design. The first test was the baseline test and was conducted using the standard electrode design and engineering-scale system, with the electrodes placed in the soil to a depth of 7.5 cm. The second test reproduced the conditions of the first test, except the electrode design was modified to produce the hot-tip electrodes and the electrodes were inserted to a depth of 18 cm. The baseline case reached the targeted 1-m depth in 29 hr and the hot-tip case reached depth in 25 hr, representing a 17% reduction in time required for the hot-tip case to reach the target depth. The baseline case consumed 749.1 kWh to produce a 727-kg block, corresponding to a specific energy consumption of 1.03 kWh/kg. The hot-tip case consumed 664.8 kWh to produce a 636-kg block, corresponding to a specific energy consumption of 1.045 kWh/kg. The slightly higher specific energy consumption for the hot-tip case may be due to differences in heat loss out the top surface of the melt.

Melting Low-Alkali Soils

Soils obtained from the Savannah River Site (SRS) were used in a series of crucible melts and two engineering-scale tests to assess the soil's potential to melt during the ISV process. Because of their low concentration of alkali and alkali earth compounds, SRS soils have been difficult to melt in previous tests. The crucible tests evaluated the feasibility of introducing chemical fluxants into the soil in a semi-intrusive manner. The concept tested involves pressing lances containing fluxant material into the target vitrification zone. This concept relies on the ability of the fluxant to percolate through the target vitrification zone from a relatively confined initial configuration. Three fluxant materials were tested: sodium bicarbonate, sodium hydroxide, and calcium carbonate. All three additives mixed with the soil to produce significant melts of the crucible contents. However, concerns remain regarding the density of the fluxant lances that must be placed to obtain the necessary concentration of the alkali oxide material throughout the soil/waste matrix.

Both engineering-scale tests successfully treated the entire staged depth of SRS soil. Higher power densities were used in both tests to achieve the high temperature needed to vitrify this soil (~2000°C). In the first test, an overburden layer of SRS soil mixed with 14-wt% starter material was placed over a soil plug containing only SRS soil. In the second test, the entire target zone was composed of just SRS soil. The presence of the SRS soil and overburden layer of starter material smoothed the startup transient. However, both cases required substantially more energy to process the full depth of the soil plug than is usually required to vitrify Hanford soil (1.5 to 2 times more specific energy consumptions). These higher specific energy consumptions are to be expected because of the nature of the SRS soils and do not preclude the successful use of ISV on such low-alkali soils.

SCHEDULE OF DEVELOPMENT

Efforts associated with the low-alkali soils portion of this task are driven by the immediate needs of the SRS. If ISV is selected for remediating some of the contaminated sites at SRS, the technology could be applied immediately incorporating the improved techniques developed by this task.

The depth enhancement portion of the task was conducted in collaboration with Geosafe Corporation. Benefits from this effort will be realized in the near term by both the private sector and DOE.

COLLABORATION/TECHNOLOGY TRANSFER

The low-alkali soil portion of this task is being performed to address the concerns of EM-40 at the SRS. The modified electrode concept is being developed in collaboration with the Geosafe Corporation and has potential for becoming the baseline technology for all ISV applications.

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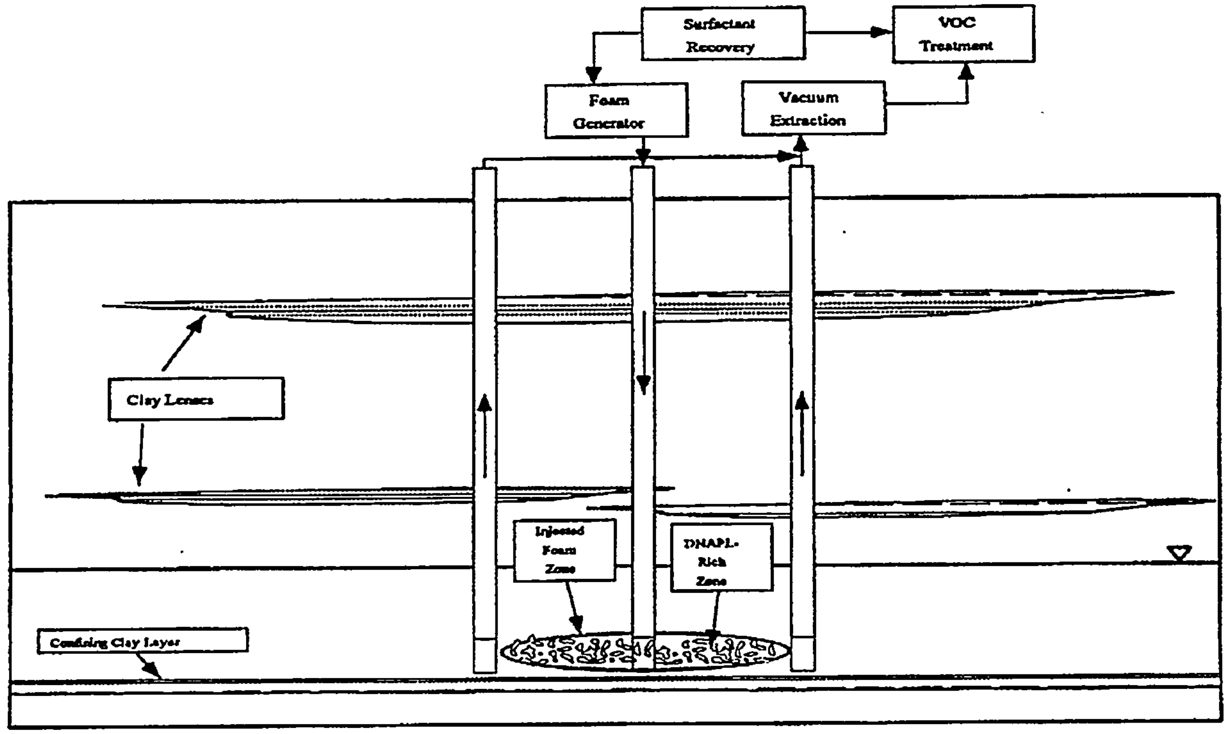
NAPL CONTAMINATED SOIL/GROUNDWATER REMEDIATION USING FOAMS

TASK DESCRIPTION

Current technologies for environmental remediation of nonaqueous phase liquids (NAPLs) are either ineffective or leave pollutants in the soil matrix that continue leaching into the groundwater. The innovative technology proposed for this task uses foams, coupled with bioremediation (either in situ or ex situ), to release and mobilize NAPL contaminants in the subsurface.

Unlike surfactants, foams remove contaminants by physical scouring, in addition to surface tension reduction and solubilization. This concept was originated by the Gas Research Institute (GRI). The foam can either be produced in situ or above ground and injected into the contaminated zone. Injection/ production wells (either vertical, horizontal, or Bladen-lysimeters) can be used to assist in delivering, transporting, and monitoring the foams through the subsurface. The Bladen-lysimeters are able to monitor and treat the contaminants



Conceptual Diagram Depicting Vertical Well Orientation for Delivery and Extraction of Foams simultaneously and are relatively inexpensive. The delivery of the foam, its sweep front, the foam stability, its efficacy to release NAPLs in the subsurface, and the resultant biodegradability of the foam/NAPL mixture can be aided through the proper selection of foaming agents, nutrients, and gas/oil core aphrons (OCAs). The foam should drive the contaminants upward in the subsurface, thereby lessening the potential for driving the contamination offsite. The plume should not migrate offsite; the treatment is limited to the affected area of contamination. This technique also has the potential to mobilize and biodegrade the contaminants either simultaneously or sequentially. The technology is well adapted for use with either horizontal or vertical wells. It is anticipated that this technology can be supplied to both the saturated and vadose zones for remediating soils contaminated with either chlorinated organics, such as trichloroethylene (TCE), or polyaromatic hydrocarbons (PAHs), such as chrysene, benz(a)anthracene, anthracene, fluoranthene, or phenanthrene. Further, this technology will treat soils having either scattered contaminants or pools of NAPL-contaminants in the subsurface.

This technology allows either aerobic or anaerobic environments to be established in the subsurface, depending on the carrier gas used. Either environment enables the foam-pollutant system to be adequately biodegraded for the particular contaminant of concern. The foam system can be tailored to provide either an aerobic or anaerobic system, or a combination thereof. For example, TCE can be biodegraded aerobically, whereas tetrachloroethylene and CCl_4 may need to be degraded anaerobically because their aerobic methanotrophic degradation may not be feasible.

TECHNOLOGY NEEDS

The bioavailability of surface-associated contaminants is a major concern in the remediation of soil and groundwater systems. The failure of many pump-and-treat processes is thought to be due in part to the slow release of contaminants, either because of desorption-limited release of sorbed material or because of the limited mobility of polled and interstitially held NAPLs.

Foam is a dispersant of gas bubbles separated by a thin liquid film containing surfactants. While successfully applied commercially for enhanced oil recovery, foams have not yet been systematically applied to near surface (relative to oil recovery applications) in situ remediation problems. Foams are currently used by the oil industry to improve crude oil recovery, resulting in 20% to 50% higher recoveries of oil for some applications.

In recent years, there has been considerable work in previously unrelated areas that has the potential to contribute to a new remediation technology having great flexibility and specificity. These areas include the development of "designer" foams, physical/chemical methods for removing pollutants from soils, and presumably lower cost methods for in situ bioremediation. This new foam technology combines these areas and has several potential advantages over existing technologies (e.g., surfactant flooding), including those listed here.

- The technique has the potential to mobilize and biodegrade the contaminants, either simultaneously or sequentially.
- The foam can either be generated in situ or above ground and injected into the contaminated zone.
- Because the applied surfactant dosage in the foam(s) is several orders of magnitude below the critical micelle concentration, the biodegradation is not expected to be significantly inhibited (as occurs with surfactant floods).
- The foams should drive the pollutants towards the surface (particularly when coupled with a vacuum extraction system to pull the foam/pollutant mixture upwards). As a consequence, the potential for driving the contamination offsite is minimized.
- By performing the treatment in situ, pollutants cannot be moved from one place to another as might happen with a pump-and-treat option.
- Because the foams are generated in situ, no volatile organic compound emissions are encountered.
- The technology is well adapted for use with either horizontal or vertical wells.
- The technology allows either aerobic or anaerobic environments to be established in the subsurface. Additionally, the foams can carry nutrients and microorganisms to enhance biodegradation of the mobilized pollutant.
- This technology has the potential to increase the applicability of in situ bioremediation. Unlike other approaches, foams can be designed to simultaneously remove pollutants from soil and enhance bioremediation.

If applied to the much shallower depths involved in waste remediation, foams have the potential to 1) be tailored to the particular pollutant, soil, or remediation scheme, 2) reduce remediation costs when compared with surfactant flooding, 3) be simpler to use because the foams tend to float rather than sink, and 4) enhance bioremediation by carrying nutrients, bacteria, and specific gases.

ACCOMPLISHMENTS

Key issues that could require further experiments before a successful field demonstration of foam remediation can be implemented were identified this year. These issues include impact of foam flow through porous media, pressure drops, foam stability,and extraction efficiency for contaminants from actual site soils.

Several experimental methods for addressing the issues in laboratory experiments were developed. It has been demonstrated that foams can remove

NAPL contaminants at 10x the efficiency of surfactant flushing solutions. This greater efficiency results because foams flow through media in a plug-flow fashion instead of channeling, thereby effectively scouring NAPLs from the soil. This results in NAPL removals as high as +90% in a soil column, compared to a maximum of 10% removal by surfactant flushing in about five-pore volumes. The advantage of foam use is that its higher removal efficiency is achieved with surfactant concentrations 100x less (i.e., two orders of magnitude lower) than those needed for surfactant flushes.

The research also identified key issues that need to be addressed to properly design and use a foam remediation system. One of the major issues is the observation from laboratory experiments that there can be a significant pressure drop in some situations. To address this issue, a three-dimensional (3-D) computer model was developed to predict pressure drops as a function of foam rheology, characteristics, and soil matrix. The results suggest that pressure drops may be lower for a field application as a result of 3-D flow effects. In addition, several strategies for reducing the pressure drop were suggested, including reducing microbubble size (10 to 20 μm); using foam flow to fracture soil, thereby increasing permeabilities (previously used in enhanced oil recovery); using multilevel injection/extraction wells; and coupling with other technologies for increasing foam flow rates (e.g., vapor extraction and electrokinetics). Another approach considered involves using OCAs, which are small drops of oil dispersed in water. OCAs require little or no surfactant and do not experience significant pressure drops, but they tend to channel like surfactant solutions and do not provide physical scouring. Optimization of foam characteristics for site-specific soils will be necessary to lower pressure drops.

Based on results from the laboratory experiments, the following conclusions were drawn:

- The principal factor affecting foam flow in porous media is its apparent high viscosity, which in most medium- and fine-grained matrices is a strong function of the foam quality (% gas in the foam) and the soil permeability (which is a strong function of the grain size distribution). Apparent viscosity of foams can be 15 to 20x that of water, based on equal volume delivery rates of foam versus pure water to a soil matrix. To a lesser extent, surfactant type and concentration, foam stability, and soil chemistry are important. With coarser soils, the bubble size is expected to play an important role in generating smaller microbubbles, approaching the pore size opening which could markedly reduce pressure drop and enhance flow through the porous media.

- The best chance for minimizing bubble size, which should enhance flow through coarse matrices, is to concentrate on surfactants, which reduce surface tension. Any efforts to achieve more intensive shearing when forming microbubbles should reduce bubble size. Thus, study of high shearing devices, such as low-clearance positive displacement pumps, fine sand packs, and a series of in-line mixers, should be investigated.

- The primary advantage of foam scouring over surfactant flushing is its ability to treat effectively with good sweep efficiency through high-viscosity contaminated zones and to minimize channeling. Second, treatment seems to be effective as the dispersed concentration of dense nonaqueous phase liquids (DNAPLs) drops to 5000 ppm or lower. The scouring ability serves to mobilize and emulsify for removal and/or disperses and spreads the contamination on the matrix surface, thereby enhancing the solubilization rate and subsequent localized biodegradation. Results from our experiments indicated that foam scouring was 10x more effective at removing DNAPLs from porous soils than was surfactant flooding.

- The use of OCAs, while not apparently effective for scouring, showed significant promise for extracting and concentrating dissolved PCE. The very high distribution coefficient of 1000 or more for straight-chain paraffins makes ex situ treatment of PCE, CCl_4, and TCE of considerable interest; in situ treatment also warrants further investigation. Droplet stability, separation, and recovery of the oil droplets, and concentration of the chlorinated organics, require further study.

- The development of a foam model has verified most of the physical and chemical factors affecting the pressure drop and scouring observations. The results further show that unless foam bubble size is diminished, the use of foam injections at 5- to 50-ft depths for in situ remediation of shallow, low-to-medium permeable matrices will be limited to 1- to 5-ft penetrations unless coupled with pneumatic fracturing, closely spaced wells, or development of injection/recovery techniques through the same well. At greater depths, allowable delivery pressure without fluidization to the surface will be greater, and injections could be more aggressive.

SCHEDULE OF DEVELOPMENT

Research efforts in the next 6 to 12 months will be directed towards work to bring foam remediation technologies to the demonstration stage by early 1996. Several DOE sites have been identified as potential sites where foam remediation technologies could provide improved environmental restoration at lower costs. The projected remediation strategy is to use foams to remove or solubilize chlorinated organics (such as TCE) by scouring and emulsification mechanisms. Residual TCE concentrations not removed would then be in the range favorable for in situ bioremediation. Foams will remove contaminant concentrations that either are not presently bioavailable or exist at levels toxic to biodegradation processes.

COLLABORATION/TECHNOLOGY TRANSFER

The team is discussing the technology with additional companies and plans to hold a workshop with various industry, government, and academic experts to identify major issues that need to be addressed. Small business innovative research proposals and requests for proposals have been submitted on variations of the foam remediation technologies with the following companies: OHM, Envirogen, Inc., Aphron Technologies, and Golder Associates.

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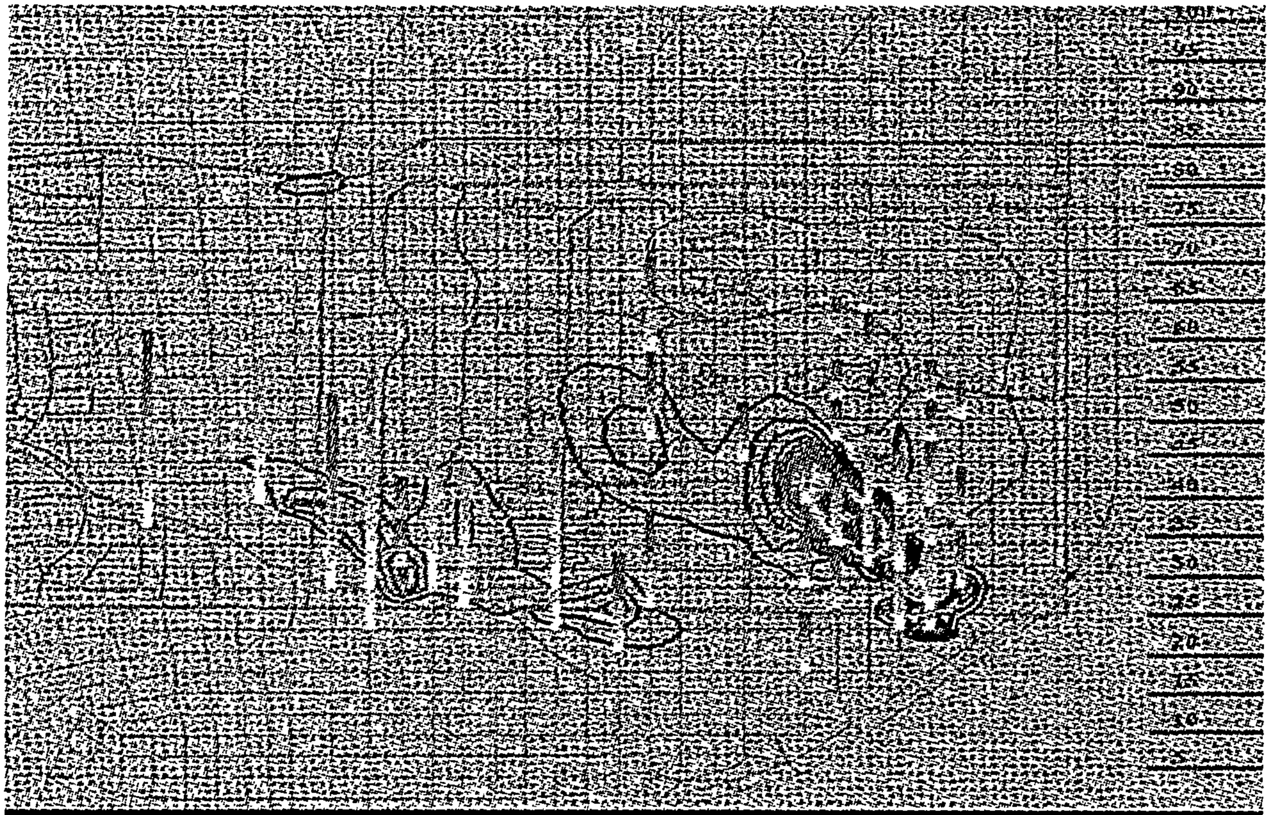
OPTIMAL REMEDIATION DESIGN: METHODOLOGY AND USER-FRIENDLY SOFTWARE FOR CONTAMINATED AQUIFERS

TASK DESCRIPTION

Groundwater remediation is an expensive problem that will persist for decades. The critical question within the U.S. Department of Energy's (DOE) complex, and the United States in general, is how to manage and optimize the long-term groundwater remediation process. Both containment and decontamination strategies must be applied to the subsurface remediation process. The locations and rates of pumping for each groundwater remediation well, which may change with time, must be selected carefully, as must the locations and sampling intervals of monitoring wells. Operation and maintenance costs associated with these decisions can be enormous when projected over realistic remediation periods. Therefore, the benefits to DOE from design optimization can also be enormous.

This task focuses on developing a methodology and associated tools for managing and optimizing strategies for remediating contaminated groundwater. The methodology segment of the task will



Example of output from optimization tool.

lead to a decision support tool for incorporating information on contamination risk, remedial requirements, optimal remedial design alternatives, and associated engineering costs. Contributions will include user friendly interfaces so a broad range of potential users can benefit from this effort. This will include graphical interfaces that can be used on different types of computers.

Optimization tools will be developed to apply non-convex objective functions to problems using two- or three-dimensional simulators of groundwater systems. Optimization tools will extend MODFLOW, an existing three-dimensional groundwater flow and transport code for saturated groundwater systems, to employ graphically oriented hydrological and numerical data manipulations. Unsaturated flow and transport conditions will then be incorporated. Improved problem formulation and expression will be incorporated with objective and constraint functions, including improved economic descriptions with the above physical parameters.

TECHNOLOGY NEEDS

Operation and maintenance costs associated with techniques selected for groundwater remediation are enormous when projected over realistic remediation periods, which may range from 30 to 100 years. Pump-and-treat, one remedial alternative, is often selected for groundwater remediation because the process simulations needed to design a remediation strategy are well developed. However, this alternative is generally implemented with only minimal consideration of the best location of extraction/injection wells. The result may be zones of contamination in which the contaminant mass is held static for a very long time, or transportation of contaminants to new subsurface locations where their removal is more difficult. Methods to manage and optimize the groundwater remediation process over long time periods are needed.

The approach taken for this task is to provide a general description of project-specific tasks to be accomplished. The more general description of tasks is preferred, because it provides freedom to the University of Vermont graduate students to take innovative approaches.

A major task is the refinement of optimization tools for contaminated groundwater systems. This task is broken into several subtasks described below:

- Subtask 1 investigates more efficient tools for optimization of large-scale three-dimensional groundwater systems that are hydrodynamically constrained. Despite recent advances in optimal design techniques, a number of open problems remain, including the addition of clay caps, horizontal drains, and cutoff walls directly into the optimization schemes.

- Subtask 2 relates to contaminated groundwater systems. In this subtask, we will address nonlinear optimization directly, in particular addressing nonconvex problems in solute transport in groundwater systems. Research on more robust and efficient optimization methods, such as the outer approximation method and modifications of existing techniques, will be emphasized to serve these problems. The research pursued under this task will be directly applicable to other important subsurface contaminant problems, such as multiphase flow and the use of subsurface chemical treatments.

- Subtask 3 extends the work into unsaturated groundwater systems. Extension of the codes to incorporate algorithms used in Subtasks 1 and 2 will allow optimal design of both saturated and unsaturated systems. Optimization problems for such contaminated systems are quite nonlinear, and research on more robust and efficient optimization methods will thus emphasize the development of emerging methods, such as the outer approximation method, as well as modifications of existing techniques to solve non-convex problems.

- Subtask 4 is to develop graphical interfaces that can be compiled and executed on different types of computers. This is a central aspect of the project and will accompany the previous subtasks. Project results can be effectively disseminated to end-users only if the results are used. The user interface provides end-users with access to the optimization tools and must be developed with the end-user in mind. A graphical user interface will not only increase the potential for technical transfer, but will provide an important tool for the exploration of data, proposed solutions, and other "what if" scenarios that involve large amounts of numerical information.

Another major task involves more directly the critical issue of remediation problem formulation and expression. Work will be performed on the development of more realistic objective and constraint functions that include improved economic descriptions. This will allow the quantitative optimization problem under consideration to be closer to a decision-maker's verbal description of the problem. This task will incorporate the optimization solution procedures developed in the above tasks.

A final task relates to technology transfer. Any enhancement to optimization tools would have an immediate impact on Lawrence Livermore National Laboratory's (LLNL) remediation implementation. This is the reason for the close coordination between LLNL and the University of Vermont. Because LLNL is acting as a client for the optimization tools being developed by this work, technical transfer is anticipated to be rapid and ongoing.

ACCOMPLISHMENTS

During the past year, MODLP, a program for solving linear optimal hydraulic control of groundwater contamination based on MODFLOW simulation, was developed and delivered to investigators preparing the remedial design for the LLNL main site Comprehensive Environmental Response, Compensation and Liability Act of 1980 (CERCLA) cleanup. MODLP is a computational tool that helps design capture zones for controlling the movement of contaminated water. It creates and solves linear optimization problems that contain constraints on hydraulic head or head differences in a groundwater system. A user document describing the general structure of the computer code, the types of constraints that may be imposed, detailed input instructions, interpretation of output, and the interaction with MODFLOW simulation kernel is available along with the computer code itself.

COLLABORATION/TECHNOLOGY TRANSFER

This work is being performed in collaboration with Dr. George Pinder of the Research Center for Groundwater Remediation Design, University of Vermont. Additional faculty participants are David E. Dougherty of the University of Vermont and David P. Ahlfeld of the University of Connecticut.

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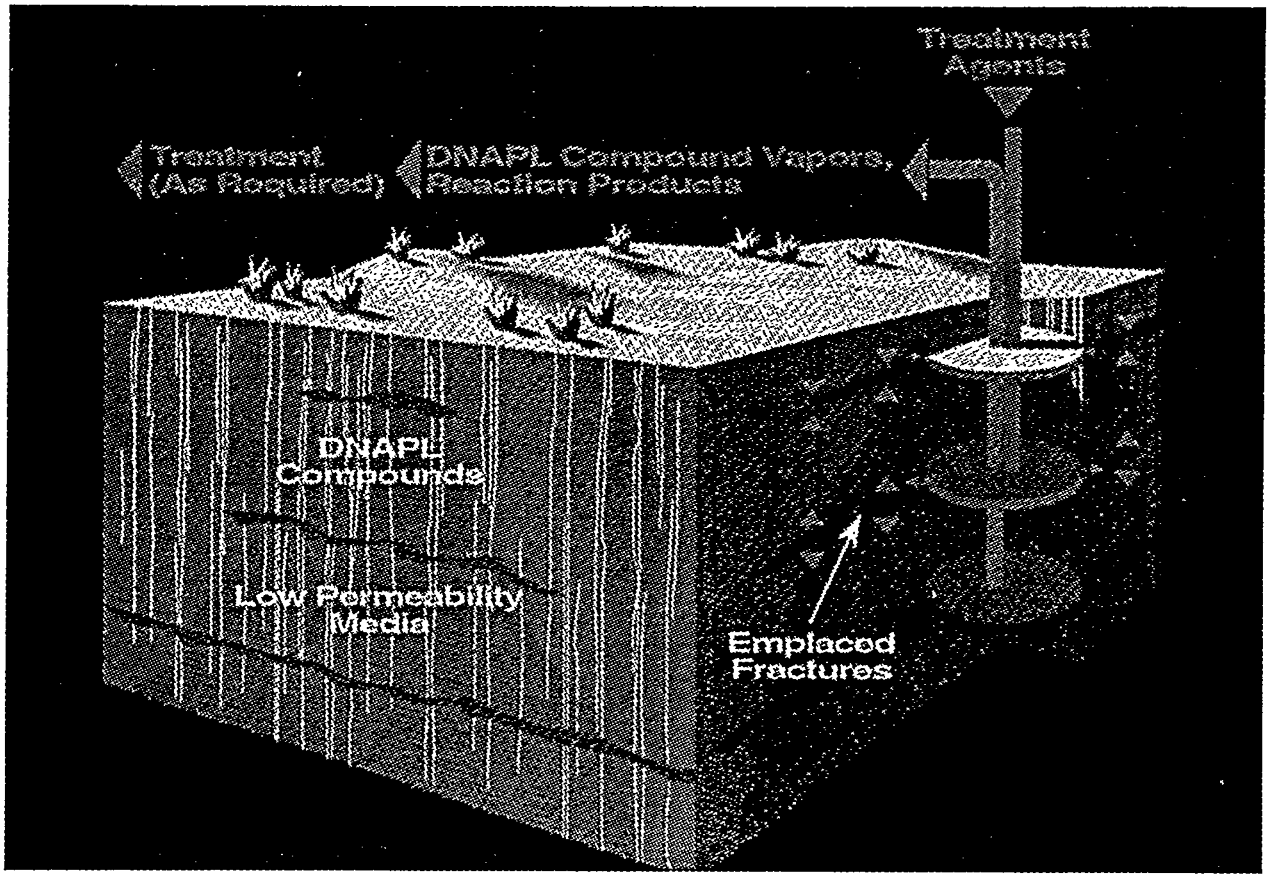
REMEDIATION OF DNAPLS IN LOW K SOILS

TASK DESCRIPTION

This task is being conducted as a joint effort under sponsorship of the U.S. Department of Energy (DOE) and the American Petroleum Institute (API). In situ remediation technologies will be tested and evaluated for both source control and mass removal of dense nonaqueous phase liquid (DNAPL) compounds in low permeability media (LPM). This effort is focused on chlorinated solvents (e.g., trichloroethylene and perchloroethylene) in the vadose and saturated zones of low permeability, massive deposits, and stratified deposits with inter-bedded clay lenses. The task includes technology evaluation, screening analyses, and field-scale testing at both clean and contaminated sites in the United States and Canada.

The initial phase of the work includes preparation of a series of focus papers by a consortium of experts to document the state of the art for various emerging in situ remediation technologies for DNAPLs in LPM. The focus papers will cover transport/fate processes and in situ



treatment technologies, including separation and transfer processes (e.g., vapor extraction and subsurface mobilization) and destruction processes (e.g., chemical and biological degradation). Thermal enhancement methods will also be assessed, including hot air and steam injection, and electromagnetic and resistance heating. Finally, enabling technologies, such as hydraulic and pneumatic fracturing, and mixing will be studied.

The second phase of the work includes field-scale testing of promising technologies at clean- and controlled-release test sites near Sarnia, Ontario, and Cincinnati and Portsmouth, Ohio. Capabilities also exist to conduct large-scale laboratory experiments with packed lysimeters or field-collected cores. Eventually, field testing will be conducted at a contaminated site such as the X-231A or X-701B units at the DOE Portsmouth site. Throughout this work, activities will be directed to understanding the processes that influence DNAPL migration and treatment in low permeability media, and assessing the operation and performance of the remediation technologies developed and tested.

TECHNOLOGY NEEDS

The presence of DNAPLs such as trichloroethylene and perchloroethylene in low-permeability soil and geologic media represents a common contamination problem that is very difficult to treat. DNAPL compounds can migrate in low permeability media by preferentially moving into and through naturally occurring fractures where they partition between the gas, aqueous, and sorbed phases within the fracture and matrix system. They may also form isolated "blobs" and "ganglia" known as residuals, as well as connected DNAPL pools. In the vadose zone, DNAPL compounds can continually volatilize into the soil air or leach into percolating water. In the saturated zone, DNAPLs can slowly dissolve and contribute contaminants into flowing groundwater.

Soil vapor extraction or groundwater pump-and-treat technologies have been used to remove DNAPLs from low-permeability media, although the success of these approaches has been limited. While these technologies provide a means to control gaseous and dissolved contamination, they have little effect on removing or controlling the mass of DNAPLs within the subsurface.

This task is developing in situ technologies for both source control and mass removal of DNAPL compounds in low-permeability media. An objective is to remove the sources of DNAPL contamination rather than merely treat DNAPL compounds in soil air or groundwater.

ACCOMPLISHMENTS

A Memorandum of Understanding (MOU) between DOE's Office of Technology Development and API has been prepared to provide a framework for DOE and API to work together in a wide range of subject areas. This project is the first effort being conducted under this MOU, and it has been merged with an existing effort by

API that has focused on remediating light nonaqueous phase liquids (LNAPLs) in low permeability media. The LNAPL project was initiated in 1992 to investigate and study remediation of petroleum hydrocarbons, such as gasoline in fine-grained soils. Results from the LNAPL effort will be made available and used to address DNAPL questions whenever applicable. The LNAPL work has produced a series of focus papers describing processes and technologies for LNAPLs. This work was followed by a controlled release of gasoline within a 100-m^2 sheet-pile enclosed test cell near Sarnia, Canada. Transport and distribution of the gasoline was monitored and a series of soil vapor extraction tests was made during the summer of FY 1993. In FY 1994, the project was also directly linked to the Environmental Restoration Program at the DOE Portsmouth Gaseous Diffusion Plant since that site provided funding to the effort and sought solutions for near-term implementation.

The DNAPLs in the LPM project was initiated in late summer FY 1993. Contracts were placed with multiple universities and private industries. A series of transport/fate and remediation technology focus papers was prepared and will be completed by May 1995. During FY 1994, tests were conducted at field sites located near Sarnia, Canada, and Portsmouth, Ohio. At the DOE Portsmouth site, a clean test site was established adjacent to several contaminated sites. A pneumatic fracturing test was conducted for enhancing the hydraulic conductivity of saturated silty clay soils. Also, a comparative study of reactive fluid injection and dispersal using multipoint vertical lancing equipment was completed. The multipoint injection system was able to deliver seven different fluids (aqueous tracers, lime slurry, hydrogen peroxide, potassium permanganate, biosurfactant, iron powder, and air) at volumetric loading rates of 5% v/v into different test cells and abruptly modify soil matrix properties affecting DNAPL and contaminant behavior. Draft reports were completed for both tests and are undergoing revision. At the Sarnia site, enhanced soil vapor extraction was tested during FY 1994 and a pilot-scale hydraulic fracturing study was conducted. Two cores were collected; two additional cores from within and two from outside the cell are scheduled for collection. These cores will be used for leaching experiments. Draft reports were also completed on pilot study work at the Sarnia site and on the vapor extraction work.

As currently planned, field-scale testing will continue during FY 1995 at the test sites in Sarnia, Canada, and near Cincinnati and Portsmouth, Ohio. The work will continue to evaluate the effects of pneumatic and hydraulic control, heat and mass transfer, and fracturing methods coupled with hot air and steam injection. Intensive monitoring of subsurface properties before, during, and after pilot tests will be used, along with tracer experiments, to describe process operation and performance and to calibrate existing models. Laboratory tests will focus on describing the fracture/matrix system to help understand short- and long-term process performance. A field demonstration to compare multiple technologies is planned and will be conducted at a contaminated land treatment site at the DOE Portsmouth facility.

COLLABORATION/TECHNOLOGY TRANSFER

This project will initiate cooperation in the environmental restoration and waste management area between API and its members (250 corporations in the petroleum and allied industries) and DOE and its national laboratories and sites. BP Research is currently managing the LNAPL project for API and is co-managing the joint DOE/API project with Oak Ridge National Laboratory. The joint project currently includes participants from over six universities and six private industries. Linkages are already in place for testing technologies at DOE sites (e.g., Portsmouth), which will facilitate project co-funding as well as rapid transfer of promising results into full-scale implementation within DOE environmental restoration programs.

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SECTION 3.0

CONTAINMENT

- *Containment technologies* (subsurface barriers) are required to prevent the migration of contaminants. Two types of subsurface barriers are being developed, impermeable barriers and permeable barriers.
- Impermeable barriers could be emplaced around a source term to contain the waste and could be used in conjunction with a remediation technology, such as soil flushing or electrokinetics, to prevent further migration of waste during treatment. Permeable barriers allow water or aqueous waste to pass through the barrier, but remove and retain the contaminants.
- Significant progress has been made in developing new barrier materials. The major issues to be resolved focus on the functional requirements for deploying a barrier, the emplacement of the barrier, and the verification of barrier emplacement and performance.

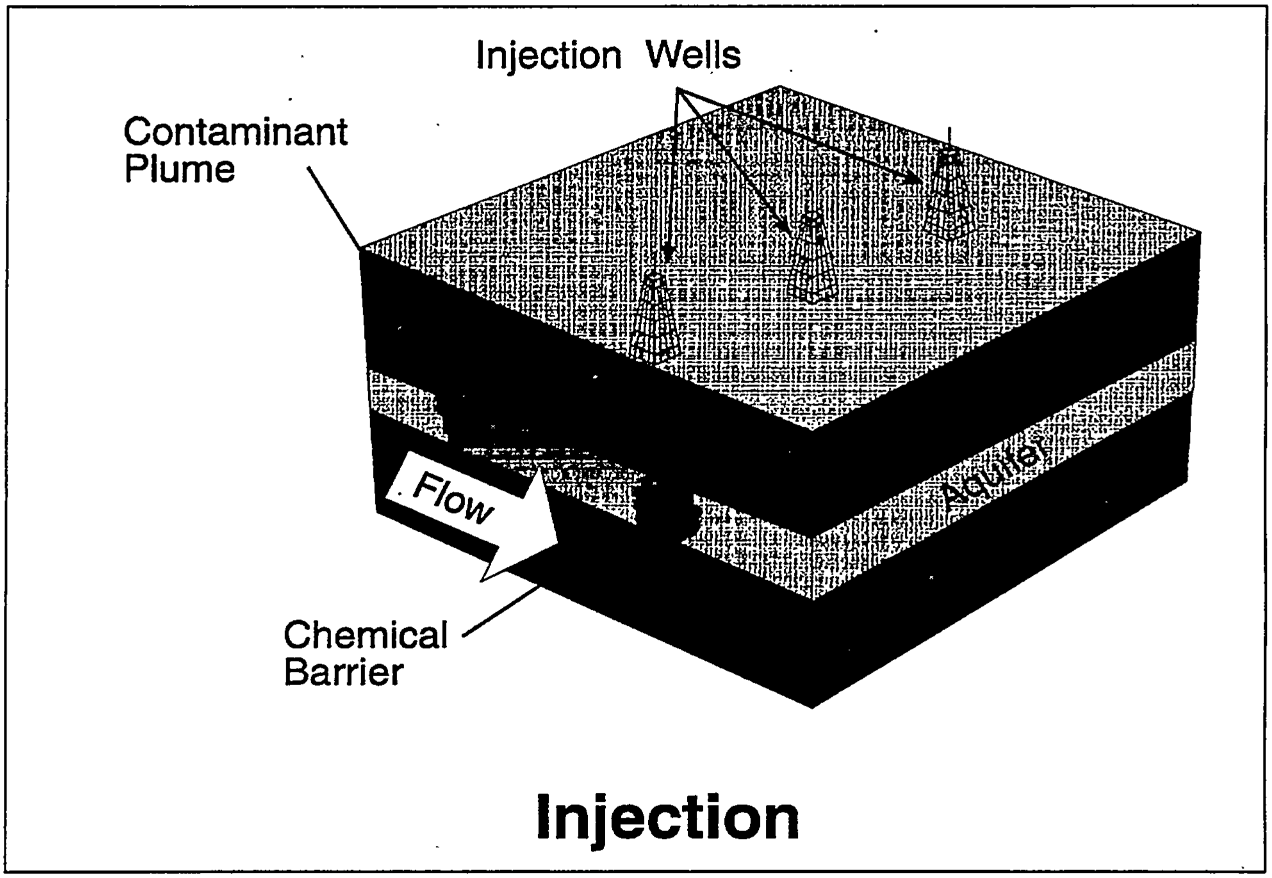
CHEMICAL BARRIERS FEASIBILITY AND FIELD DEMONSTRATION

TASK DESCRIPTION

This task is examining the sorption and immobilization capacity of a natural iron mineral for numerous site contaminants, and the mineral's use in the in situ formation of a permeable barrier that removes target contaminants without impeding groundwater flow.

Ferric oxyhydroxide or hydrated iron oxide is a naturally occurring, non-hazardous substance that has sorption affinities for many inorganic contaminants found at U.S. Department of Energy (DOE) sites. Contaminants such as uranium, molybdenum, chromium, arsenic, copper, lead, zinc, and radium can potentially be removed from groundwater by this mineral.

To form a barrier, the iron is injected as a solution in water. Reaction underground with aquifer mineral alkalinity converts it to the sorbing phase. Precipitation within the aquifer pores coats the rock particles, forming a barrier zone around the contaminated area. This coating extracts the contaminants moving with the groundwater and confines them in the barrier zone.



The objectives of this task are to 1) determine the absorptive capacity of the iron mineral for target contaminants, the mobility of the iron mineral, and the permeability modifications that occur when the mineral is introduced into the subsurface, and 2) design and field test a low-cost, water-permeable barrier system formed in situ.

TECHNOLOGY NEEDS

This effort is directly applicable to remediation of uranium contamination at the Monticello Mill Site (Monticello) in Utah. Because uranium or metal contamination in groundwater is prevalent at many DOE, U.S. Department of Defense, U.S. Environmental Protection Agency, and industrial waste sites, this technology has widespread application. DOE sites with uranium or metal groundwater contamination include the Uranium Mine Tailings Remedial Action Program facilities, Pantex, Fernald, Nevada Test Site, Y-12, and the Gaseous Diffusion Plant at Oak Ridge.

ACCOMPLISHMENTS

The results of laboratory studies on ferric oxhydroxide were submitted to a journal for publication. The results indicated that ferric oxyhydroxide forms from the injection of ferric chloride into carbonate-bearing aquifer sediment. The ferric oxhydroxide formed in this manner is sorptive for uranium and molybdenum and is immobile. Emplacement causes little or no decrease in the permeability of the aquifer.

SCHEDULE OF DEVELOPMENT

The results of the laboratory testing phase are sufficient to justify a field demonstration. The construction phase for a field demonstration at a uranium mill site in Monticello, Utah, was completed but the project has been suspended because of scheduling issues at the Monticello site.

COLLABORATION/TECHNOLOGY TRANSFER

Laboratory studies on the use of this sorbent for uranium mill tailings remediation have been carried out under the Surplus Facilities Management Program and the Grand Junction Projects Program Support Research and Development Program. Published papers and participation in technical conferences have led to inquiries from DOE and private industry interested in testing this technology.

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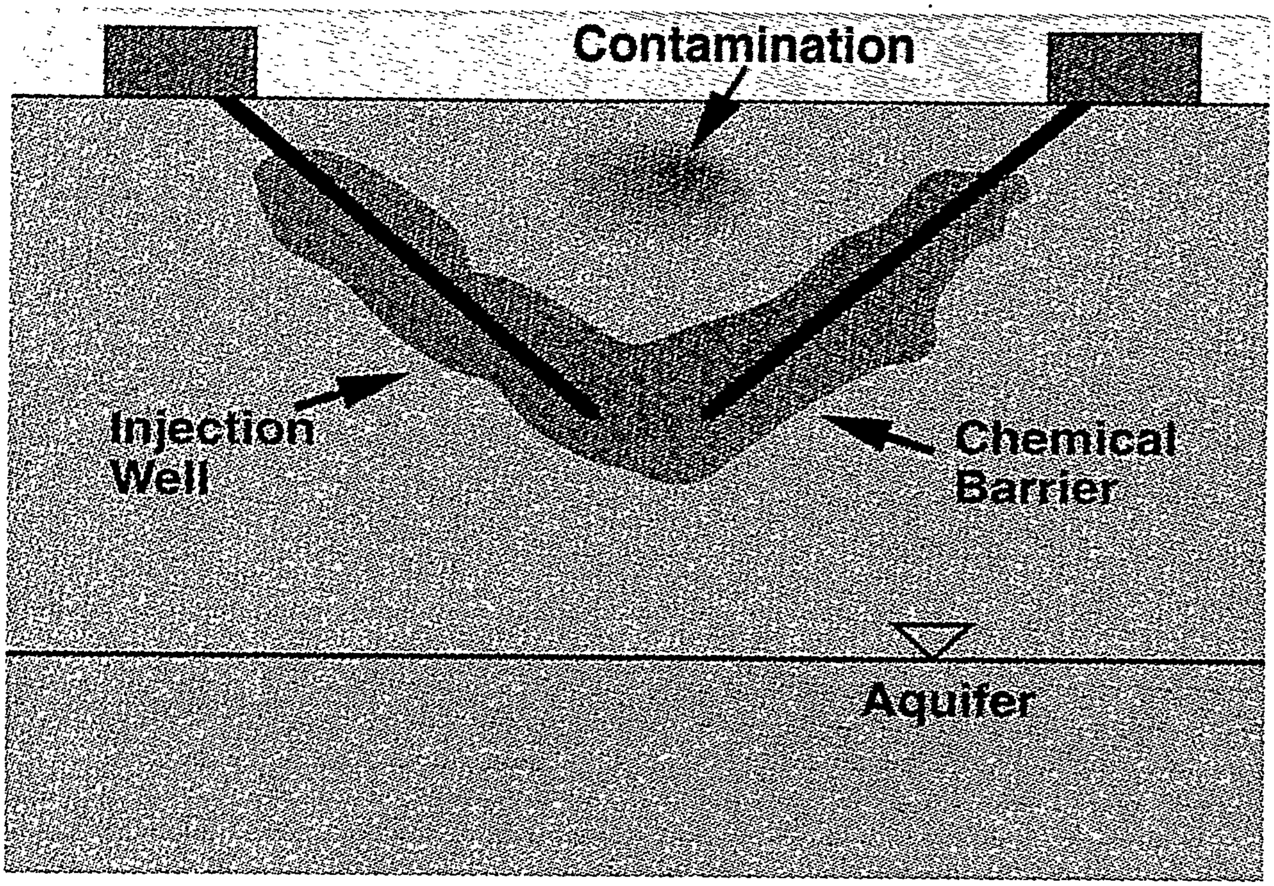
CHEMICALLY ENHANCED BARRIERS TO MINIMIZE CONTAMINANT MIGRATION

TASK DESCRIPTION

This task is developing permeable reactive barriers to be used in aquifer sediments or the vadose zone to minimize contaminant migration. Sequestering agents in the form of barriers that will minimize transport of some of the most mobile contaminants are being evaluated, as are methods to emplace the agents without excavating the waste sites.

Five major task areas must be addressed to develop a useful barrier: 1) identify contaminants of concern; 2) perform literature reviews and conduct scoping experiments to identify suitable sequestering agents; 3) develop adsorption isotherms, adsorption kinetics data, hydraulic conductivity data, and other necessary chemical, physical, and long-term stability data required to design a barrier; 4) design barriers and model performance; and 5) conduct a field demonstration to evaluate performance of the barrier under field conditions.



TECHNOLOGY NEEDS

Much of the U.S. Department of Energy's (DOE) hazardous waste has been disposed to the ground as liquid waste that remains in the unsaturated sediments above aquifers. These contamination points within sediments and near-surface burial grounds serve as a source term that can provide contaminants to the recharge water. Although conventional pump-and-treat or dig-and-treat methods can be used to remove the contamination, these methods are expensive and produce a secondary waste stream. Permeable reactive barriers that do not significantly restrict the flow of groundwater, but selectively remove hazardous components, may be a cost effective substitute for conventional treatment methods. Selective barriers are needed for a range of contaminants, including organic solvents, radionuclides, and toxic metals. For contaminant mixtures, a combination of different barrier materials could be used. This investigation will provide data on a variety of selective sequestering agents and examine emplacement methods that do not require excavation.

ACCOMPLISHMENTS

In Task 1, the most problematic contaminants of concern with respect to groundwater contamination at DOE sites were found to include Sr-90, Cr, chelated Co-60, U, Tc-99, and chlorinated hydrocarbons. A number of DOE sites were identified that are suitable as field demonstration sites.

In Task 2, a number of sequestering agents were identified that have good potential as effective sequestering agents for many of the contaminants of concern.

Currently, the focus of work is on Tasks 3 and 4, which will develop the sequestering agents and complete the engineering calculations for the barrier. Some effort has been applied towards Task 5, which includes a literature review of emplacement technologies, a preliminary field demonstration plan, and meetings with regulators to discuss the acceptability of this technology from a regulatory standpoint. We expect to be ready to initiate a field demonstration by the end of FY 1995. Results of FY 1994 work in Tasks 3, 4, and 5 are described below.

Zeolite Barrier to Contain Strontium

Equilibrium isotherm data for the adsorption of Sr onto three zeolites showed clinoptilolite to be the most cost effective as a barrier material. A preliminary barrier design based on further experimental work with clinoptilolite indicates that a 1.0-m-thick barrier will reduce Sr-90 concentrations in groundwater to zero for 200 years and to less than 0.1% beyond 200 years.

Novel Adsorbents as Potential Barrier Materials for Strontium

The performance of several novel Sr-adsorbents in a simulated Ca-rich Hanford groundwater at 15°C was tested. Among the adsorbents tested were sodium- and silicotitanates, a hydrous titanium oxide, a Sr-selective mica, two commercial zeolites, and a natural zeolite. Tests consisted of a batch kinetic adsorption study followed by an adsorption isotherm after the equilibration period was established. Strontium-85 was used as a tracer. Test results demonstrated significantly higher Kds (1 to 2 orders of magnitude) for the silicotitanates, hydrous titanium oxide, and Sr-selective mica samples than for the zeolite samples. However, it is not clear to what extent the form of the titanate and mica materials (fine powders) relative to that of the zeolites (engineered forms) affected relative performance. The times required to reach equilibrium were surprisingly long (several weeks to equilibrium) and similar for all materials except the mica sample, for which significantly longer periods (>4 months) were required. Again, with the exception of the mica sample, the adsorbents having the highest affinity for Sr also had the highest rates of Sr uptake. The novel adsorbents performed very well and decisions regarding their potential use in barriers may well be based on their cost effectiveness.

Tethered Organic Chelates as a Barrier to Sr Migration

Use of a highly selective chelating agent attached to a tetraalkyammonium cation is being considered as a potential barrier-forming reagent. This sequestering agent could be injected into the subsurface where it will attach to clay particles in the aquifer and greatly increase the sequestering capacity of the surrounding aquifer material. Attempts to synthesize the reagent are now underway. Currently, four of the six synthesis steps have been completed. If the synthesis is successful, the material will be tested for its ability to sequester Sr under typical groundwater conditions.

Mixed Waste Barrier Formed by Injection of Metallic Iron Colloids

A chemically reactive barrier is being developed by injecting a suspension of metallic-iron (Fe^0) colloids into the flow path of reducible contaminants. A time series of batch-type studies was conducted to determine the ability of Fe^0 to chemically reduce a number of highly mobile, oxidized metals into their immobile reduced species. When these contaminants were spiked into Hanford groundwater, Fe^0 filings were able to substantially lower (as much as 4 orders of magnitude) the dissolved contaminant concentrations. These studies also showed that the rate at which these contaminants were removed from the dissolved phase varied between metals in a manner commensurate with thermodynamic consideration, a benefit in terms of modeling and predictive efforts. Further study with various Fe^0 colloids showed interactions between influent colloid concentration and injection flow rate that affect colloid placement in aquifer sediments.

Phosphate Co-precipitation Barrier for Chromate

The co-precipitation of chromate and other anions, such as pertechnetate, sulfate, and selenate with phosphate, may be useful for remediating contaminated groundwaters. The concept involves using slowly soluble sources of phosphate (sodium or calcium-dihydrogen phosphate) and calcium (calcium carbonate) to precipitate an insoluble neutral or basic calcium-phosphate mineral. Contaminant anions present in trace quantities will be co-precipitated as this mineral forms and, because of the mineral's insoluble nature, prevented from re-entering the groundwater. Batch studies under diffusion-controlled conditions have demonstrated the procedure. However, preliminary column studies that attempted to reproduce the diffusion-controlled release of phosphate at Hanford groundwater flow velocities were not successful and suggest the approach is best suited for use in stagnant water-flow regimes.

Hydrotalcite Barrier for Chromate

Adsorption can also be used to remove chromate from groundwaters. Hydrotalcites (layered double hydroxides) are easily synthesized and are effective adsorbents for chromate and other anions in slightly alkaline and alkaline solutions. Batch testing was conducted using several hydrotalcites in solutions ranging in Cr(VI) concentrations from 100 ppb to 30 ppm. Adsorption constants (Kds) from 200 to as high as 1000 mL g^{-1} were observed with a MgAl hydrotalcite. Higher Kds are expected with removal of interlayer carbonate ions. Column studies also showed effective removal of chromate from a simulated groundwater solution for at least 30 pore volumes.

CCl_4 Barriers Composed of Granulated Rubber Tire Material

Initial results indicate that granulated rubber tire will work well as an adsorbent for chlorinated organic compounds. The low cost of this waste product makes its use as a barrier material especially attractive. Some concern has been expressed concerning the potential for this material to release hazardous materials. In a 1989 study by J & L Testing Co., a series of tests was conducted to determine if any hazardous constituents can be leached from granulated rubber tire material. It was found that no constituents in the tire leachates occurred at levels above the drinking water standard.

Emplacement Technologies

Available technologies having potential to be applied for emplacement and monitoring of permeable barriers were reviewed and summarized in a Pacific Northwest Laboratory document. Two emplacement technologies currently being evaluated in more detail are 1) the MecTool™ emplacement method for installing zeolite and other granular materials and 2) installation by injectable colloids (metallic iron in particular).

COLLABORATION/TECHNOLOGY TRANSFER

This investigation will be carried out in collaboration with EBASCO Services, Inc., and Westinghouse Hanford Company, Richland, Washington. In addition, we are working with collaborators from various institutions that will synthesize some test compounds. These include Pennsylvania State University, Eastern Montana College, Sandia National Laboratories, UOP Company, and Allied Signal. Collaboration and funding has also been provided through the Efficient Separations and Processing Cross-Cutting Program.

Data and results from this work will be published in DOE technical reports and journal articles.

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CONTAINMENT OF CONTAMINANTS THROUGH PHYSICAL BARRIERS FROM VISCOUS LIQUIDS EMPLACED UNDER CONTROLLED VISCOSITY CONDITIONS

TASK DESCRIPTION

This task is investigating liquids that, when injected into the subsurface, form nearly inert impermeable barriers through great increases in viscosity. Injecting these liquids into the subsurface through inclined or horizontal wells effectively contains the contaminated zone by entrapping and immobilizing both the contaminant source and the plume. Two general types of liquids are being investigated: 1) colloidal silica (CS), a silicon-based chemical grout; and 2) silicon-based polymers from the polysiloxane (PSX) family.

The CS grouts provide containment through a gelation process. The barrier liquids are injected into the subsurface at ambient temperatures and the sealing gel forms after a controlled gel time. Its containment performance is controlled by the gel time, which depends on pH, temperature, the chemistry of the injected suspension, and the chemistry and

Barrier Liquid Technology, First-Level Field Demonstration
Los Banos, California

mineralogy of the aquifer porous medium. The PSX liquids provide containment through cross-linkage of the injected substances and the formation of a matrix of infinite viscosity. The PSX barrier liquid is a mixture of two fluids that are unaffected by the aquifer or waste chemistry. Its containment performance depends on temperature and the ratio of the two constituents.

TECHNOLOGY NEEDS

Contaminants from buried wastes or from contaminated soils in the vadose zone can be mobilized, forming plumes that migrate toward uncontaminated regions of the aquifer. The source of contaminants can be any kind of underground storage facility that may be subject to leakage and/or leaching. Contaminants cling tenaciously to subsurface materials, particularly clays, and traditional physical extraction methods are slow and ineffective. Excavating the contaminated soils and disposing the soil in protected facilities is an expensive and often impractical solution.

Containment technologies have largely been limited to expensive, invasive approaches involving trenching or cut-off and slurry walls. This investigation is addressing more economical containment methods that may have broad applicability at a wide range of sites.

There are three ways to apply this containment technology. The first, conditions permitting, permanently immobilizes the contaminants by sealing and entombing them in a monolith of inert and impermeable material. With the second method, an inert, impermeable structure is created to surround and isolate the contaminated area, which can be treated at a later time. Alternatively, the structure could enhance or even make possible remediation techniques (such as soil flushing) that mobilize contaminants. The work described here focuses on this use of barriers. Finally, the third method allows permeable aquifer zones to be sealed, thus helping to maximize the effects of traditional cleanup techniques (such as pump-and-treat) in inaccessible and difficult-to-treat less permeable zones.

ACCOMPLISHMENTS

Successful laboratory studies and collaborations with industry and academia have moved this technology to the point of field demonstration in less than 2 years. Alternative processes to alleviate possible effects of soil chemistry on the CS gel time were developed, as were ways to control the gel time and gel texture. Protocols for the sequential injection of CS were designed. Laboratory studies demonstrated the capability to reduce permeabilities to less than 10^{-8} cm/s after two injections. Processes to control the viscosity and gel time of PSX polymers were developed. The PSX crosslinkage times are far less sensitive to the soil chemistry than is CS. Permeabilities could be reduced to 10^{-10} cm/s after a single injection. In collaboration with the manufacturers, new CS and PSX formulations were developed to meet barrier fluid requirements. Preliminary waste compatibility tests concluded that neither CS nor PSX are significantly affected by the types of waste in the Hanford tanks.

Collaborations were established with Bechtel in the area of barrier fluid emplacement, leading to plans for an initial injection test and a field demonstration at a site in California. One of the factors in selecting this site was its similarity to geologic conditions at Hanford. The field demonstration is now under way and will be reported in FY 1995.

COLLABORATION/TECHNOLOGY TRANSFER

While the bulk of the work is conducted at Lawrence Berkeley Laboratory (LBL), there is significant collaboration with other organizations. Texas A&M University in College Station, Texas, is a participant in this study. Their principal responsibility has been to evaluate the performance of barrier fluids in large two-dimensional laboratory experiments using their specialized (dual gamma attenuation) facilities. The University of California Berkeley is involved in the rheological study of polymer-type barrier fluids.

LBL is actively exchanging information and exploring possible collaborations with other private firms, including Bechtel, DuPont Chemicals, Dow-Corning, and Philadelphia Quartz. A collaborative agreement is in place with Bechtel to work on the issue of barrier fluid emplacement. A confidentiality agreement has been established with DuPont Chemicals (Office of Corporate Remediation) to collaborate on the application of CS grouts, and potential future collaborations with DuPont are being discussed. A similar confidentiality agreement has been established with Dow-Corning, the manufacturer of PSXs that have specific initial viscosities and final-product properties. Moreover, the investigators have seen significant interest and received invitations for presentations and discussions from the U.S. Environmental Protection Agency (EPA), the U.S. Navy (Naval Air Weapons Station and Hunters Point Shipyard), the U.S. Army, the McClellan Air Force Base, the Lawrence Livermore National Laboratory, and the State of California (Regional Water Quality Control Board).

The new technologies and corresponding design package will be made available for use throughout the U.S. Department of Energy (DOE) Environmental Restoration program, as well as to other government agencies (EPA and the U.S. Department of Defense). Contamination problems expected to be especially amenable to barrier containment include localized (point-like) sources. Applications include underground storage tanks, buried wastes, and localized sources. Potential DOE sites include Hanford, Idaho, Oak Ridge, Rocky Flats, Savannah River, and Lawrence Livermore. Many industrial sites with point-like contamination problems are also candidates for the application of these technologies.

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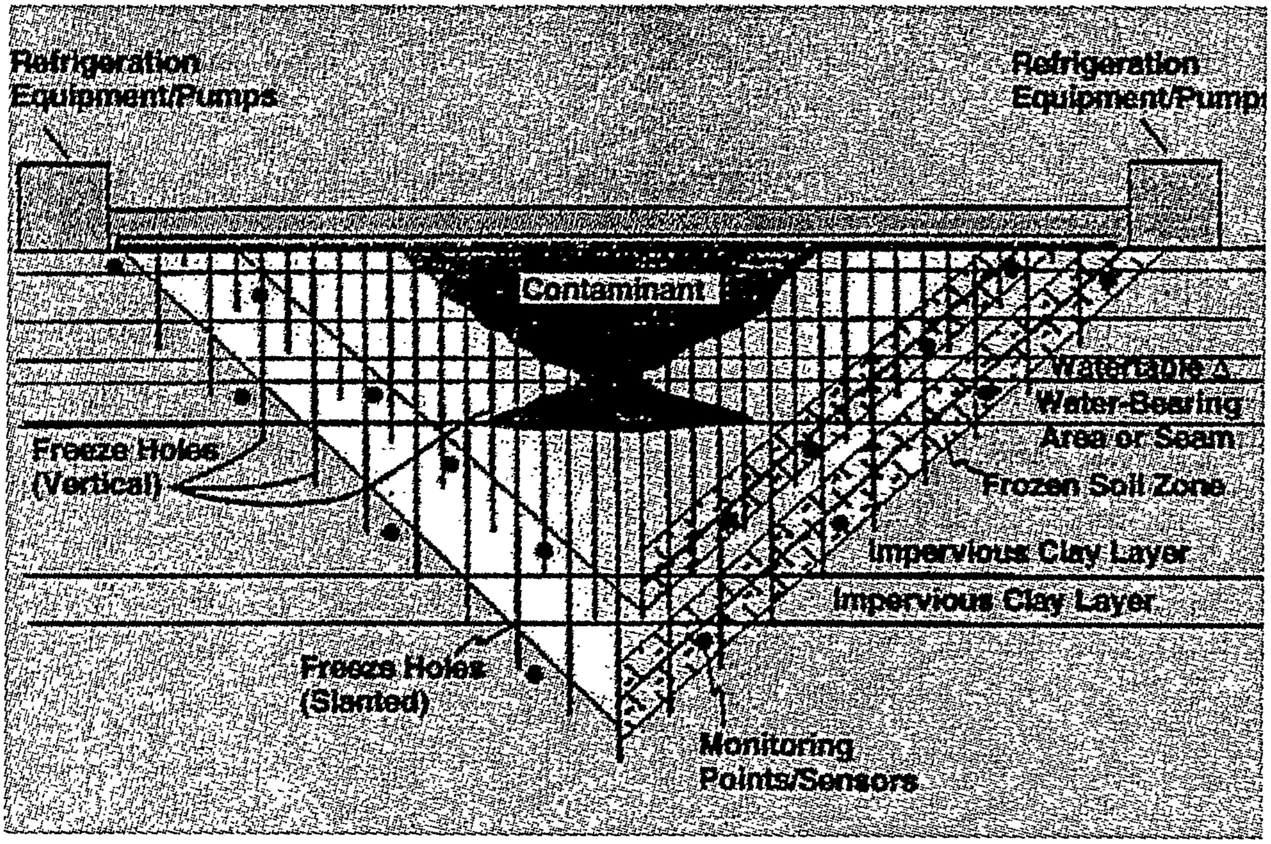
CRYOCELL TECHNOLOGY APPLICATIONS AT NON-ARID SITES

TASK DESCRIPTION

This task is addressing the feasibility of establishing frozen soil barriers to contain radionuclide-contaminated soil in a nonarid setting. Because ground freezing has long been used in civil engineering applications (such as bonding soil to provide load-bearing strength during construction of foundations, and to seal tunnels and mine shafts against groundwater flooding), the foundation of the technology is already established. To form a frozen barrier, series of holes are drilled and refrigerant is circulated. The refrigerant freezes the soil around the holes to create a confined volume, thereby preventing contaminant migration.

The objective of this work is to design, install, and pre-test a soil freezing facility at an uncontaminated site. After successfully completing these objectives, a soil freezing technology demonstration will be performed to show construction of a containment system around an instrumented underground tank and associated piping. Data from this demonstration will be provided for analyzing other possible field applications


Source: Cryocell® - Registered Trademark of RKK, Ltd.

within the U.S. Department of Energy's (DOE) complex. The tests planned include

- a well casing installation test (to maximize the accuracy of freeze pipe placement)
- a barrier diffusion test (to demonstrate barrier integrity)
- a moisture addition test (to verify the ability to adjust moisture content throughout the barrier)
- a test to assess containment of a leaking underground tank
- a soil movement (e.g., heave) analysis both inside and outside the barrier
- a heat grid test to verify the ability of heat pipes to control barrier size
- a freeze pipe heat-transfer test to verify the ability of freeze pipes to remove heat from the soil zone and form overlapping ice columns
- a test to determine computer modeling as a predictive tool.

TECHNOLOGY NEEDS

A frozen soil barrier may meet containment needs and minimize adverse impacts to the environment because

- it uses environmentally benign materials (refrigerants are circulated within a dual tube borehole)
- it does not create unwanted reactions and byproducts in the subsurface
- it provides a means to fully contain waste, without the need for soil excavation (soil disturbance)
- it can be removed by thawing, if necessary
- it offers significant advantages over current containment technologies because it can be repaired in place by adding water if a breach occurs.

Other advantages are minimal operation and maintenance requirements and applicability to a wide range of contaminants.

ACCOMPLISHMENTS

The technology demonstration was performed and completed by Scientific Ecology Group (SEG), under contract to DOE, at a nonhazardous SEG site in Oak Ridge, Tennessee. The dimensions of the frozen soil barrier region were 56 ft x 56 ft (outside) and 33 ft x 33 ft (inside), once the barrier was fully formed. Freeze pipes were installed in a double row to form a V-shaped bathtub with vertical end walls. The sides of the bathtub were formed with freeze pipes installed at 45 degrees. The bottom of the frozen barrier extended to a maximum of 28 ft below grade. Approximate costs for construction, operation (5 months), and maintenance of the ice barrier consisted of the following:

- drilling and piping costs - $50,000
- refrigeration plant (two 40-ton units) rental - $50,000
- equipment mobilization and site preparation - $30,000
- energy costs - $30,000
- field labor for installation - $20,000
- supervision engineering (installation, removal, formation, and maintenance) - $70,000
- design engineering - $20,000
- brine disposal and expendibles - $6,000
- maintenance costs - $6,000.

It should be emphasized that the given costs pertain to an initial demonstration of a previously untested technology being conducted on a nonhazardous site. Cost projections for future demonstrations or projects should consider variances resulting from site soil and contaminant conditions (i.e., radioactive sites/HP coverage, drilling monitoring and cuttings disposal, permitting, drilling costs [Hanford vs. Oak Ridge], etc.).

Tests were performed during freeze barrier installation, formation, and operation. Generalized results of these tests are described here.

Well Casing Installation Test

Inclinometer surveys of 3.5-in. hollow stem, auger-drilled boreholes showed some deviation between the desired and actual location of the freeze piping. To correct this, four boreholes were redrilled.

Barrier Diffusion Test and Leaking Tank Containment Test

The tracer (rhodamine-WT) was restricted to within the confines of the freeze barrier system, indicating barrier integrity within the sand trench area.

Computer Model Validation

Soil temperature monitoring over the performance period indicated an approximate maximum deviation of 20% between theoretical and actual observed temperatures. The actual energy consumption of 420,800 kW-hr showed good agreement with predicted values (approximately 380,000 kW-hr). This indicates that the model would be an effective analytical tool for predicting freeze barrier formation times to the design thickness and shape of the freeze wall.

Soil Movement Test

Based on past experiences with fine-grained soils in civil engineering projects, soil movement was theoretically predicted to be within 1.20 to 2.24 ft during the first 70 days of freezing. This prediction showed good agreement with the observed result of 1.65 ft, indicating that soil movement can be accurately predicted.

Heat Grid Test

Temperature increases in the diffusion testing wells and subsequent temperature equilibrium upon operation of the heat grid system indicates the heat pipes can control the growth of the frozen barrier.

Freeze Pipe Heat Transfer Test

Heat transfer characteristics of the freeze pipes were determined during this test.

In addition to the tests described above, it was determined that additional tests were required to verify the formation characteristics and integrity of the freeze barrier. Electro-potential studies were conducted by Isotron Corporation. These tests, which used the frozen soil's low electrical conductivity properties, showed low ionic transport across the frozen soil barrier. This was determined after conductivity effects caused by ambient temperature, moisture, and brine piping leaks in a nonfrozen surface (approximately 18 in.) were electrically eliminated. This indicates that the barrier would be an effective deterrent to ionic transport. Additionally, the inner area contained by the frozen soil barrier was excavated and ground-penetrating radar (GPR) studies were performed by Massachusetts Institute of Technology, Earth Resources Laboratory. The excavated area and GPR studies showed 1) the inner area was in the predicted formation (V-shaped), and 2) the frozen wall thickness was approximately 15 ft thick in the sand trench area and approximately 5 ft thick in clay-dominated areas.

Laboratory studies for Hanford and Oak Ridge soils concerning barrier formation (moisture addition, etc.) and contaminant diffusion properties were conducted and completed at the University of Washington. These studies demonstrated 1) an effective procedure for producing a barrier of frozen saturated soil, of arbitrary thickness, regardless of the initial soil moisture level (soil pre-freezing and subsequent water injections); and 2) maximum permeability of approximately 4 x 10E-10 cm/s for tests conducted with chromate and trichloroethylene solutions. Tests with cesium-137 showed no detectable diffusion of radioactivity through the barrier, although sorption on the soil grains may have been responsible for the immobility.

COLLABORATION/TECHNOLOGY TRANSFER

Martin Marietta Energy Systems, Inc., will provide project management and SEG will perform the design, construction, and testing of the frozen soil barrier.

SEG and its teaming partner, RKK, Ltd., have significant experience in frozen soil applications from the civil engineering industry. In radioactive and hazardous waste applications, their design and supporting software have received substantial peer review by technical experts.

Assuming a frozen soil barrier can be successfully installed and tested, the technology could then be deployed at contaminated sites across the DOE complex. The initial barrier would also be available as a test bed/barrier within which other researchers could test, develop, and refine new treatment methods, perhaps even using actual hazardous materials.

Contaminated sites under the responsibility of other government agencies (e.g., U.S. Department of Defense) or private industry are also candidates for frozen soil barrier containment technology.

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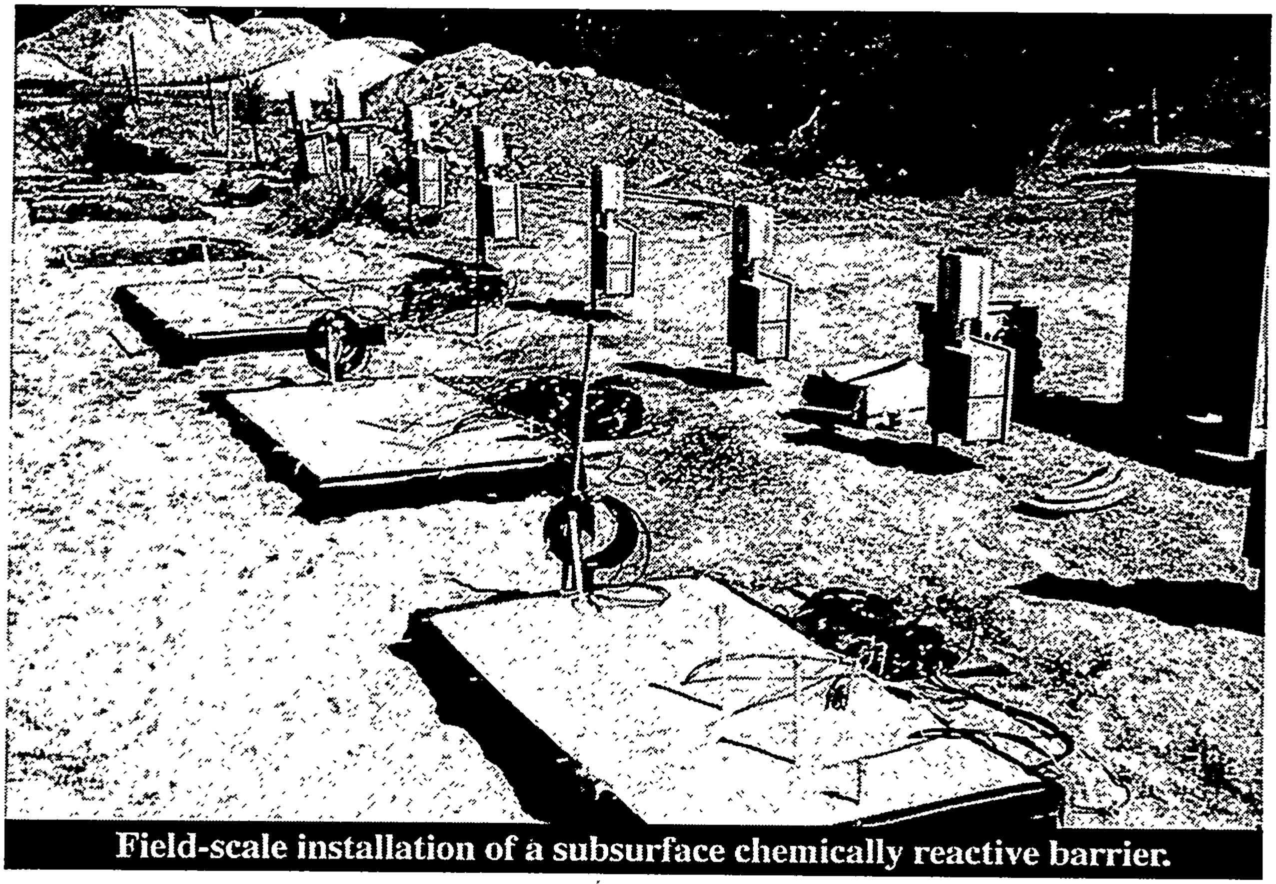
DEVELOPMENT AND TESTING OF A WATER-PERMEABLE REACTIVE BARRIER

TASK DESCRIPTION

This task is developing water-permeable, chemically reactive barriers, coupled with extensive monitoring technology, in integrated environmental containment systems to prevent dispersal of near-surface contaminants. Site closure and post-closure monitoring are regulatory requirements, and it is anticipated that the regulatory environment will become increasingly stringent regarding the discharge of toxic and radioactive mixed wastes. Three potential applications of reactive barriers have been identified for this purpose: containment of sites undergoing characterization and remediation planning, containment of sites undergoing active remediation, and long-term control of residuals. Permeable, reactive barriers have been the focus to avoid requirements for active systems while containing near-surface contaminant dispersal. Integration of common sorptive, extractive, and reactive materials, and gel materials/technology from the petroleum industry, provides broad-ranging capabilities at a low cost for near-term



Field-scale installation of a subsurface chemically reactive barrier.

application. Directly coupled monitoring and tracer activities result in quantitative testing and defensible evaluation of both demonstration experiments and applications.

TECHNOLOGY NEEDS

Numerous materials have been proposed as subsurface chemically reactive barriers to contaminant transport, ranging from peat moss to synthetic silica titanates. While many of these proposals appear promising in laboratory studies, the real world poses many hazards that may decrease or completely destroy a barrier's effectiveness. Unlike in a laboratory, in a field application the barrier will be subjected to meteorological cycles, matrix heterogeneities, biological disturbances (from microorganisms to elk), and imperfections in emplacement. Multicomponent, gel-enhanced barrier materials, chemical tracer characterization approaches, reservoir management technology, and remote monitoring of the hydrologic systems are, therefore, being evaluated in this project in an integrated field-scale system prior to direct application and evaluation on contaminated sites. Evaluation will occur at several different levels, including technical performance, chemical and process engineering, cost-effectiveness (in comparison to alternative technologies such as surface treatment and physical extraction), regulatory action levels, compliance and acceptance, operational safety/risk, quality assurance, and technology transfer.

ACCOMPLISHMENTS

A suite of three permeable-reactive barrier test cells was constructed during the start of this project in late FY 1992. These field-scale experimental systems were developed to allow baseline testing of several relatively simple natural components that had been proposed - zeolite, peat, and clay - subject to environmental conditions typical of the arid west. In addition, several polymer systems were selected from those available and in use in the petroleum industry - Ludox (colloidal silica gel), Floopam (a polyacrylamide), and Xanthan Gum. Of these materials, only the silica gel and Floopam were available in time for emplacement during test cell construction. The test cell systems focused evaluations in two major areas: 1) could relatively small amounts of simple extractive materials and gels provide an effective, easily and consistently emplaced barrier for a range of low-level contaminants, and 2) would the gels provide substantial structural stability and potential for chemical enhancements in the widely variable near-surface environment? The physical testing of barrier mixtures and components and hydrologic testing of the field-scale experimental cells were the focus of this study. Since their emplacement, these barriers have been subjected to temperatures ranging from -15°C to 35°C, rain (including summer monsoons), up to 60-cm snowpack, and repeated elk and rodent activity. Conservative and reactive tracer flow is carefully controlled across the barriers, while an array of transducer-equipped sampling ports, time domain reflectometry probes, and thermistors provides detailed data on conditions within the cells. Ongoing field and laboratory measurements quantify extended-term hydraulic and chemical behavior of the barrier materials.

At the conclusion of the studies, controlled excavation and laboratory testing will provide detailed information on the chemo-mechanical behavior. The field test cells are providing essential demonstration, evaluation, and testing capabilities generally applicable to installation and acceptance/compliance in an actual remediation situation. In particular, test cell activities provide important information on strategies for characterizing and monitoring field applications.

Potential applications of permeable-reactive barrier technology, emplacement techniques, and general regulatory acceptance have been evaluated. Field and laboratory test plans were developed and implemented in FY 1994. Test results from the field-scale systems, coupled with laboratory comparative survey results on a broader variety of commercially available extractive materials, provide the basis for selection or elimination of permeable-reactive barrier approaches for specific DOE and industrial sites and contaminants. Selected DOE sites presently undergoing characterization are being evaluated for pilot-scale implementations and permitting. Combination strategies are particularly emphasized in defining such implementations.

Qualitative evaluation of the physical condition and stability of gel materials that were subjected to saturated, variably saturated/unsaturated and surface conditions over 2 years, and to seasonal cycles, confirms laboratory indications of moderate-term stability for field implementations. Organic gels proved to be a stable, yet hospitable, environment for natural biologic activity. Multicomponent tracer tests of barrier hydrologic and reactive properties demonstrated consistent properties over the experimental period. Metal contaminant tracers (slightly to moderately interacting), however, failed to be mobilized through the test cells to the barrier system, indicating significant operational complexities in scale-up and pilot-scale field testing. Similarly, the long-term stability of commercial monitoring probes proved to be limited in these semi-saturated systems.

The full suite of data developed for relatively simple contaminants provides a baseline to define approaches to characterize reactive-permeable barrier systems for more complex environments, including those with contaminants at very low levels and posing complex/expensive analytical and handling requirements (e.g., actinides). Pilot-scale testing opportunities are developing in parallel with characterization and evaluation activities at a range of U.S. Department of Energy and industrial sites.

COLLABORATION/TECHNOLOGY TRANSFER

This effort has relied on close linkages to industry and university collaborators. Dupont researchers participated early in providing Ludox and expertise in gel production. Pfizer Oil Field Chemical provided information from their previous development efforts on polymers and cross-linkers for petroleum applications. Cross-linking using aluminum instead of chromium appeared reasonable. In contrast to requirements for staged injections in petroleum reservoirs, which has limited aluminum cross-linker applications, our trench-based approach allowed mixing and initial gel formation before emplacement of the barrier. In addition, the aluminum cross-linked gel is softer, providing a more stable and flexible barrier system based on laboratory experiments and field observations to date.

Continued progress with characterization and regulatory plans at Los Alamos have resulted in definition of problems that are opportune for near-term evaluations of permeable-reactive barrier approaches. In particular, cesium and barium near-surface groundwater contamination have been singled out for evaluation this year based on site-driven needs. We are also working closely with principal investigators developing enhanced extractants and are particularly building on experience with silica titanates for cesium, so that direct comparisons for permeable barrier applications can be made to simpler natural materials. In addition, we have participated in compiling information on potential barrier approaches as part of a report for the Rocky Flats Technology Office.

A series of additional information exchanges is ongoing. Discussions and exchange visits with Scientific Ecology Group personnel led to the definition of potential linkages with soil washing systems as either a parallel approach or a barrier material recycling approach and the identification of significant overlap in process characterization needs. Discussions and exchanges of information with Rocky Mountain consultants regarding previous experiences and lessons from slurry wall environmental applications has continued to enhance our understanding of current and past industry practice. Similarly, discussions with personnel from Law Environmental, Mission Research, Inc., and Harding Lawson Associates provided valuable information and identification of options for conventional trench emplacement, cassette systems for trench emplacements, and enhancement of jet grouting and directed hydrofracture as potential specialized emplacement approaches, among others.

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DEVELOPMENT OF FROZEN SOIL BARRIERS FOR ARID SITES

TASK DESCRIPTION

This task is addressing the feasibility of using frozen soil barriers (ground-freezing technology) to contain hazardous and radionuclide-contaminated soil in an arid setting. The first phase is a laboratory-based investigation of containment of frozen water in soil, including the behavior of associated solutes, transport mechanisms through unfrozen water films or pockets, mechanical effects such as heave, and other freezing-related processes. Assuming favorable results from the laboratory-scale investigation, a frozen soil barrier will be installed at an uncontaminated site. Installation involves drilling to install pipes through which refrigerant is circulated. The holes are positioned to create a confined subsurface volume as the soil around the boreholes freezes.

A critical aspect of this project is the successful, controlled addition (and removal) of water to the unsaturated subsurface to create the barrier. Water movement in response to 1) the negative pore pressures of the unsaturated zone and 2) thermal gradients around freeze pipes

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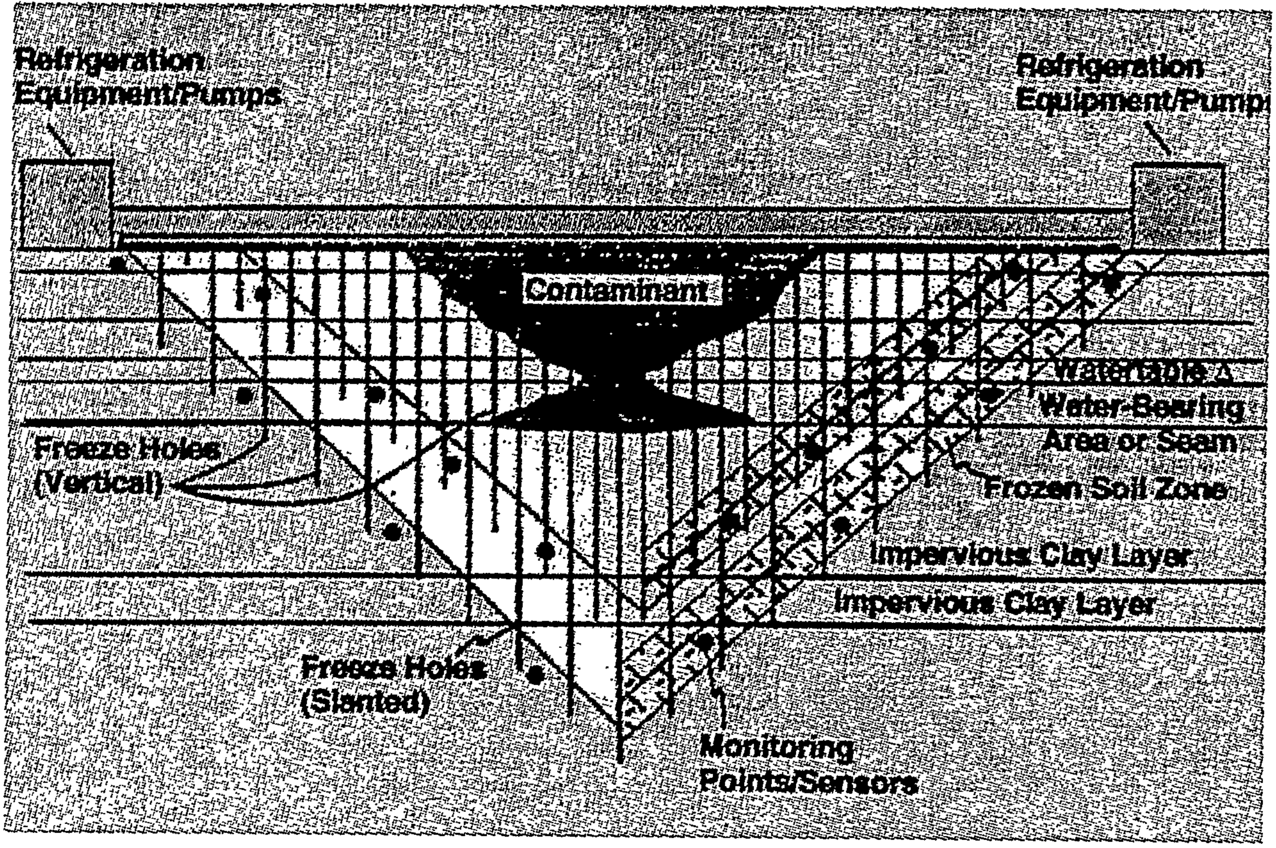

complicates barrier formation beyond that of a saturated site. Upon completion, the project must establish capability for removing water to prevent contaminant migration should that be a requirement in the technology's future use at unsaturated contaminated sites. Assuming the successful addition of water, barrier integrity/performance would then be evaluated by means of tracer tests, monitoring thermal conditions, and other suitable methods.

Furthermore, the barrier would then be available as a test bed other investigators could use to conduct studies of hazardous waste treatment technologies.

TECHNOLOGY NEEDS

Many of the U.S. Department of Energy's (DOE) contaminant sources (e.g., landfills, dry wells, evaporation ponds, etc.) are located in arid climates and are typically far above the natural groundwater level. Frozen soil barriers are thought to be useful in providing containment at these sites. However, most experience with their hydraulic performance is associated with natural, fully saturated environments. Under arid conditions, performance may be affected by the need to first create full saturation (i.e., achieve near-zero air porosity), then maintain this condition under the frozen state. This project will examine potential performance factors arising from arid site conditions and evaluate specified measures to mitigate or minimize adverse effects.

ACCOMPLISHMENTS

Laboratory-scale studies have been completed by Michigan State University. Permeability measurements of frozen sediment were made for a wide range of moisture conditions and in the presence of solutes. Methods to increase the moisture content of the frozen barrier were tested. A final report on the laboratory activities was completed.

SCHEDULE OF DEVELOPMENT

Laboratory-scale testing will be completed in FY 1994. Based on the laboratory results, a decision will be made on whether or not to proceed with a field demonstration.

COLLABORATION/TECHNOLOGY TRANSFER

Project scientists are working with Hanford personnel so that laboratory-scale results will meet the needs of EM-30 for containing waste from underground storage tanks.

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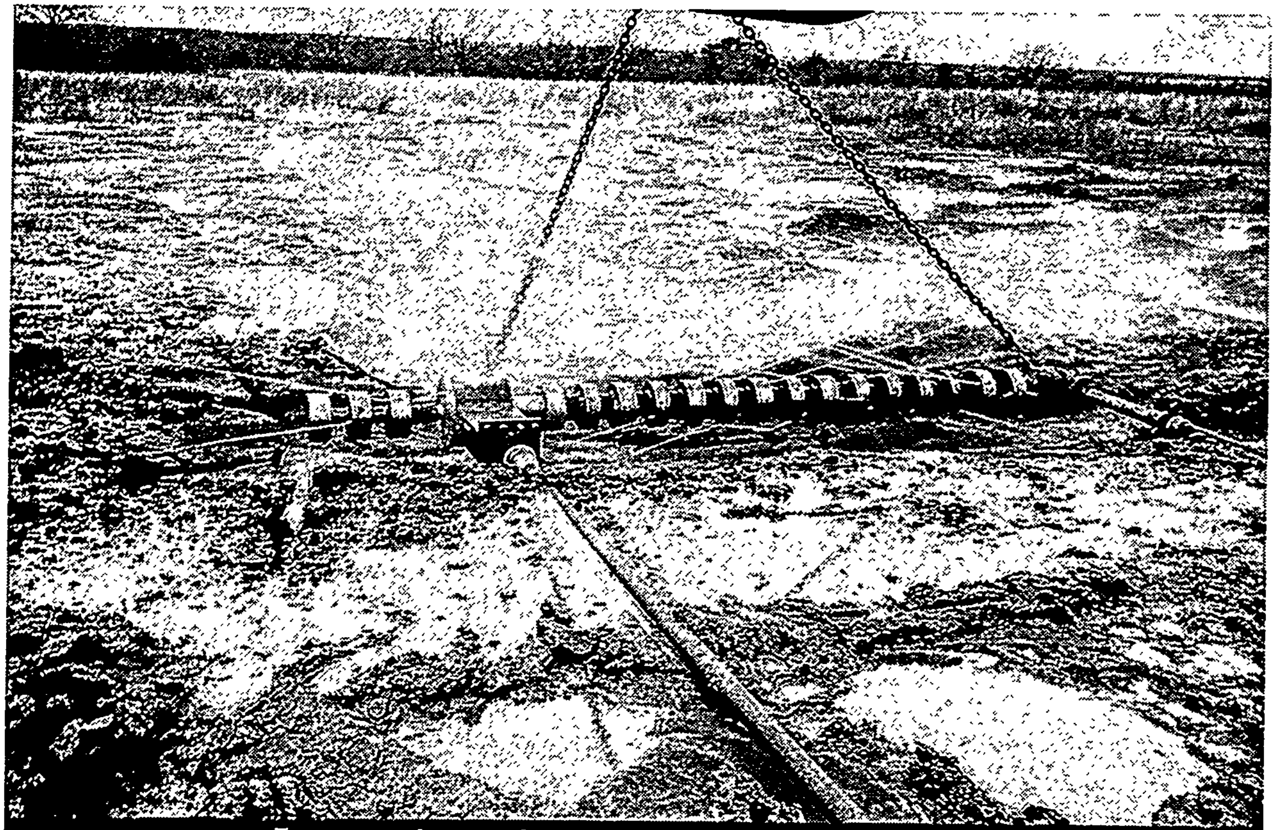
DEVELOP/DEMONSTRATE METHODS OF PLACING A HORIZONTAL IN SITU GROUT BARRIER

TASK DESCRIPTION

This task examines a method of in situ emplacement of barriers beneath a waste site. The process begins with two horizontal drill holes curving down from the surface at one end of the area, passing beneath the waste, and returning to the surface at the other end. The drill stem threaded through the hole is attached to a winch or tractor. At the opposite end, jet grouting equipment is attached to the drill stem and connected to jet grouting pumps.

The jet grouter itself is a hydraulically driven injector/mixer that leaves a soil-grout mix in a slab about 10 ft wide and 1.5 ft thick.

The investigation is focusing on laying a series of four strips and joining the edges into a contiguous sheet, forming a horizontal barrier or containment floor. Emplaced panel strips will be excavated and tested for gaps or zones of inadequate grout-soil mixing. Additional development may address widening the panels and



Jet grouting to form a subsurface grout barrier.

placing this type of barrier in soils with rock fragments and other characteristics that restrict grout tool movement and/or complete mixing.

TECHNOLOGY NEEDS

Temporary or long-term containment of mobile contaminants from existing waste sites requires effective surrounding barriers. Vertical barriers are relatively well known from standard construction project work, but methods for building horizontal barriers in situ have not been developed. For old sites, the problem is to place a containment barrier without disturbing the waste. Any excavation of the waste represents additional health and regulatory problems that are both expensive and difficult to solve.

A technology that allows barrier construction with minimal waste, is amenable to changes in barrier materials, and works in a wide variety of soil matrices would be a powerful tool for site containment and remediation.

ACCOMPLISHMENTS

- A single-pass panel 1.5 ft x 12 ft x 100 ft has been designed and emplaced at a depth of 12 ft.
- The panel has been excavated and the workability of the concept has been verified.
- Prototype equipment for making a larger panel has been designed, manufactured, and field tested.
- Lessons learned from the prototype testing were incorporated into improved tools which have been manufactured and shop tested.
- Surface support equipment for supplying grout and moving the tooling has been field tested.
- The grout design has been selected and a test plan has been approved.
- Special test equipment/apparatus (tiltmeters and infiltrometers) have been built and tested.
- A work plan to install a multiple panel horizontal barrier has been approved. The multiple panel will be installed at Fernald in FY 1995.

COLLABORATION/TECHNOLOGY TRANSFER

This work will be supported through collaboration with the technology owner, Halliburton NUS, with consulting support on grout and barrier materials from Brookhaven National Laboratory. Performance testing of the emplaced panels will be performed by the University of Cincinnati.

Potential users of this technology are widespread throughout the U.S. Department of Energy's (DOE) complex and the country. A method for in situ emplacement of horizontal barriers is needed for the waste sites and tanks at Hanford. The technology may also have applications to the waste pits at Fernald.

Because the need is so widespread, this technology is readily transferable for application to containment problems outside DOE as well. Uncontrolled dump sites, leaking chemical and fuel storage tanks, and engineered but failing waste disposal facilities represent additional opportunities for this in situ containment system.

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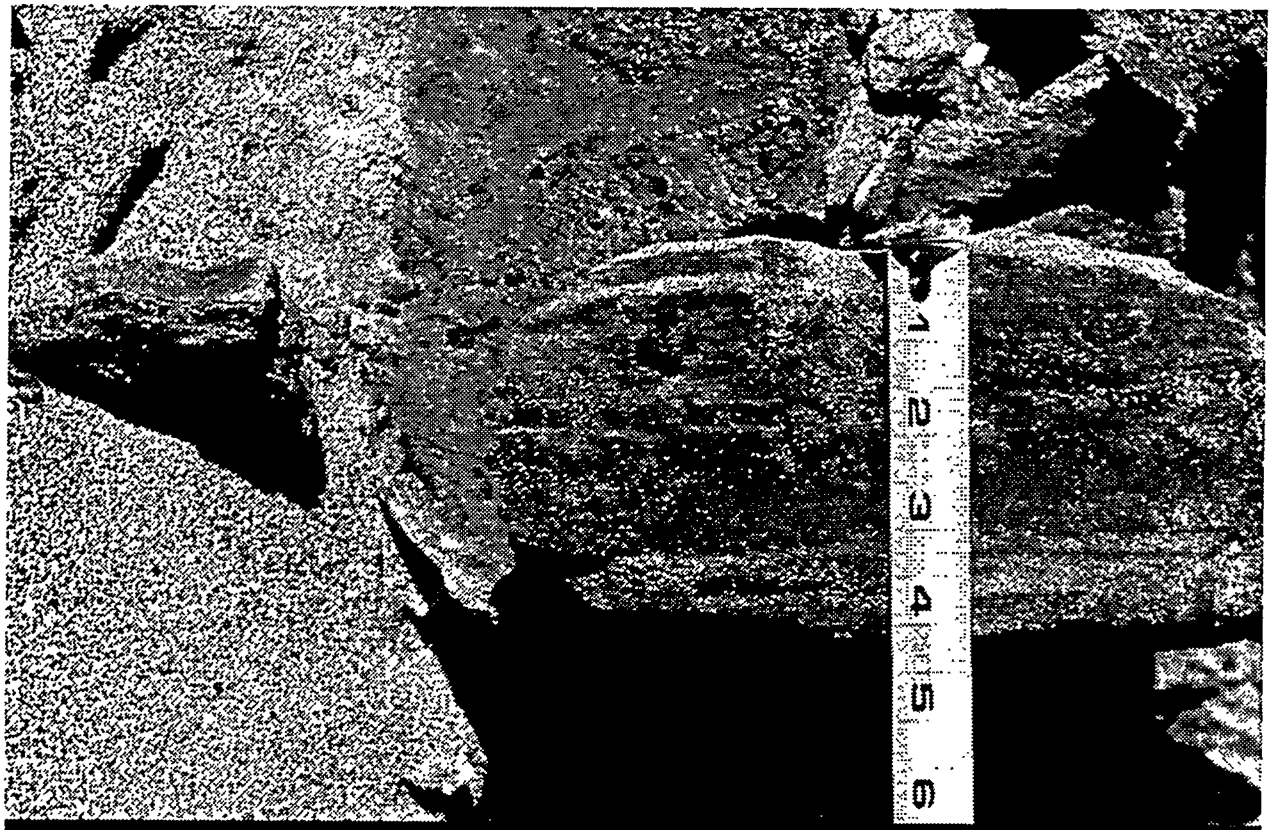
EVALUATION OF TWO NEW FLOWABLE GROUT TECHNIQUES FOR IN SITU BARRIER CONSTRUCTION

TASK DESCRIPTION

This task is evaluating the potential application of two new grouts as barrier materials for U.S. Department of Energy (DOE) sites: a mineral wax/bentonite emulsion developed in Germany (montan wax) and a glyoxal-modified sodium silicate grout developed in France. The montan wax was developed by two German companies, MIBRAG and DBI, with over $9M invested in product development and testing, including three field-scale pilot studies performed in Germany. The sodium silicate grout was developed by the French chemical company Société Française Hoechst. No field tests for the suitability of this grout as a barrier have been performed before this study, but the grout had been used extensively as a soil strengthener. Because these materials are being used abroad in various grouting applications, regulatory and public acceptance of this barrier technology within the United States should be rapid.



Layer of montan wax injected to form a barrier in a section of soil.

The evaluation involves both laboratory and field tests. The laboratory phase was completed in FY 1993 and involved grout injection experiments with soils from several DOE sites to evaluate the effectiveness of the grouts in reducing hydraulic conductivities of unconsolidated soils under ideal conditions. Soil samples from three Integrated Demonstration (ID) sites were used in the tests: the Buried Waste ID at Idaho National Engineering Laboratory (INEL), the Underground Storage Tank ID at Hanford, and the Mixed Waste Landfill ID (MWLID) at Sandia National Laboratories (SNL). The laboratory program also evaluated the compatibility of the grouts with common types of industrial and hazardous wastes.

The field tests are being conducted in two phases: single-borehole injection tests begun in FY 1993 and a multiple-borehole injection test performed in FY 1994. The single-borehole tests were performed in unsaturated soils at SNL in conjunction with cement grout injection studies conducted by SNL as part of the MWLID. The first phase involved relatively small-scale injection tests to evaluate permeation characteristics of the grouts in a range of soil types and conditions. Multiple-borehole tests were performed at a site adjacent to the City of Richland, Washington, Municipal Landfill in FY 1994. The objective of the multiple-borehole tests was to demonstrate the feasibility of constructing a subsurface barrier using permeation grouting methods. Technical challenges include lateral permeation within soils to form horizontal barriers, physical and hydrologic stability of the barrier over time, and the regulatory acceptance of the overall approach and grout materials.

TECHNOLOGY NEEDS

A groundwater/pore-water flow control system is needed that can be injected from the surface and will form within the aquifer or vadose zone, thereby eliminating the need to excavate trenches and construct barriers. A material that is resistant to deterioration from soil, groundwater, and contaminant chemistry would meet significant waste site remediation needs throughout the complex.

This investigation is examining some currently available injectable grouts that have shown promise for this application in Europe. The feasibility of using conventional grout permeation methods to place a barrier and the resistance of the materials to waste components are the focus of this study.

ACCOMPLISHMENTS

A preliminary laboratory assessment of grout penetration characteristics was completed for both the montan wax and sodium silicate grouts using soils from several DOE sites. The reduction in permeability resulting from grout penetration was quantified for the soil samples.

Several small-scale injection tests were performed under field conditions at SNL's MWLID site, with permeation of grout confirmed. The tests indicated that both the montan wax and sodium silicate grouts can be emplaced in unconsolidated vadose zone soils with conventional grout permeation methods, provided the soils have sufficiently high permeability. The minimum hydraulic conductivity for permeation grouting appears to be around 5 x 10^{-4} cm/s for both grouts.

Downhole geophysical methods were used to track the movement of grout away from the injection boreholes. The results are consistent with soil samples collected during post-test characterization.

Two reports were issued: *Laboratory Test Results for Evaluating the Performance of Montan Wax and Sodium Silicate Barrier Materials in Unconsolidated Soils* and *Preliminary Results of Permeation Tests using Montan Wax and Sodium Silicate Barrier Materials in Unconsolidated Soils at the Mixed Waste Landfill Integrated Demonstration Site (MWLID).*

Final agreements between DOE and the technology vendors on licensing and non-disclosure have been secured.

A Test Plan was issued entitled *Multiple-Borehole Permeation Tests Using Montan Wax and Sodium Silicate Grout Materials in Unconsolidated Soils Adjacent to the City of Richland, Washington, Municipal Landfill.*

Multiple-borehole tests were performed on City of Richland, Washington, property adjacent to the municipal landfill. Both montan wax and sodium silicate grouts were used in the test program. The primary goal of the test was to place continuous horizontal grout barriers. Geophysical data were obtained during the tests and are under evaluation at this time. Initial data suggest that permeation grouting with the montan wax did not achieve a laterally extensive barrier. Indications are that other placement methods besides permeation grouting would be more successful in producing a laterally extensive barrier. Other emplacement methods are being considered.

SCHEDULE OF DEVELOPMENT

Post-test characterization and data evaluation for the multiple-borehole tests will be performed in FY 1995. A summary report of the multiple-borehole tests will be prepared.

COLLABORATION/TECHNOLOGY TRANSFER

This project is being carried out by Golder Federal Services, Inc., in cooperation with the European grout licensees MIBRAG (Germany) and Société Française Hoechst (France). The materials were identified through the International Technology Exchange Program. Results will be made available through this and other international efforts.

Site treatment at landfills and underground storage tank sites at Hanford, Oak Ridge, Savannah River, Fernald, and INEL may benefit from these relatively advanced technologies. Other potential users include a number of U.S. Department of Defense sites with leaking underground storage tanks and industrial facilities such as refineries and fuel terminals. The single-borehole injection tests were conducted at SNL's MWL. The multiple-borehole injection tests were conducted at a site adjacent to the City of Richland, Washington, Municipal Landfill.

With DOE's assistance, this technology should mature rapidly. The German company is searching for an American affiliate to manage applications in North America. The French group has a United States division to manufacture and distribute its grout formulation. Rapid transfer to the private sector is anticipated.

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HYDRAULIC AND DIFFUSION BARRIERS IN THE VADOSE ZONE SURROUNDING BURIED WASTE

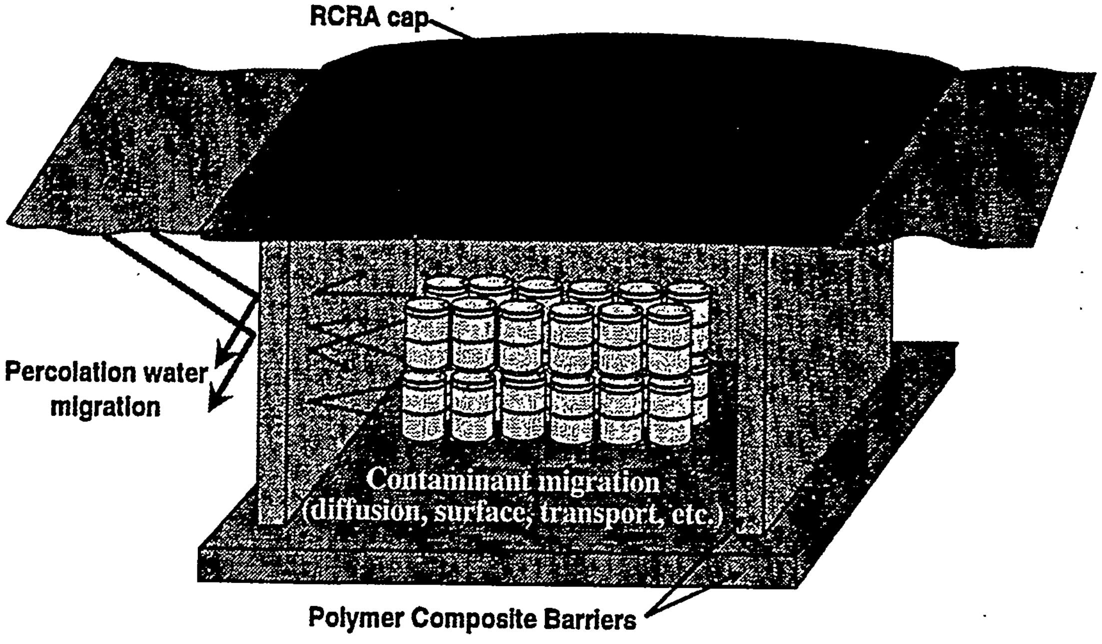
TASK DESCRIPTION

This task is developing advanced polymer barrier materials for use as subsurface barriers and investigating the materials' durability and performance under typical waste site conditions. As part of this work, methods to verify complete placement of a subsurface barrier are also being developed. "Placement verification" is defined as determining what, if any, breaches (gaps, cracks, etc.) exist in the barrier following its installation and curing time.

Formulation studies have optimized aggregate type/quantities (stone, crushed glass, and sand) and the binder used to produce the study samples. Formulations that can be placed vertically and horizontally using conventional construction methods have been developed.

The materials evaluated for this application include sulfur polymer cement, vinylester styrene, polyester styrene, furfuryl alcohol, a high molecular weight acrylic, and asphalt. The performance of these materials was compared to that of a typical

Hydraulic and Diffusion Barriers



Portland concrete used in hydraulic dams. Bench-scale samples of each material were evaluated for their permeability to water, ionic (chloride) diffusivity, wet/dry cycling, and chemical resistivity to acid, base, and solvent conditions. Compressive, tensile, and flexural strengths were also measured as indicators of the structural integrity of a monolithic barrier wall. Tests indicate good performance and durability characteristics can be achieved.

TECHNOLOGY NEEDS

Contaminated soils, buried waste, and leaking underground storage tanks (USTs) pose a threat to the environment because of the potential for contaminant migration from these buried waste sites. One option to control contaminant migration is to construct a subsurface barrier consisting of a wall of low permeability material that completely surrounds the waste site. Using subsurface barriers instead of dig-and-retrieve methods can reduce exposure by several orders of magnitude, also reducing remediation costs by many millions of dollars compared to retrieval and treatment alternatives. Interim subsurface barriers can also provide waste management operations sufficient time to evaluate and select appropriate remediation alternatives. As an example, many USTs within the U.S. Department of Energy's (DOE) complex are currently leaking or are estimated to lose their integrity soon. These tanks can be surrounded by subsurface barriers to prevent contaminant plumes from migrating until tank operations or tank physicochemical conditions can be addressed. Vertical barriers will enhance treatment methods by removing pathways for contaminant transport caused by water infiltration, vapor- and gas-phase transport, transpiration, etc. In addition, subsurface barriers can be used to direct contaminant movement to collection sumps/lysimeters or treatment zones.

Portland cement grout curtains have been used to form barriers around waste sites. However, large castings of hydraulic cements invariably crack because of shrinkage and thermal stresses induced by the hydration reactions. Because the permeability of Portland-based grout cannot be assured, this material is undesirable as a construction material for waste site barriers. Other low permeability, high integrity materials are needed to form subterranean barriers.

ACCOMPLISHMENTS

Brookhaven National Laboratory (BNL) has investigated the regulatory issues, assumptions, and drivers associated with using barriers and advanced polymer systems around buried waste sites and has issued a summary report.

During FY 1994, BNL completed a review and feasibility study of barrier verification technologies. Verification is required to determine what, if any, breaches (gaps, cracks, etc.) occur in a barrier after installation and curing. Existing waste site monitoring methods were reviewed for their applicability to barrier placement verification. BNL also determined the feasibility of using existing technologies not originally designed for waste site or subsurface monitoring. For example, perfluorocarbon tracers developed at BNL for atmospheric studies are detectable at extremely dilute concentrations and their use has been accepted by regulatory agencies. BNL proposes to inject small amounts of such materials on the inside of the barrier and use a series of detectors external to the barrier to detect the tracer. This method will identify leaks and thereby verify barrier integrity and performance.

Also during FY 1994, BNL developed formulations and characterized the performance and durability of several polymer systems for use in subsurface barriers. Formulation and optimization of 18 barrier materials, sample fabrication, preliminary testing, and final testing were completed. A final report was issued. Testing indicates good performance and durability characteristics have been achieved, and polymer materials have been shown to be durable under a wide range of waste site conditions. The final database of polymer barrier materials provides a wide range of material choices for hazardous, low-level radioactive, and mixed waste landfills. Polymer materials are available to meet most, if not all, the DOE-complex performance requirements and environmental conditions. The final database was the subject of an expert review panel workshop that included BNL, DOE, and industry personnel. The BNL polymer barriers program is now ready for the demonstration stage.

SCHEDULE OF DEVELOPMENT

BNL is in the final planning stages of a full-scale field demonstration of subsurface barriers using polymers. In conjunction with several collaborators, the project will develop and demonstrate a close-coupled, engineered subsurface barrier system to contain waste forms. A close-coupled barrier system consists of a primary and secondary barrier. The primary barrier is closest to the waste form and is composed of a low viscosity material having outstanding resistance to the waste constituents. The secondary barrier provides secondary containment in case the primary barrier leaks. The targeted waste forms include hazardous and mixed landfills, leaking underground storage tanks, underground nuclear fuel cycle waste storage and disposal tanks, hazardous waste piping, and trench or evaporation disposal pits and ponds.

The demonstration will emplace a low permeability barrier beneath a simulated waste site without disturbing the waste form, evaluate stresses induced on the waste form during emplacement, and conduct subsequent barrier integrity evaluations. The containment will be a multibarrier of a cementitious grout followed by a polymer grout. The two grouts will be close-coupled to bond the polymer barrier to the cementitious barrier. The project will demonstrate at field-scale that a close-coupled barrier can be installed for halting or substantially slowing the migration of mobile waste contaminants from a waste site.

Following the barrier installation, BNL will conduct performance verification testing to evaluate the barrier. Such testing will verify the success of the barrier demonstration in duplicating the performance achievements of laboratory studies. Following the performance verification activities, intrusive verification may be conducted. Samples may be cored from the primary and secondary barriers for laboratory testing, and the site will be excavated and visually inspected.

Laboratory testing of core samples will include tests of unconfined compressive strength, hydraulic conductivity, wet-dry cycling, rapid chloride penetration (diffusivity), and chemical resistivity. Testing will be conducted by BNL.

COLLABORATION/TECHNOLOGY TRANSFER

The field test is planned to include the following participants:

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Technology transfer will include a final report detailing the demonstration results. Additional technology transfer will include publication and presentation of information at symposia and society meetings.

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SECTION 4.0

HOW TO GET INVOLVED

WORKING WITH THE DOE OFFICE OF ENVIRONMENTAL MANAGEMENT

The U.S. Department of Energy (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, management, and operating contractors, the Office of Environmental Management (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

EM will facilitate the development of subcontracts, research and development (R&D) contracts, and cooperative research and development agreements (CRADAs) 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 nonfederal 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 is 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 acquisition policy and strategy supporting environmental management technology development that uses phased procurements to span the research, development, design, testing, and evaluation continuum from applied R&D concept feasibility through full-scale remediation. DOE EM-phased procurements make provision for unsolicited proposals, but a formal solicitation is the preferred response. The principal 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 design, testing, and evaluation 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 CRADAs. 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 *Financial 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 CRADAs.

EM awards grants and CRADAs if 51% 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 United States' 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 United States' 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 nondisclosure 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 business 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 Program Office and interfaces with other DOE small business offices as well.

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