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Technology Development In Situ Remediation Integrated Program

Annual Report

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OFFICE OF TECHNOLOGY DEVELOPMENT
IN SITU REMEDIATION INTEGRATED PROGRAM

Preface

The Department of Energy (DOE) established the Office of Technology Development (EM-50) as an element of Environmental Restoration and Waste Management (EM) in November, 1989. EM manages remediation of all DOE sites as well as wastes from current operations. The goal of the EM program is to minimize risks to human health, safety and the environment, and to bring all DOE sites into compliance with Federal, state, and local regulations by 2019. EM-50 is charged with developing new technologies that are safer, faster, more effective and less expensive than current methods. The organizational structure of EM-50 is shown in Figure 1. The In Situ Remediation Integrated Program (the subject of this report) is part of EM-541, the Environmental Restoration Research and Development Division of EM-54.

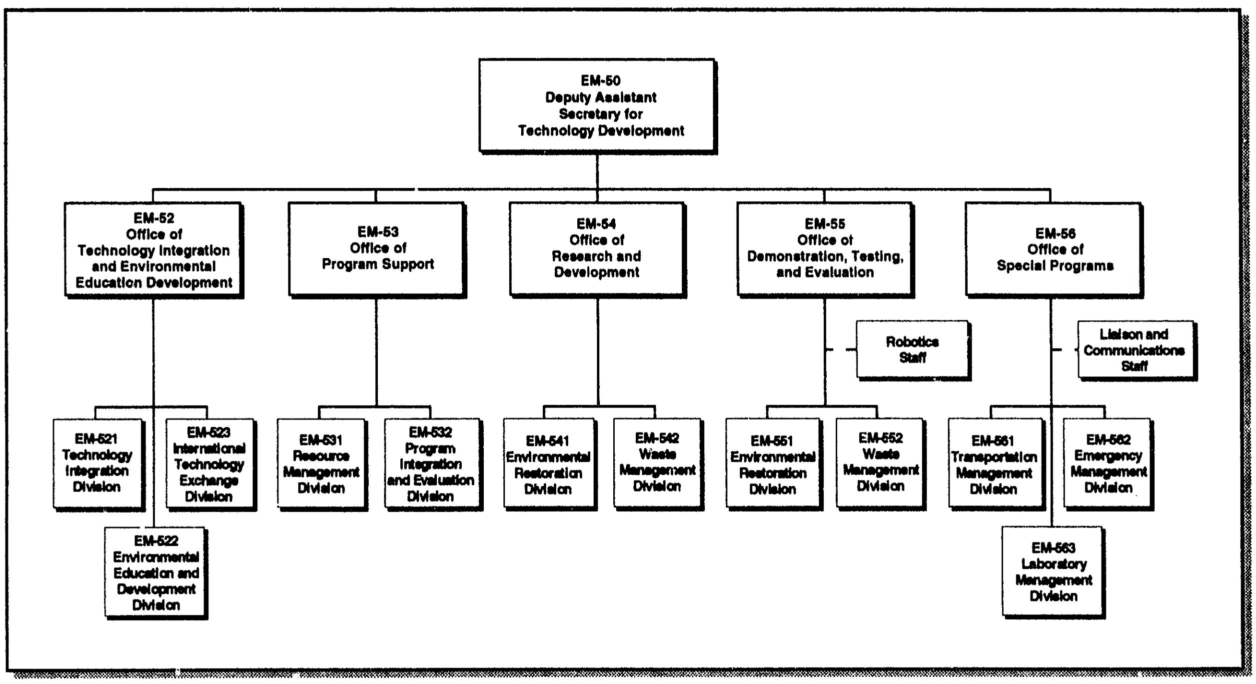

Figure 1. EM-50 Organizational Structure.

IN SITU REMEDIATION INTEGRATED PROGRAM ANNUAL REPORT

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IN SITU REMEDIATION INTEGRATED PROGRAM OVERVIEW

PURPOSE

The In Situ Remediation Integrated Program (ISR IP) was instituted out of recognition that in situ remediation could fulfill three important criteria:

- Significant cost reduction of cleanup by eliminating or minimizing excavation, transportation, and disposal of wastes;
- Reduced health impacts on workers and the public by minimizing exposure to wastes during excavation and processing; and
- Remediation of inaccessible sites, including:
  - deep subsurfaces
  - in, under, and around buildings.

Buried waste, contaminated soils and groundwater, and containerized wastes are all candidates for in situ remediation. Contaminants include radioactive wastes, volatile and non-volatile organics, heavy metals, nitrates, and explosive materials. The ISR IP intends to facilitate development of in situ remediation technologies for hazardous, radioactive, and mixed wastes in soils, groundwater, and storage tanks. Near-term focus is on containment of the wastes, with treatment receiving greater effort in future years.

TECHNOLOGY NEEDS

ISR IP is an applied research and development program broadly addressing known DOE environmental restoration needs. Analysis of a sample of 334 representative sites by the Office of Environmental Restoration has shown how many sites are amenable to in situ remediation:

- Containment 243 sites
- Manipulation 244 sites
- Bioremediation 154 sites
- Physical/Chemical Methods 236 sites

This needs assessment is focused on near-term restoration problems (FY93-FY99). Many other remediations will be required in the next century. The major focus of the ISR IP is on the long term development of permanent solutions to these problems. Current needs for interim actions to protect human health and the environment are also being addressed.

Substantial cost reduction can be achieved through successful development of in situ remediation methods. For example, the recent Record of Decision for Pit 9 at Idaho National Engineering Laboratory (INEL) containing 14,000 cubic meters of buried TRU waste estimates the cost of excavation/disposal (the baseline technology) at $24K per cubic meter, whereas the cost of using in situ vitrification would be about $2K per cubic meter.

WINDOWS OF OPPORTUNITY FOR ISR IP

- Near-term development (FY93-FY97) of Containment Technology for interim actions and to provide a basis for advanced in situ techniques;

- Mid-term development (FY94-FY00) of Manipulation Technology to transport or stabilize wastes; and

- Development of Bioremediation and Physical/Chemical In Situ Treatment Technology by 2005 to meet final remediation needs.

Technologies now being actively developed through ISR IP support are listed in Figure 2, with more detailed summaries of their status appearing in the following pages. When promising results warrant full-scale field demonstration, that work would normally be performed as part of an integrated demonstration.

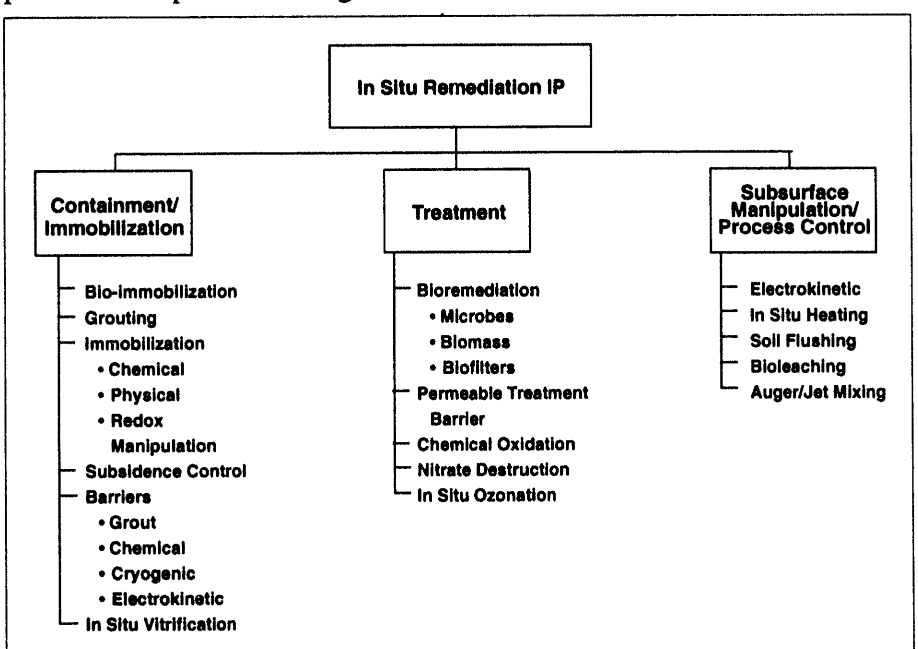

Figure 2. In Situ Remediation Integrated Program.

ACCOMPLISHMENTS

In addition to its sponsorship of individual Research and Development projects, ISR IP has taken a lead role in the assessment and encouragement of innovative technologies that may have application to DOE. For example, an ISR IP Workshop on Electrokinetics in Atlanta, Georgia, in January, 1992, brought acknowledged experts in the theory and practice of this remediation technology into direct contact with potential users, with the result that the potentialities and limitations of electrokinetics were better understood by all. That workshop defined the Research and Development needs for bringing this technology into practice, and sponsored projects are now addressing those questions. Field demonstrations in both arid and non-arid sites are anticipated in FY95. A workshop on "Mercury Contamination at DOE Facilities" will be held in 1994, at Oak Ridge, sponsored by ISR IP.

Technologies under development by ISR IP that exhibit greatest promise to date include:

- Frozen Soil Barriers - would provide a temporary barrier to quickly halt the migration of contaminant plumes or would permit construction of large reactors for in situ treatment.

- Reactive Barriers - the feasibility of using permeable colloidal suspension barriers, in situ microbial filters, and chemically enhanced vadose zone barriers to provide an in situ filter is being evaluated.

- In Situ Magnetic Separation - selective adsorption of radioactive/heavy metals from groundwater on magnetically separable particles has been demonstrated in bench-scale experiments. Field demonstration is planned by the Resource Recovery project at the Berkeley Pit in Butte, Montana, and at the Savannah River National Laboratory.

- Uranium Biosorption - use of beaded bacterial biomass for adsorption of uranium from groundwater as a selective adsorption process for low levels of uranium is being evaluated.

- In Situ Redox Manipulation - oxidation or reduction of inorganic species to insoluble forms, and the subsurface conversion of organic contaminants to harmless species is an attractive source-specific technique that, nonetheless, has wide applicability.

- Electrokinetics - application of direct current between buried electrodes causes movement of ions and water. Electrically mobile and soluble contaminants can be collected at the electrodes for disposal. The process is especially attractive for clay soils, where hydraulic flushing is ineffective.

Other promising technologies being studied are:

- Bioremediation of mixed chlorinated solvents;

- In situ corona discharge for treating non-volatile contaminants; and

- Physical barriers formed from viscous liquids.

FUTURE DIRECTIONS

The ISR IP will assist development of remediation technologies that will be faster, safer, cheaper and more effective than today's alternatives. To meet the technology goals of the Office of Technology Development (EM-50) by the year 2005, ISR IP will:

- expand development of containment technology to meet near-term requirements while continuing to pursue final remediation strategies;

- expand innovative bioremediation support;

- maintain innovative manipulation technology support; and

- begin expanding in situ physical/ chemical treatment in the near future.

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EM-54

Technology Development
In Situ Remediation
Integrated Program

Subprograms

Section 1.0

Containment

.0 CONTAINMENT SUBPROGRAM

Contaminant migration to areas surrounding a pollution source is a major environmental concern and methods are needed to control the spreading of pollution. The Containment Subprogram seeks to develop in situ technologies for pollution containment and is supporting investigations of new barrier materials, contaminant absorbers or neutralizers, and emplacement methods for barrier formation that do not require soil excavation. These technologies could provide short-term containment while the source plume is being remediated or long-term containment for sites presenting no immediate danger or requiring development of new remediation methods.

Barriers can be designed to be impermeable to water flow (hydraulic barriers), or can be semi-permeable, allowing water to pass but retaining the pollutant. Both types are being studied in this subprogram.

Impermeable barriers made with clays or cement/clay mixtures are widely used in construction. These barriers are effective in slowing water flow, but their use at contaminated sites can be limited by the need to excavate (and dispose of) contaminated soil from the placement trench. Clay may also be chemically attacked by leachates from the waste material, leading to degradation of the plugging effect of the clay and diffusion of contamination. Proper moisture content must be maintained to prevent shrinkage cracks in the clay. These deficiencies may be overcome through development of new barrier concepts, materials, and construction techniques. New synthetic binders and polymers are being evaluated for long-term stability and effectiveness as sealants. Inorganic grouts are also being studied for use with or without clays.

Developing semi-permeable barriers that control contaminant mobility without affecting groundwater flow is a major goal of the Containment Subprogram. By placing a substance in the barrier zone that absorbs or reacts with the target contaminant(s), pollutants can be physically trapped or chemically converted to a harmless form. Capacity and long-term effectiveness of such barriers are principal concerns of this research.

Forming barriers in situ by injection from the surface can decrease construction and waste disposal costs and can be useful for replenishing barriers that have lost their effectiveness over time. Development of barrier emplacement methods that do not involve soil excavation would be an important advancement of this technology. Frozen barriers in both non-arid and arid soils are being evaluated as part of this R&D effort.

1.1 CHEMICALLY ENHANCED BARRIERS TO MINIMIZE CONTAMINANT MIGRATION

TASK DESCRIPTION

This investigation is examining a number of substances that can immobilize chemical and radionuclide contaminants in groundwater beneath waste sites. Substances and processes under investigation include adsorption of chlorinated hydrocarbons from groundwater using a variety of organic materials, reductants to destroy chlorinated hydrocarbons and induce precipitation of various metals and oxyanions, and zeolites to sequester mobile metals.

Significant changes in mobility can be achieved through changes in oxidation state. Immobilization can also occur through surface adsorption of active substances, such as iron oxide or clays, or with ion exchange materials.

In addition to examining barrier technologies that involve construction to place the barrier, this program will also be investigating various methods to inject reagents into the subsurface. These techniques would minimize the excavation and management of potentially contaminated soils (see Figure 1.1).

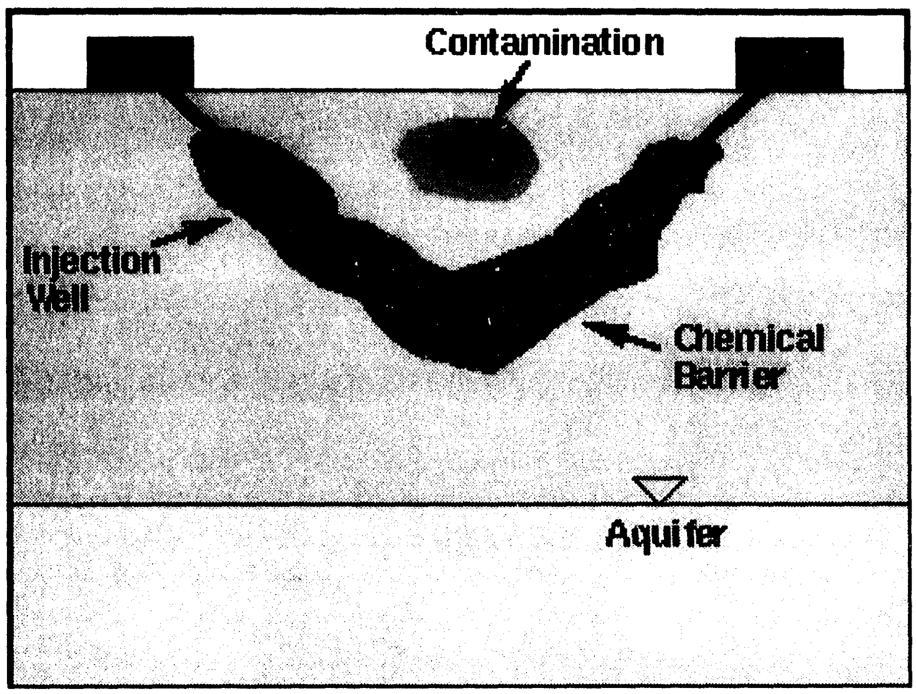

Figure 1.1. Develop and determine effectiveness of permeable barriers.

TECHNOLOGY NEEDS

In situ remediation of contaminants at disposal sites would be significantly enhanced if techniques existed that could target mobile substances without restricting groundwater movement. Control of groundwater requires limiting surface water penetration and vadose zone movement. Errors in control can lead to release of contaminated water. Complete control may require caps, liners, lateral barriers, and possibly, the installation of a pumping system.

Barriers with partial permeability allow selective immobilization of the hazardous components.

Selective barriers are needed for a range of substances including organic solvents, anions, and cations. For contaminant mixtures, a combination of different barrier sorbents may be necessary. This investigation will provide data on a variety of selective sorbent materials and examine methods of barrier placement that avoid excavation.

ACCOMPLISHMENTS

- Critical contaminants selected for investigation are: chelated cobalt, strontium, chromate, pertechnitate, and chlorinated hydrocarbons.
- Sequestering and sorption agents include: zeolites, macerated synthetic rubber, hydrotalcite, and immobilized organic chelates.
- A laboratory test plan was finalized and work is in progress.
- A preliminary site test plan is in preparation.

COLLABORATION/ TECHNOLOGY TRANSFER

This investigation will be carried out in collaboration with Ebasco Services, Inc. (Richland, Washington), and the Westinghouse Hanford Company. Laboratory investigations using an unsaturated flow apparatus (UFA™) will be performed at Washington State University. A co-investigator will synthesize some test compounds at Eastern Montana College.

Details on the efficacy of various chemical reagents in sequestering contaminants and the use of the UFA™ will be published in DOE technical reports and outside journal articles. Details on barrier emplacement and non-destructive monitoring will be shared in appropriate engineering literature.

Because chemical barrier reagents have applications in other containment activities such as caps and liners, data and results will be available to designers and engineers of these waste management systems.

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

TASK DESCRIPTION

This investigation is examining liquids which, when injected into the subsurface, produce nearly-inert impermeable barriers through a very large increase in viscosity. Appropriate emplacement of these substances provides an effective containment of the contaminated zone by trapping and immobilizing both the contaminant and the plume. (See Figure 1.2).

This project will identify and characterize promising materials and evaluate their containment potential by means of laboratory pilot-scale experiments and field testing and demonstration. The general purpose TOUGH2™ model, developed at the Lawrence Berkeley Laboratory (LBL) is being modified to simulate barrier fluid behavior and to design experiments.

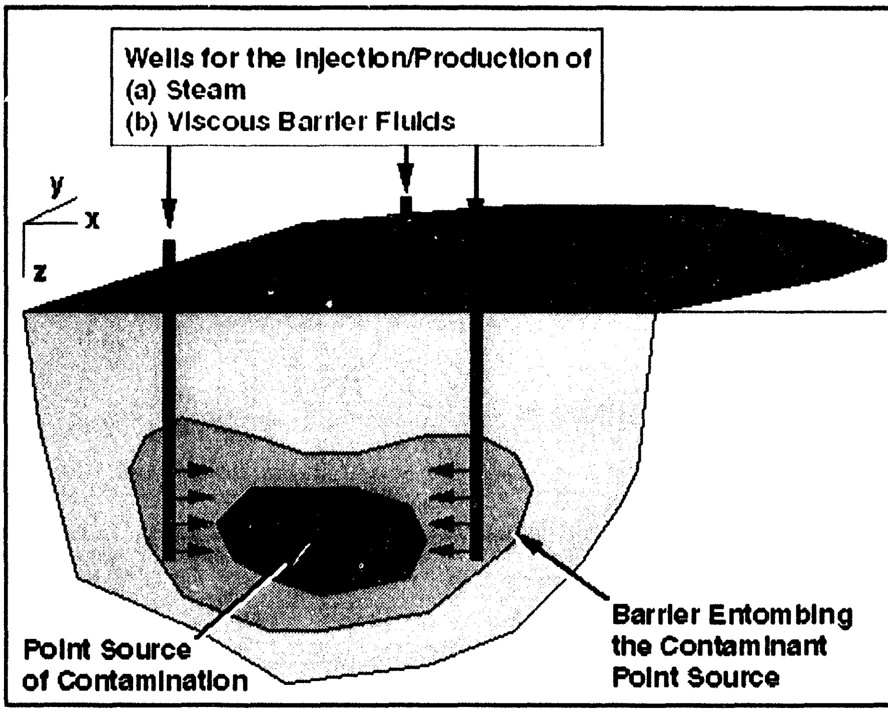

Figure 1.2. Identify and evaluate the feasibility of producing in situ barriers.

The first type of barrier fluid under examination belongs to the polybutene family. Polybutenes are chemically and biologically inert, hydrophobic and impermeable to water and gases, and are approved by the Federal Drug Administration for food contact. Their performance is unaffected by the soil and waste type, and is only controlled by their drastic viscosity dependence on temperature. The second type, colloidal silica, is a silicon-based chemical grout that poses no health hazard, is unaffected by filtration, and is chemically and biologically inert. Its containment performance is controlled by the gelation time, which depends on pH, temperature, the chemistry of the injected suspension, and chemistry and mineralogy of the aquifer porous medium. The third type of barrier fluid is polySiloXane. These fluids are chemically and biologically inert silicon-based polymers used for medical implants. They are mixtures of two fluids, are unaffected by the aquifer or waste chemistry, and their containment performance depends on temperature and the ratio of the two constituents.

TECHNOLOGY NEEDS

The strong adsorption of many contaminants to soil particles makes physical extraction slow or ineffective. Excavation of contaminated soils and disposal in protected facilities is very expensive. Containment on-site and control of groundwater transport can limit the off-site threat, and may supply a long-term solution.

A barrier containment system that does not require excavation would be a useful groundwater contamination control technique. Formation of a barrier with surface injected components that polymerize or change their viscosity under aquifer temperature and pressure conditions would allow barrier emplacement without excavation. In situations where complete control is necessary, an impermeable barrier is preferred over the sorption barrier.

In some areas aquifer mineralogy or regulatory restrictions may preclude the use of one or another barrier component. A variety of barrier systems must be available to match the range of contaminants and circumstances.

ACCOMPLISHMENTS

- Completed a wide search for fluids with desired properties;
- Identified three types of promising substances for evaluation as barrier fluids: polybutenes, colloidal silica, and polysiloxanes, and selected the most promising uses of these fluids;
- Completed analysis of the rheological properties of the barrier fluids;
- Conducted laboratory studies of barrier fluid flow and emplacement in porous media in columns and three-dimensional flow chambers. Determined that all three types of liquids are effective in sealing porous media; and
- Identified the dominant mechanisms in colloidal silica gelation in porous media. Developed processes to control the gel time and the texture of the gels. Determined the need and designed protocol for the sequential injection of colloidal silica.

COLLABORATION/ TECHNOLOGY TRANSFER

Texas A&M University in College Station is evaluating the performance of barrier fluids in large two-dimensional laboratory experiments using their specialized facilities. UC Berkeley is involved in the selection and rheological study of polymer-type barrier fluids.

The new technologies and the corresponding design package will be made available for use throughout the DOE Environmental Restoration program, as well as other U.S. agencies (EPA and DOD). Contamination problems expected to be especially amenable to barrier containment include localized ("point-like") sources. Many DOE sites would be candidates for the pilot- and field-scale application of the technologies, including the Hanford Underground Storage Tanks Integrated Program, Mixed Waste Integrated Program, the Buried Waste Integrated Demonstration Program, as well as the Rocky Flats site, the Nevada Test Site, the Savannah River site (for localized sources), and the Lawrence Livermore National Laboratory (where much pertinent information may be available from the "clean site" steam injection pilot). Many industrial sites with "point-like" contamination problems are also candidates for the application of these technologies.

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1.3 EVALUATION OF TWO NEW FLOWABLE GROUT TECHNIQUES

TASK DESCRIPTION

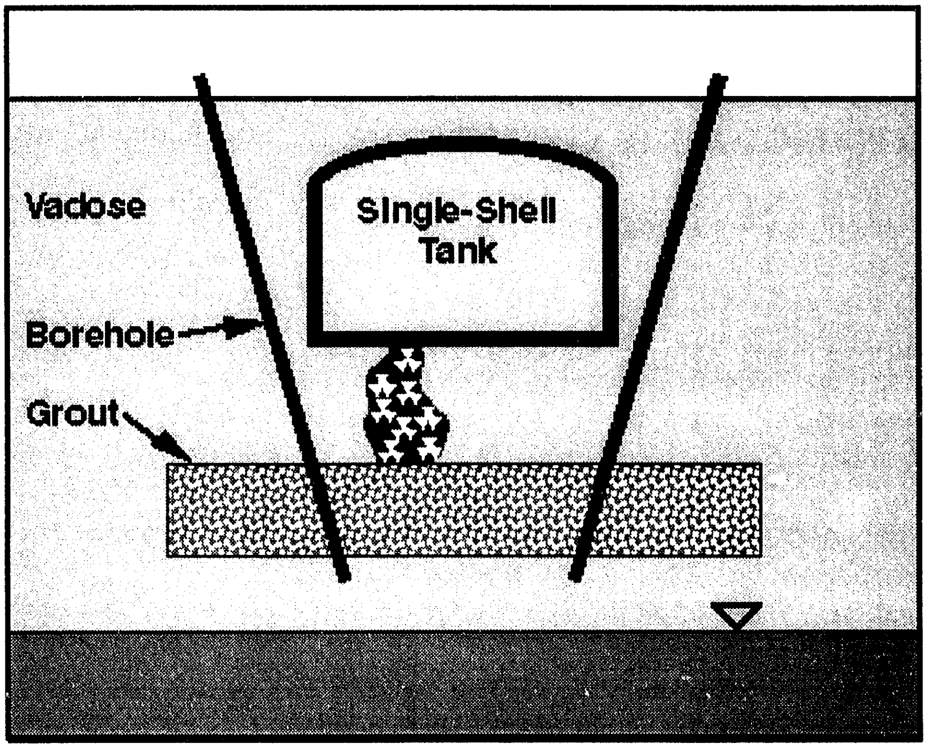

Figure 1.3. Evaluation of new grout barriers.

This project is examining the potential application of a bentonite/ mineral wax formulation, developed in Germany, and an inorganic grout, developed in France, as barrier materials for DOE sites (see Figure 1.3). Because these materials have been used for grouting, bringing them to regulatory and public acceptability within the U.S. should be rapid.

This investigation is examining the compatibility of these barrier formulations within the range of DOE soils and waste types. Technical challenges include lateral permeation of the soils, physical and hydraulic stability of the barrier over time, and the regulatory acceptance of the overall approach and grout materials.

TECHNOLOGY NEEDS

A groundwater control system that is injectable from the surface and forms within the aquifer removes the need to excavate trenches and construct barriers. A material that is resistant to deterioration from aquifer and contaminant chemistry would meet significant waste site remediation needs throughout the complex. Materials that do not contain synthetic compounds or have been used elsewhere may gain regulatory acceptance faster than those using unusual or manufactured substances.

This investigation is examining some currently available injectable grouts that have shown promise in Europe. Their application to the arid site conditions and resistance to waste components are the focus of this study.

ACCOMPLISHMENTS

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

- Grouts are being formulated to match the permeability of several soils.
- Sandia National Laboratory has agreed to a field test of the technology and has identified a drilling contractor.

COLLABORATION/ TECHNOLOGY TRANSFER

This project is a cooperative effort of Golder Associates and the European licensees MIBRAG (Germany) and Societe Hoechst Francaise (France). The materials were identified through the International Technology Exchange Program (ITEP). Results will be made available through this and other international efforts.

The Underground Storage Tank Integrated Demonstration sites at Hanford, Oak Ridge, Savannah River, Fernald, and INEL will all potentially benefit from these relatively advanced technologies. The Sandia Mixed Waste Landfill is the probable site for demonstration of effectiveness. Other potential users include a number of DOD sites with leaking underground storage tanks as well as industrial facilities such as refineries and fuel terminals.

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 U.S. division to manufacture and distribute its formulation. Speedy transfer to the private sector is expected.

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1.4 CHEMICAL BARRIERS FEASIBILITY AND FIELD DEMONSTRATION

TASK DESCRIPTION

This research is examining the sorption and immobilization capacity of a natural iron mineral for a number of site contaminants, and its use in the formation in situ of a permeable barrier that removes target contaminants but does not impede groundwater flow.

Ferric oxyhydroxide or hydrated iron oxide is a naturally occurring non-hazardous substance that has sorption affinities for a number of inorganic contaminants found at DOE sites. Such contaminants as uranium, molybdenum, copper, lead, zinc and radium can potentially be removed from groundwater.

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 (see Figure 1.4).

The objectives of this investigation are:

- to determine the absorptive capacity of the iron mineral for target contaminants; and
- to design and field test a low-cost water-permeable, barrier system formed in situ.

TECHNOLOGY NEEDS

Construction of an impermeable barrier system can be expensive in terms of excavation, hazardous waste disposal, and groundwater management.

Important aspects being studied in this project include the sorption capacity for a variety of contaminants and the relative immobility of the sorbing phase under aquifer flow conditions.

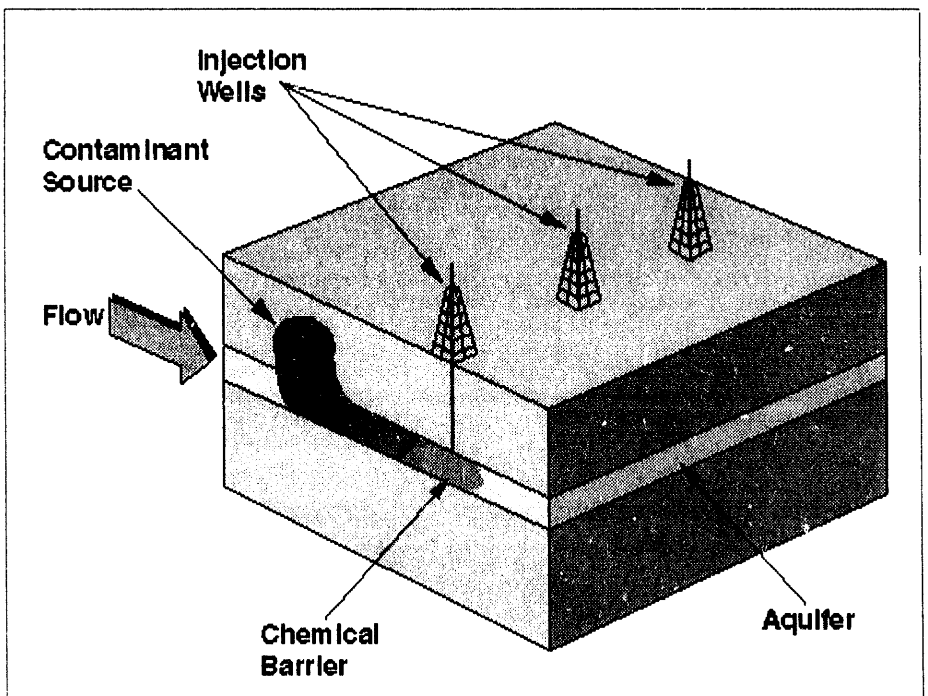

Figure 1.4. Chemical Barriers Feasibility and Field Demonstration.

ACCOMPLISHMENTS

- Ferric oxyhydroxide has been identified as an effective sorbent for such species as uranium, molybdenum, lead, copper, zinc and radium.
- The sorption characteristics of uranium and molybdenum at the Monticello Uranium Mill Waste site in Utah have been completed.
- Methods to enhance the attachment of ferric oxyhydroxide to the aquifer minerals have been examined.
- Laboratory studies on the use of this sorbent for uranium have been carried out under the Surplus Facilities Management Program, and the Grand Junction Project's Office of Research and Development Program.
- Preliminary acceptance from regulators has been received for an injection experiment at the Monticello field site.
- Laboratory column studies are underway to examine aquifer permeability changes.
- The rate at which the aquifer would accept fluid was determined in an injection test at Monticello using clean water.

COLLABORATION/ TECHNOLOGY TRANSFER

This project is being carried out by Chem-Nuclear Geotech, Inc. (Rust International), with the cooperation of the Monticello Remedial Action Project of the DOE Office of Environmental Restoration.

This effort is directly applicable to remediation of uranium contamination at the Monticello Mill site. Because uranium contamination in groundwater is prevalent at many DOE sites, this technology has widespread application. Other DOE sites with uranium contamination include UMTRA facilities, uranium groundwater contamination at Pantex, Fernald, the Rocky Flats Plant, Nevada Test Site, Y-12, and the Gaseous Diffusion Plant at Oak Ridge.

In addition, the application of this type of barrier may be appropriate for many different metals at DOE, DOD, EPA, and numerous commercial and industrial waste sites.

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1.5 HYDRAULIC AND DIFFUSION BARRIERS IN THE VADOSE ZONE SURROUNDING BURIED WASTE

TASK DESCRIPTION

This investigation will develop and test new barrier materials specifically for buried waste control. (see Figure 1.5). Tests will determine the long-term durability of the material, permeability to groundwater, ionic diffusivity, response to wet/dry cycling, and chemical resistance to acid, base, and organic solvent conditions that might occur at waste sites.

This study will also examine the effects of aggregate type and quantity on barrier performance. Inert aggregate substances such as clean sand and recycled glass used to produce the test specimens will be optimized to binder, geological, environmental and waste conditions.

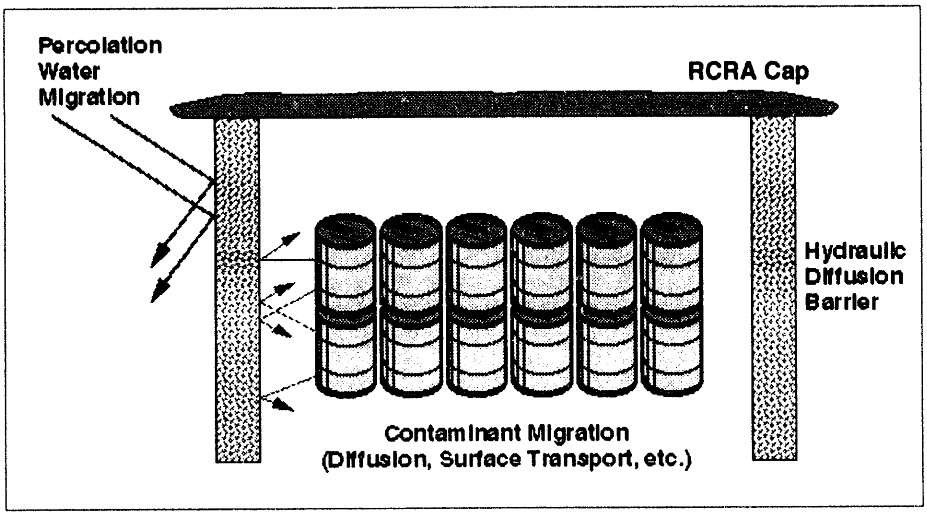

Figure 1.5. Reduction of contaminant migration and mobility using hydraulic/diffusion barriers.

Because the investigation will examine new applications of barrier constituents, regulatory issues affecting approval of barrier construction have been surveyed. This survey was a general overview of the regulatory concerns for emplacement of polymers and binders in soils, and included a specific focus on the use of thermoset resins.

TECHNOLOGY NEEDS

Sites with components that are not controllable with contaminant-specific sorbents will require barriers that prevent the movement of contaminated groundwater. Systems that use direct injection of barrier reagents as liquids, and subsequent in situ formation of the barrier, are preferred over those involving excavation.

Currently approved clay-based barriers may not be as effective as some synthetic polymers and resins. These agents may cement and seal sediments to form impermeable, chemically-resistant barriers to water movement. In some situations where in situ formation is not possible, and excavation costs are not prohibitive, barriers constructed with synthetic binders and an inert matrix provide an alternative. This investigation includes the search for appropriate matrix aggregates.

ACCOMPLISHMENTS

- The report, "Regulatory Issues and Assumptions Associated with Barriers in the Vadose Zone Surrounding Buried Waste", was issued.

- Inert barrier aggregate mixes of sand, sand and stone, and sand and recycled glass were selected.
- Binders and resins chosen included vinyl ester styrene, polyester styrene, polyacrylate, a furfuryl polymer, and petroleum bitumen.
- Over 1000 test samples were evaluated for compatibility and engineering performance; testing has been initiated.

COLLABORATION/ TECHNOLOGY TRANSFER

All work on this project is currently being accomplished through the facilities of the Brookhaven National Laboratory's (BNL) Waste Management Group. Because one of the planned aggregate mixes involves recycled consumer glass waste, some cooperation with a municipal or commercial recycled glass supplier is envisioned.

Communication of the results of this investigation will be through an expert review panel workshop. Attendees will include BNL, DOE, and industry personnel. A summary report will be issued containing workshop results. Further technology transfer will include dissemination of study results at symposia and meetings of professional and industrial associations.

Potential demonstration sites are through the Buried Waste Integrated Demonstration, the Mixed Waste Landfill Integrated Demonstration, and the Underground Storage Tank (UST) Integrated Demonstration. Discussions at the Brookhaven Waste Management Group are identifying when and how the results of this investigation will be used.

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1.6 SOIL FREEZING TECHNOLOGY APPLICATIONS

TASK DESCRIPTION

This investigation addresses the feasibility of frozen soil barriers (ground freezing technology) as a means of containing hazardous and radionuclide-contaminated soil in a non-arid setting. Because ground freezing has long been a civil engineering technique for ground control, water entry control, etc., this project is essentially a new application of an established technology. A series of holes are drilled and refrigerant is circulated, freezing the soil around the holes such that a confined volume is created, thereby preventing contaminant migration (Figure 1.6).

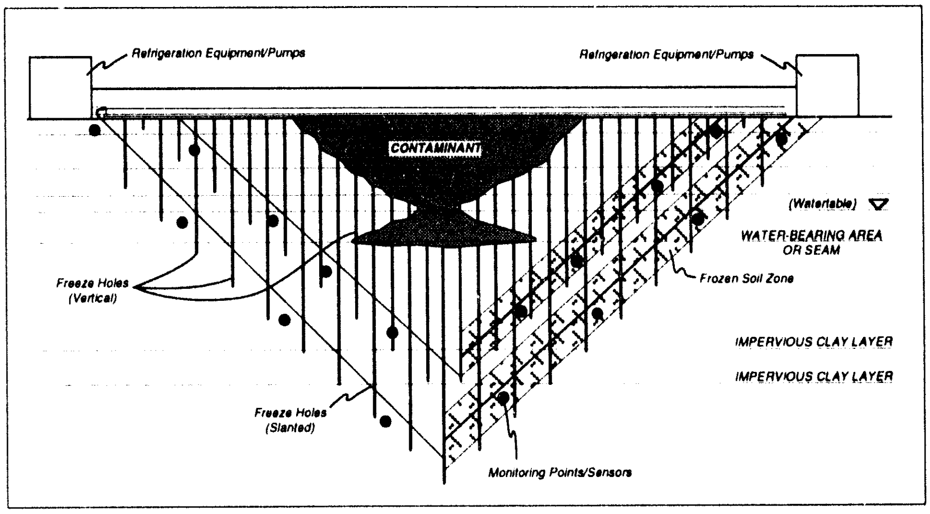

Figure 1.6. Frozen Soil Barrier at a Non-Arid site; cross-sectional view.

The objective of this project is to design, install, and pre-test a soil freezing facility at an uncontaminated site. After successful completion of these objectives, a soil freezing technology demonstration would 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 the analysis of other possible field applications within the DOE complex.

A series of tests is planned, including:

1) a well casing installation test (to maximize freeze pipe placement accuracy);

2) a barrier diffusion test (to demonstrate barrier integrity);

3) moisture addition test (to verify the ability to adjust moisture content throughout the barrier);

4) leaking underground tank containment test;

5) soil movement (e.g., heave) analysis both inside and outside the barrier;

6) a heat grid test to verify the ability of heat pipes to control barrier size;

7) a freeze pipe heat transfer test to verify the ability of freeze pipes to remove heat from thesoil zone and form overlapping ice columns; and

8) computer modeling as a predictive tool.

TECHNOLOGY NEEDS

A frozen soil barrier may meet containment needs by minimizing 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 by-products in the subsurface;
- it provides a means to fully contain waste, including a bottom, without excavation (soil disturbance);
- it is removable if necessary (by barrier thaw); and
- it offers significant advantages over current containment technologies because it can be repaired in place by adding water, should a breach occur.

Other advantages of this type of containment technology are its minimal operation and maintenance requirements, and its applicability to a wide range of contaminants.

ACCOMPLISHMENTS

This project is a new start for FY93. DOE has selected Scientific Ecology Group, Inc. (SEG), to perform the technology demonstration. Negotiations on the scope of work are underway. The project is working on a completion of barrier installation and associated testing by the end of the third quarter of FY94.

COLLABORATION/ TECHNOLOGY TRANSFER

Martin Marietta will provide project management, and SEG, Inc., will perform the design, construction and testing.

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., Department of Defense) or private industry are also candidates for frozen soil barrier containment technology.

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1.7 DEMONSTRATION OF A FROZEN SOIL BARRIER AT AN ARID SITE

TASK DESCRIPTION

This investigation addresses the feasibility of using frozen soil barriers (ground freezing technology) to contain hazardous and radionuclide-contaminated soil in an arid setting (see Figure 1.7).

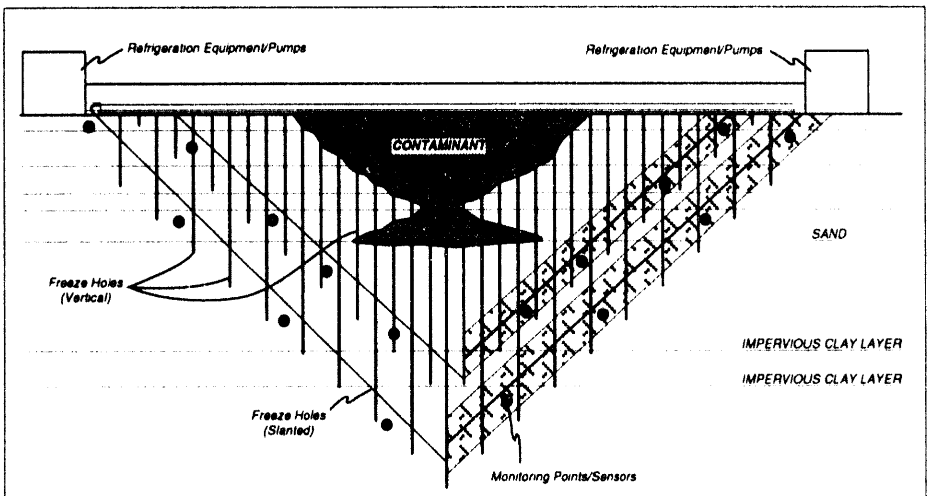

Figure 1.7. Cryogenic Barrier at an Arid site; cross-sectional view.

The first phase is a lab-based investigation of containment aspects 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 lab-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 complicates barrier formation beyond that of a saturated site. Upon completion, the project must also be able to remove 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 of thermal conditions, and other suitable methods.

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

TECHNOLOGY NEEDS

Many of DOE's 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 specific measures to mitigate or minimize adverse effects.

ACCOMPLISHMENTS

- A series of technical workshops and planning sessions on frozen soil barrier formation and performance have been held, leading to an acceptable Technical Task Proposal (TTP).
- Procurement of services for various tasks within the project has begun.
- The project is working towards a Summer 1994 demonstration.

COLLABORATION/ TECHNOLOGY TRANSFER

Overall project management is the responsibility of DOE's Grand Junction Projects Office. The lab-based investigation of the behavior of water and solutes in frozen soil will be awarded to a subcontractor in late FY93. The design of the field installation and the subsequent testing is the responsibility of Chem Nuclear Geotech, Inc., a contractor to Grand Junction Project Office. Soil freezing and associated equipment are available commercially, but a subcontractor has not yet been selected.

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1.8 SURFACE CONTROLLED EMPLACEMENT OF HORIZONTAL BARRIERS BENEATH WASTE SITES

TASK DESCRIPTION

This investigation is examining 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. Steel cables are threaded through the holes and attached to a winch or tractor. At the opposite end, jet grouting equipment is attached to the cables and connected to grout pumps. The jet grouter itself is a hydraulically-driven injector-mixer which leaves a soil-grout in a slab about ten feet wide and 2 feet thick (See Figure 1.8).

The investigation is focusing on laying down a series of six strips, joining the edges into a contiguous sheet, and tying the horizontal barrier to surrounding vertical containment. Emplaced panels will be excavated and tested for gaps or zones of inadequate grout-soil mixing. Additional development will address widening the panels and emplacement of this type of barrier in soils with rock fragments that restrict grout tool movement and 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 expensive and difficult.

A technology that allows barrier construction with minimal waste management that 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' x 12' x 100' has been designed and emplaced at a depth of 12 feet.
- The panel has been excavated and the workability of the concept has been verified.
- Prototype equipment for making a larger panel has been designed.
- A work plan to install a multiple panel horizontal barrier has been drafted.

COLLABORATION/ TECHNOLOGY TRANSFER

This work is under the supervision of FERMCO and will be supported through collaboration by the technology owner, NUS Halliburton, 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 in the DOE complex and in the country. The waste sites and tanks at Hanford need a method for in situ emplacement of horizontal barriers. The Pits and Clearwell at Fernald are also potential users.

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

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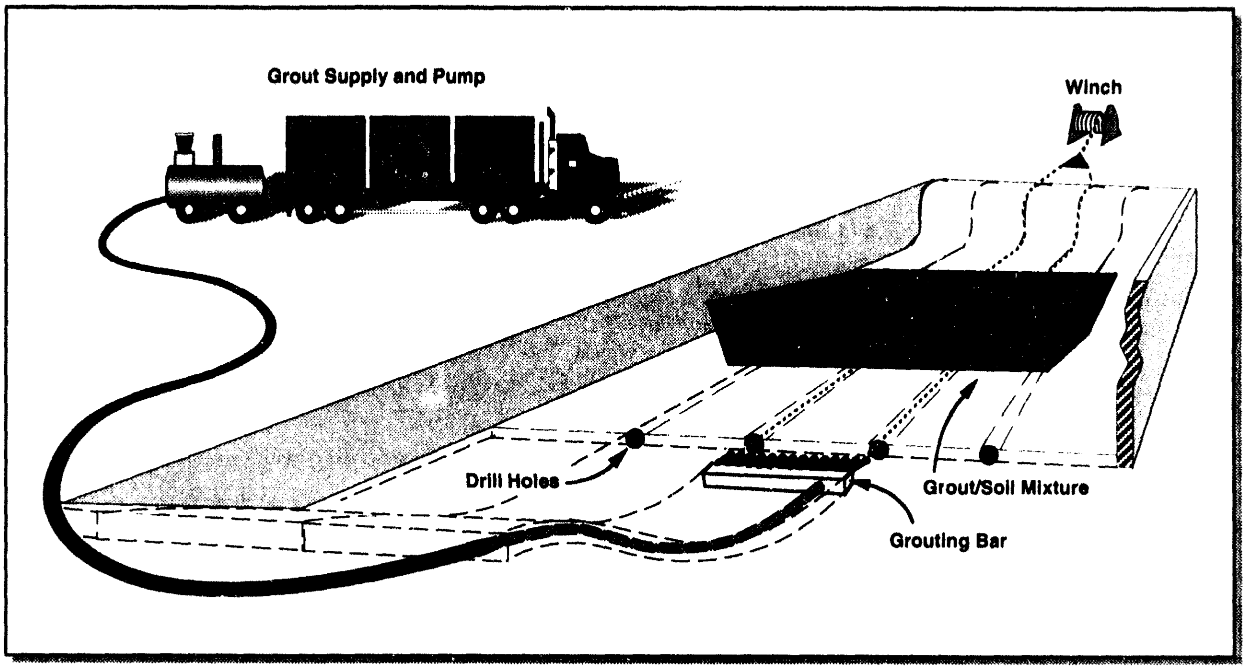

Figure 1.8. Containment vault formed in place using grouting bar.

2.0 BIOREMEDIATION SUBPROGRAM

Bioremediation refers to the use of biological systems or organisms that degrade or transform, mobilize or immobilize waste compounds. Bioremediation takes advantage of the natural abilities of microorganisms and plants to metabolize, sorb, oxidize or reduce organic and inorganic compounds. Bioremediation generally has low cost, wide public acceptance, and creates no secondary waste. The general goals of the Bioremediation Subprogram are:

- to offer effective remediation solutions for waste problems for which no other remediation technologies are effective;
- to reduce remediation costs;
- to achieve complete remediation of problem sites and create no secondary waste; and
- to offer remediation solutions for all types of waste, including mixed waste.

The following technology development needs for in situ bioremediation have been identified by EM-50:

- Criteria for performance evaluation;
- Treatment of mixed contaminants;
- Process enhancement including nutrient delivery methods;
- Treatment of chlorinated solvents;
- Standard protocols for assessing feasibility of bioremediation; and
- Treatment of non-aqueous phase liquids (NAPLs).

2.1 MODELING STRATEGIES FOR ENHANCING IN SITU BIOREMEDIATION

TASK DESCRIPTION

This task will develop and apply mathematical models of subsurface flow of halogenated aliphatic compounds to develop conceptual designs for enhancing in situ bioremediation. The research is guided by the understanding of conditions at two sites, Hanford and Rocky Flats. The primary objective is to recommend effective designs of recirculation units and strategies for improving bioremediation (see Figure 2.1). The effect of small-scale variability, such as on diffusional limits in mixing, will be evaluated.

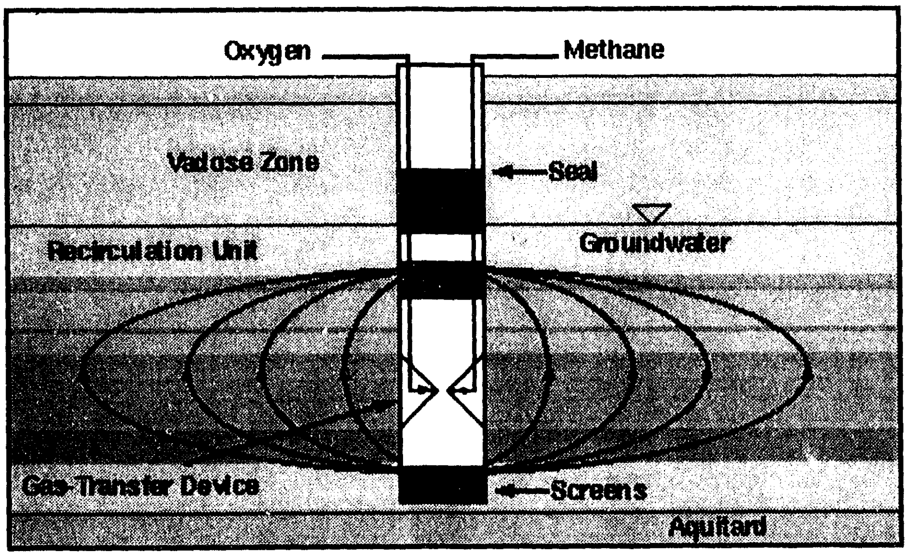

Figure 2.1. The use of mathematical models may enhance in situ bioremediation.

TECHNOLOGY NEEDS

Efficient biodegradation requires good mixing of reagents (microorganisms, nutrients, and contaminants), and methods for introducing these materials into soil at their optimum concentrations are needed. Mathematical models can be helpful in understanding the complex interaction of factors affecting in situ bioremediation, and will be useful to designers of effective delivery systems.

ACCOMPLISHMENTS

Investigation of the hydrodynamics of air sparging has begun by approximating the air/water interface as sharp. A numerical model is being formulated to locate the interface and calculate the pressure distribution and rates of flow.

A previously developed model of the hydrodynamics of pore flow has been expanded to investigate the development of biofilm. This will couple the current model with the Monod equations to calculate growth of the biofilm. This analysis will relate biomass to conductivity and porosity, and should be valuable in suggesting strategies to avoid pore plugging.

COLLABORATION/ TECHNOLOGY TRANSFER

This project involves a collaboration between the U.S. EPA and the U.S. DOE. Work is being carried out at Stanford University.

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2.2 DEMONSTRATION OF COMETABOLIC TECHNIQUES

TASK DESCRIPTION

This task will demonstrate the effectiveness of cometabolic bioremediation of groundwater contaminated by mixed organics at DOE sites. The goal is to demonstrate field scale bioreactors using techniques that cause degradation of compounds not used as a carbon or energy source by the microorganisms. Stimulation of TCE degradation by both methane and toluene-consuming microorganisms has been demonstrated in laboratory tests. Both approaches appear promising for field demonstration. Two bioreactor systems will bedemonstrated. One will use methanotrophic microorganisms and the other will utilize pseudomonad toluene degrading microorganisms. Development of each bioreactor will include culture screening and assessment, bench-scale bioreactor optimization, and in-field bioreactor demonstration. Each system's effectiveness in removing organic contaminants from the influent will be evaluated.

TECHNOLOGY NEEDS

The project directly addresses the DOE Office of Environmental Restoration's need for development and demonstration of bioprocesses for TCE-contaminated groundwater streams. By demonstrating in parallel the strengths and deficiencies of the two most promising cometabolic bioreactor technologies available for TCE degradation, this project will determine the most effective biodegradation technique for remediating TCE-contaminated sites.

ACCOMPLISHMENTS

This project began in April 1990. A skid-mounted bioreactor unit loaned to the project from the Air Force Civil Engineering Support Agency was extensively modified and installed in a van trailer. Laboratory and bench-scale pretreatment tests on the site water were completed, and the demonstration unit was started up using site groundwater as influent.

With respect to the individual bioreactor systems, in particular the methanotroph bioreactor system, laboratory work has been carried out to define bioreactor startup conditions, including nutrient and methane concentrations; gas and liquid flowrates; and microbial densities. The methanotroph bioreactor system was operated in the steam stripping pretreatment mode during the startup/shakedown period, followed by operation in the air stripping pretreatment mode, with intermittent shutdown periods for waste disposal. Initial results were inconclusive, primarily due to high variability in calculated mass balances that, in turn, were caused by irregular off-gas flow rates. Flow controllers will be added to the system.

For the toluene-degrading (pseudomonad) bioreactor system, laboratory-scale treatability tests and nutrient optimization tests have been completed. Bench-scale bioreactor tests using simulated site water proceeded concurrently with laboratory tests. This work defined the bioreactor startup conditions, including nutrient and toluene concentrations, air and liquid flow rates, and microbial densities.

COLLABORATION/ TECHNOLOGY TRANSFER

Operation of the bioreactors will be conducted jointly with the Air Force Civil Engineering Support Agency and Envirogen, Inc. (Lawrenceville, NJ).

A preliminary CRADA negotiation was initiated in March 1992 with Envirogen, Inc., to operate the bench-scale system developed by Envirogen at the K-25 demonstration site. The system was tested using simulated K-25 site water in FY91 and FY92, and successfully removed up to 80% of TCE from an influent stream containing a mixture of organics representative of the K-25 seepage flow. According to the CRADA work statement, Envirogen will provide the system and on-site technical oversight; and ORNL will prepare all necessary documentation, operational and monitoring manpower, and post-demonstration close-out activities. Both parties will collaborate in interpretation, evaluation, and reporting of the data.

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2.3 IN SITU MICROBIAL FILTERS

TASK DESCRIPTION

This task will develop and evaluate an in situ microbial filter to remediate contaminant plumes at their expanding boundaries using methanotrophic bacteria (see Figure 2.3).

In the first field demonstration, specialized non-pathogenic trichloroethylene (TCE) degrading bacteria will be injected to establish an in situ fixed biofilter around a suitable injection well located within the contaminant plume. The fixed microbial filter will be quasi-cylindrical in shape and have a height of about 2 m and a radius of about 1 m. After a predetermined period of time, the inoculation process will stop and groundwater will be extracted from the same well. Contaminated groundwater will flow through the attached in situ microbial filter, it will be decontaminated to regulatory limits by the microbes, and clean water will be produced at the well-head. After the filter has reached its longevity limit, the filter will be replenished.

In both cases, the enhanced activity of the biocurtain will cause biotransformation of TCE at a rate equivalent to the rate at which TCE is delivered to the filter. Thus, the microbe curtain will serve as a contaminant-specific fixed filter, capable of remediating substantial amounts of TCE in groundwater.

TECHNOLOGY NEEDS

TCE is probably the most prevalent chlorinated solvent contaminating groundwater at DOE and other sites, and is sufficiently soluble in water to be easily transported and broadly disseminated. Because of TCE's wide dispersion at relatively low (but unacceptable) concentrations, in situ treatment technologies are sorely needed.

ACCOMPLISHMENTS

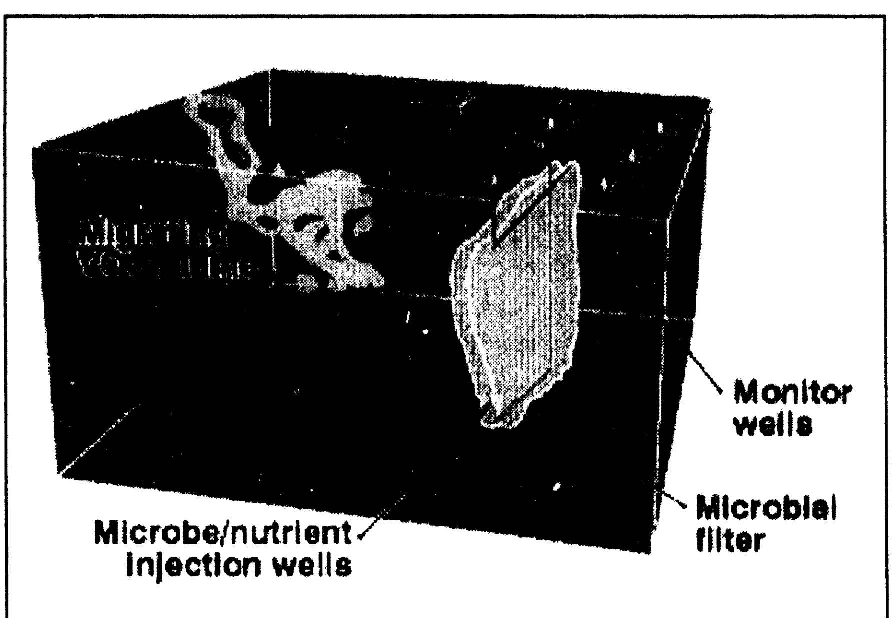

Figure 2.3. The biodegradation of trichloroethylene.

Methylosinus trichosporium strain OB3b has been optimized for use on the biofilter. Growth of the microorganism under conditions of copper starvation and careful nutrient management induced the production of large quantities of soluble methane monooxygenase (sMMO), the enzyme responsible for the cometabolic degradation of TCE. OB3b has been optimized such that the sMMO will degrade TCE for over 30 days without a need for inducer (i.e., methane). This means that once the in situ filter is injected with the microorganisms, TCE-degrading activity should last for 30 days.

A proof-of-principle experiment has been successfully completed. In this experiment, TCE-contaminated water was allowed to flow through a bench-scale, one-meter model biofilter. Microbes within the filter region degraded 100% of the TCE.

A 10 cm long column has been designed and set up, such that 100% of the TCE has been recovered. The standard flow rate of 1.5 cm/hr is being used. A greater than 3-week enzyme longevity has been established, and complete degradation of a 230 ppb pulse of TCE has been shown.

A large-scale bioreactor facility will be built for the mass production of OB3b for use on the in situ microbial filter. Cost estimates for this remodeling task have been completed, and steps are now being taken to seek a design and build contract from a bidding process.

Long term experiments have shown that the addition of a mixture of $MgCl_2$, $FeSO_4$, and agar to the aqueous media increases microbial attachment rates and reduces the rate of cell detachment. Cell detachment rates depend on fluid flow velocities, but these experiments have demonstrated that a significant enhancement of cell attachment can be achieved even at high flow velocities.

COLLABORATION/ TECHNOLOGY TRANSFER

NASA is interested in field-testing this technology.

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2.4 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 utilizes biosorbents (sorptive biomass, or biological material) immobilized in permeable beads that are in turn contained within flow-through bioreactor systems (see Figure 2.4a). Systems will be operated in a continuous or semi-continuous mode, and will be operated on-site as a pump-and-treat methodology. The system will achieve waste fixation and volume reduction. Uranium concentrations will be reduced from ppm to ppb levels.

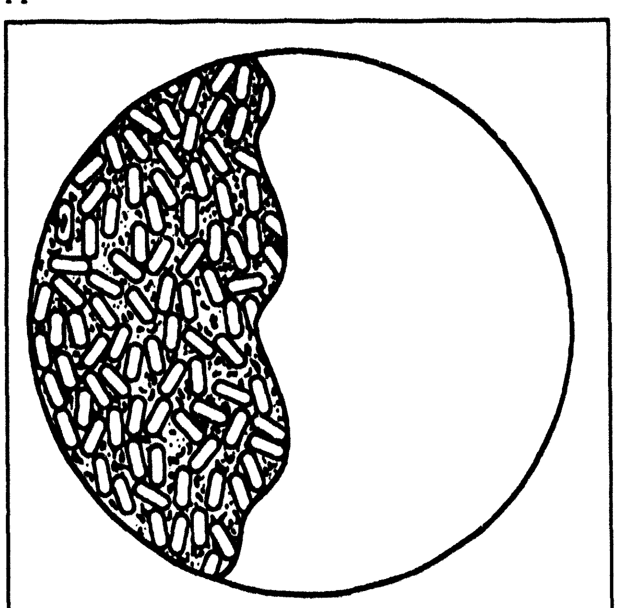

Figure 2.4a. Biobeads are formed by mixing heat-killed bacteria with a polymer.

TECHNOLOGY NEEDS

Technologies are needed for the treatment of wastewater contaminated with low concentrations of uranium. Current technologies for uranium removal include precipitation with alkali, adsorption onto activated carbon or other inorganic resins, and extraction with tributyl phosphate or other materials. These technologies 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 the binding of uranium from acidic water (i.e., pH less than 3). Isolated microorganisms in solution could bind uranium and reduce uranium concentrations from 10 ppm to 0.35 ppm. Studies are underway to find the best microbial uranium binder and the best binding conditions. Polyacrylamide will be tested for use as a matrix material in which to immobilize the biomass and form permeable beads.

In previous work *Pseudomonas aeroginosa* was found to be the best biomass for the binding of uranium at alkaline pH (pH 8.8). Heat-killed *Pseudomonas aeroginosa* immobilized within

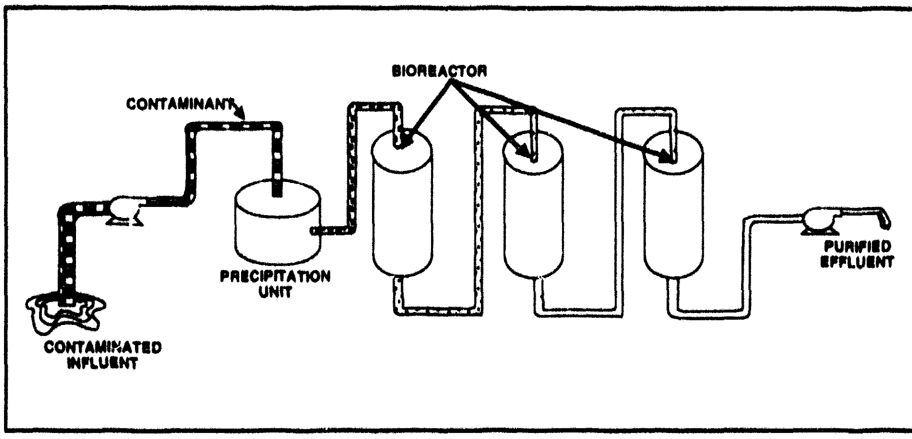

Figure 2.4b. Contaminated water is passed through a series of bioreactors.

a matrix of calcium alginate reduced uranium levels in a simulated wastewater 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 0.15M nitric acid (see Figure 2.4b).

OBJECTIVES/DATES

The major focus for 1993 includes analysis of the Ronneberg site data, development and evaluation of candidate biosorbents, and evaluation of candidate immobilization matrices. The following parameters of the Ronneberg contaminated water will be assessed as a function of depth and location: pH, redox state, total uranium, valence state of uranium, total iron, valence state of iron, total sulfate, alkalinity, major cations, minor cations, major anions, other radionuclides, total inorganic carbon, total organic carbon, and characteristics of colloids, if present. Several candidate biosorbents for uranium and iron will be identified. Microorganisms, plant tissue, and animal tissue will be considered. These candidates will be tested in parallel under conditions approximating those present in a surrogate waste, and will be ranked with respect to their ability/capacity to bind the targeted metals. Five to ten candidate immobilization matrices will be chosen. Critical parameters considered will be availability, mechanical stability, cost, and ease and scalability of matrix production.

COLLABORATION/ TECHNOLOGY TRANSFER

This technology development work is being carried out in cooperation with an industrial partner, Ogden Environmental and Energy Services, Inc. (a U.S. based company), via a CRADA with DOE. The technology will be demonstrated by Ogden at Ronneberg, an East 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 that is responsible for activities analogous to those covered by UMTRA.

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 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, and at the University of Birmingham in the United Kingdom.

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2.5 BIOMASS REMEDIATION SYSTEM

TASK DESCRIPTION

The project goal is to demonstrate the feasibility of using plants (both terrestrial and aquatic) to remediate soils, sediments, and surface waters contaminated by heavy metals and radionuclides (see Figure 2.5). Feasibility will initially be evaluated by:

1) Procuring biomass samples from plants growing or cultivated on contaminated soils and waters, determining the accumulation of heavy metals/radionuclides in the plant biomass (relative to contaminated soil); and

2) Subjecting the biomass to the Ukrainian Fractionation Separation Technology (FST) to establish the distribution of the elements or isotopes of concern in the biomass. The objective of the FST process is to concentrate and separate the contaminants of concern from the bulk biomass and/or recover uncontaminated biomass fractions that could be more easily disposed of or used for other applications (fodder, etc.).

The technology will be tested initially using plant material grown on heavy metal contaminated soils in the area of the Silver Bow Creek Superfund site (near Butte, Montana) and on Berkeley Pit water. Other plant biomass specimens derived from contaminated DOE facilities or from other sites will also be subjected to testing and evaluation in the initial feasibility study.

A small, bench-scale FST system will be built and operated at a site in Butte, Montana. Following successful demonstration and evaluation of the bench-scale process system, a larger, field-scale, mobile FST system will be tested at a DOE demonstration site (to be selected).

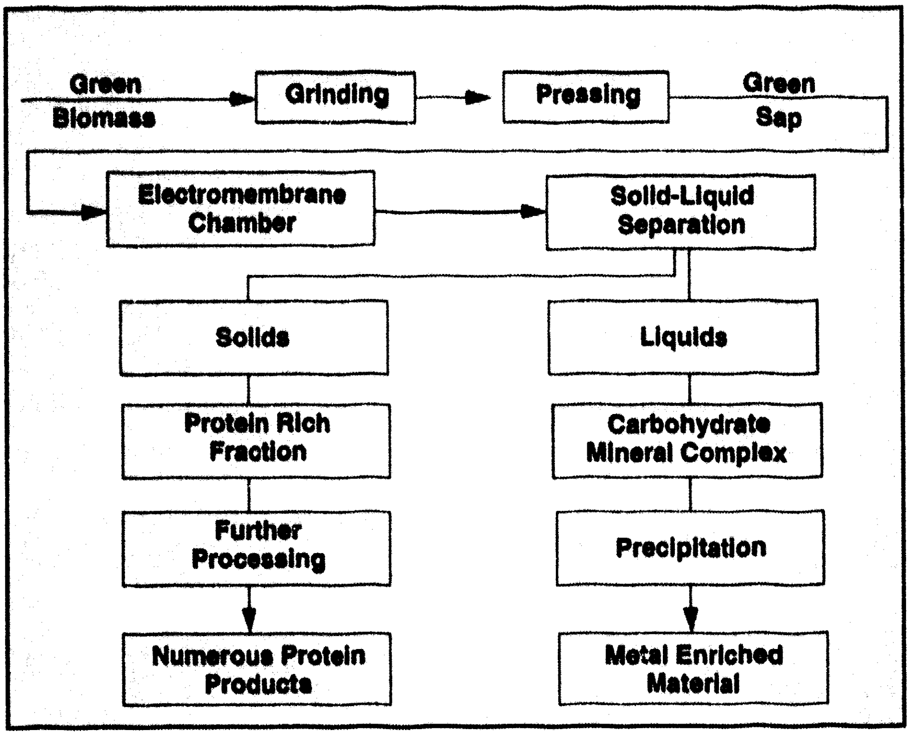

Figure 2.5. Fractionation Separation Technology Process for Macrophyte Remediation of Contaminated Soils.

TECHNOLOGY NEEDS

Considerable heavy metal contamination exists in soils and groundwater across the DOE complex, and much of this contamination is of low concentration. For such low levels of contamination in a relatively large quantity of soil and water, removal and storage or remote treatment (such as incineration, for soil) become 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 emission, 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 metals is indeed an inexpensive and publicly appealing method by which remediation of low-level heavy-metal/radionuclide contamination can occur.

ACCOMPLISHMENTS

Use of the FST to remove heavy metals from plants and to isolate useful materials from previously contaminated plants has already been demonstrated in the Ukraine. Data from the Ukraine and an initial literature review have confirmed that both aquatic and terrestrial plants accumulate radionuclides from water and soil. A draft test plan defining the sequence of experiments will be completed in October 1993. Tests are designed so that the results will allow evaluation of biomass processing technology for DOE environmental restoration needs.

Testing for the ability of the FST technology applied to soil remediation will be completed during December 1993. This demonstration will be executed near Butte, Montana, using the heavy metal fallout from a past smelting operation as a radionuclide surrogate. Metal-tolerant/accumulating native plant species, legumes and small grains will be used to determine the applicability of these biomass sources to these contaminants.

COLLABORATION/ TECHNOLOGY TRANSFER

MT International, a U.S. corporation, has established a joint venture agreement, American-Ukraine Biotech JV (AUB), with the Central Scientific Research Laboratory of Comprehensive Processing of Plant Raw Material 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 JV will provide the laboratory scale system design and personnel necessary for operation. Additionally, AUB will design and demonstrate the pilot scale system. Technical support to assist in selecting appropriate plant species for demonstration tests and evaluating the potential of applying the technology to aquatic plants for phytoremediation of contaminated water is included in the AUB tasks.

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EM-54

Technology Development
In Situ Remediation
Integrated Program

Subprograms

Section 3.0

Physical/Chemical Treatment

3.0 PHYSICAL AND CHEMICAL TREATMENT SUBPROGRAM

Contamination of soil and groundwater by a wide variety of organic and inorganic substances is prevalent at commercial and industrial sites across the United States and abroad. In situ treatment processes can remediate subsurface contaminants without excavation of the contaminated soils or extraction of the groundwater. The contaminants of interest can either be treated in place or transferred to the surface via a secondary carrier phase for subsequent treatment. In situ chemical/physical treatment processes can either be applied as an alternative to in situ bioremediation or as a pre- or post-treatment in conjunction with biological treatment. In situ chemical/physical treatment can be used in environments where microorganisms fail to thrive, can treat recalcitrant organic compounds and inorganics, and can accomplish treatment more rapidly and extensively than in situ bioremediation. The overall goal of the In Situ Chemical/Physical Treatment Subprogram is to develop a portfolio of in situ remediation technologies that employ chemical/physical processes for treatment of contaminants in situations common across the DOE complex.

The predominant sources of contamination at DOE facilities appear to be the various liquid and solid waste management units. These include liquid waste disposal facilities (e.g., land treatment units, surface impoundments, retention ponds, burning pits, french drains) and buried waste deposits (e.g., pits, trenches, and landfills). Other sources of contamination include leaking waste pipelines, high-use areas (areas surrounding waste treatment facilities, test firing sites), and leaking underground storage tanks. Leachates from the land treatment units and burial sites have in many cases contaminated subsurface soil and groundwater. In addition, contamination of surface water sediments has occurred due to off-site releases. The most prevalent contaminants are: (1) radionuclides, (2) chlorinated hydrocarbons, and (3) anions (specifically nitrates). Mixtures of contaminants are also common.

In situ chemical/physical treatment involves additions to or alterations of the subsurface that change the chemical and/or physical properties of the subsurface environment. In situ remediation technologies are increasingly being sought for environmental restoration, due to the potential advantages that in situ technologies can offer as opposed to more traditional ex situ technologies. These advantages include limited site disruption, lower cost, reduced worker exposure, and treatment under obstructed structures and at depth. While in situ remediation technologies can offer great advantages, many technology gaps exist in the application of in situ chemical/physical treatment. The technology gaps include inadequate information, particularly at the field-scale, in the areas of performance potential, implementation constraints, limitations to applicability, and verification of performance.

3.1 IN SITU GROUNDWATER TREATMENT USING MAGNETIC SEPARATION

TASK DESCRIPTION

This project will implement and demonstrate Bradtec's MAG*SEP™ technology 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) while leaving non-radioactive non-hazardous species unaffected.

The selective adsorption particles are composites manufactured in one of two forms. The particles can range in size from 1 to 15 microns, have a magnetic core, a polymer coating for durability, and either a "functionalized" resin coating or selective seed materials embedded in the polymer coating.

In treating 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 one minute). The particles are then recovered from the water using a magnetic filter. The magnetic core gives the particle a very high magnetic susceptibility. Also, because the contamination is chemically bound to the particles, adsorbing non-magnetic contaminants can be removed from water with high decontamination factors. Once the particles have been recovered on the magnetic filter, the filter is backwashed, the particles regenerated (much in the same manner as ion exchange resin is regenerated), the contaminants recovered (for recycle or treatment), and the particles reused.

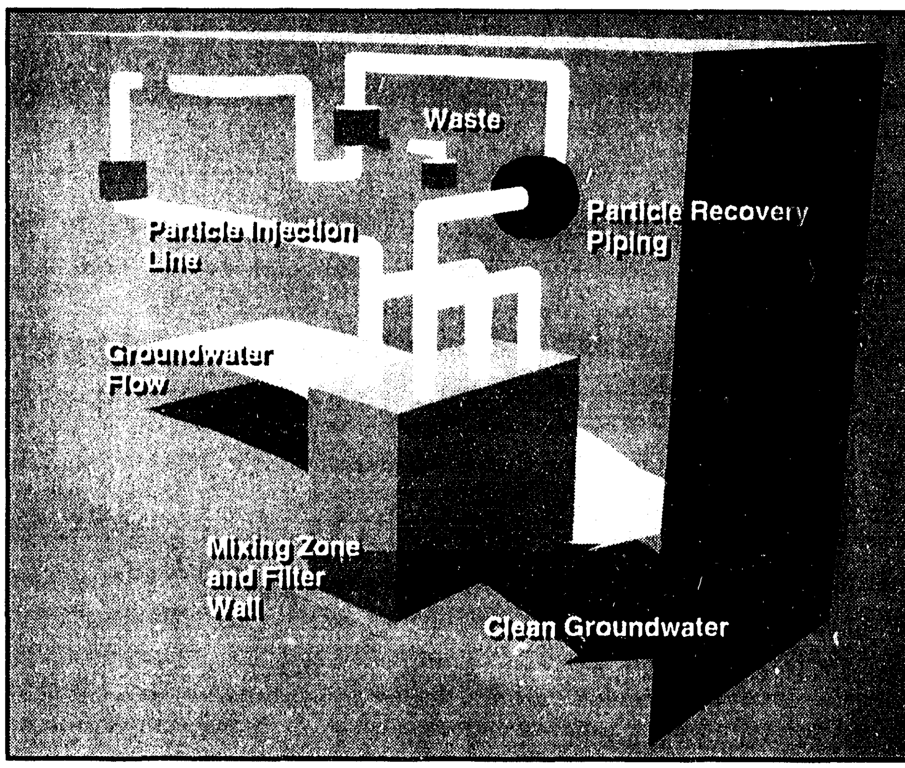

Figure 3.1. MAG*SEP™ Groundwater Treatment Concept.

The technology can be applied in situ for the recovery of radionuclides, heavy metals, and nitrates from groundwater. For in situ treatment, a "filter wall" is installed to prevent the groundwater from moving beyond the filter wall, except by passing through it. There are two zones in the filter wall: first, a mixing zone where MAG*SEP™ particles are injected and mixed with the water, and second, the magnetic recovery zone. The collected particles are then pumped to the surface for regeneration and reuse. Figure 3.1 (page 32) depicts the in situ MAG*SEP™ groundwater treatment process.

The specific tasks within this project include a pilot-scale proof of concept test that evaluates the process chemistry and specific adsorption of contaminants from water obtained from DOE sites. Adsorption kinetics, effects of competing ions, and organic/humic interferences will be evaluated along with decontamination factors and MAG*SEP™ particle regeneration.

TECHNOLOGY NEEDS

The magnetic filters and other equipment are all commercially available. Magnetic filtration, in fact, is an established technology used in water treatment for boilers and for removing iron contamination from pulp in paper manufacture. In boiler feed treatment, the iron present in water is removed by magnetic filtration. Other contaminants which are paramagnetic can also be removed. An example is copper. However, because there is no chemical bond between the iron and copper, the iron is typically removed with a decontamination factor between 20 and 100, while the decontamination factor for copper is typically 2 to 3.

The new feature of this technology is the development of the composite particles. With the MAG*SEP™ process, paramagnetics are not utilized, and the ability to recover the MAG*SEP™ particles with the contaminant is equal to the ability to recover iron which is well established with magnetic filters. No other processes use chemical treatment to prepare particles which can selectively adsorb contaminants onto a magnetic particle with a high magnetic susceptibility. To apply the MAG*SEP™ technology in situ, a means to inject and mix the MAG*SEP™ particles with contaminated groundwater, recover the MAG*SEP™ particles, and transfer the MAG*SEP™ particles to a regeneration/recovery system must be developed and demonstrated.

ACCOMPLISHMENTS

Tests conducted at Chemical Waste Management's Clemson Technical Center have removed 100% of the MAG*SEP™ particles in a liquid stream.

Site selection is complete and meetings with regulators have been initiated. Process chemistry should be complete by November 1993, and system prototype testing should be complete by December 1993. FY94 activities include the design and fabrication of the pilot plant and pilot scale testing. The final report should be issued by October 1994.

COLLABORATION/ TECHNOLOGY TRANSFER

Bradtec has exclusively licensed this technology to Chemical Waste Management, Inc., for application in North America. Bradtec has purchased a pilot-scale Electromagnetic Filter from Babcock and Wilcox Nuclear Technologies. Two test sites (Berkeley Pit and Savannah River Site) have been selected for pilot scale demonstrations.

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3.2 IN SITU CORONA FOR IN SITU TREATMENT OF NON-VOLATILE ORGANIC CONTAMINANTS

TASK DESCRIPTION

This project will develop a practical technique for decomposing non-volatile and bound organic contaminants using gas-phase oxidants that are produced in situ. The gas-phase oxidants will be produced by electrical corona made to occur on soil particles by AC electrical power delivered to 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 be insensitive to the type of organic contaminants involved and be very effective in low permeability soils (see Figure 3.2).

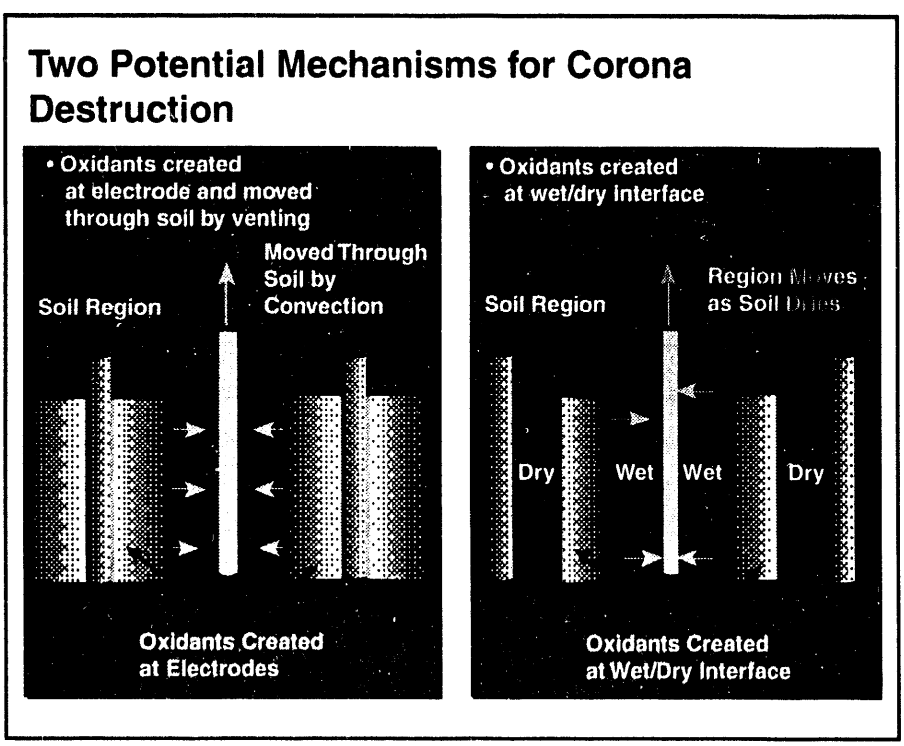

Figure 3.2. Potential Mechanisms for Corona Destruction.

Corona discharges in air produce strong oxidants capable of destroying a wide variety of compounds. These discharges occur when a strong electric field is established in a gas, causing the gas to partially ionize and form a low-temperature plasma. In simple terms, a strong electrical field will try to force current to flow by stripping electrons off of neutral gas molecules (forming positive ions). The chemical reactions that can occur depend on the average energy of the electrons, which in turn depends largely on the strength of the field (voltage gradients) used to produce them. Assuming oxygen is present, the net chemical results will be oxidation and cracking, similar to what occurs in high-temperature combustion. Studies have demonstrated the ability of corona discharges to destroy a wide variety of organic compounds. Other researchers have demonstrated the reduction of NOx using corona with ammonia as a reductant, the destruction of chemical and biological warfare agents, the removal of particulates from gas streams, and the oxidation of many metals, including gold.

Tests-to-date have investigated using simple point-to-liquid corona discharge to determine whether corona in ambient air would be capable of destroying organic contaminants in aqueous and non-aqueous liquids. This low-energy form of corona was selected because it would be expected to provide results representative of scavenging reactions that would occur in soils. Compounds tested included benzoic acid, trichloroethylene, acrylamide, benzo(a)pyrene, three organic dyes, benzene, toluene, phenol, chlorophenol, chloronapthalene, methane, and carbon tetrachloride. All compounds tested were decomposed.

Specific tasks included in this project are bench-scale and field pilot demonstrations in contaminated soil.

TECHNOLOGY NEEDS

The project consists of R&D over a 3-year period to understand the physics and chemistry of in situ corona in sufficient detail to make projections on the effectiveness and practicality of this technique for field applications, and provide baseline laboratory data on treatment efficiency, reaction by-products, energy requirements, and site applicability.

The overall approach will bring together existing knowledge of ex situ corona chemistry and in situ application of electrical fields to develop an understanding of how in situ corona can be used to accomplish the in-place destruction of diesel fuel, PCBs, heavy oils, town gas residues, and other non-volatile compounds and mixtures. The focus will be to provide sufficient laboratory data and know-how to support transfer of the in situ corona technology to DT&E.

ACCOMPLISHMENTS

The project is newly funded. A technical project team has been formed. Technical issues in moving the technology forward have been identified, and the experimental design to resolve the issues has been developed. FY93 deliverables include a site selection plan, bench-scale scoping results, and gas/liquid corona test results. During FY94, in situ bench-scale tests will be conducted using contaminated soil and the test plan for the pilot scale field demonstration will be prepared.

COLLABORATION/ TECHNOLOGY TRANSFER

Potential sites for DT&E of this technology include the Arid Soils VOC Integrated Demonstration (Hanford), Oak Ridge National Laboratory, and Rocky Flats Plant. Collaboration has been initiated with the sites.

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3.3 IN SITU CHEMICAL TREATMENT

TASK DESCRIPTION

Conventional approaches to environmental remediation have relied primarily on physical isolation or removal technologies, including groundwater pumping. It has been observed 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 by-passed 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.

This project is testing the feasibility of treating unsaturated soils by injection of reactive gases. Dilute mixtures of hydrogen sulfide in air or nitrogen will be used to treat soils contaminated with heavy metals, while chromate or uranium contaminated soils are being treated with hydrogen sulfide and sulfur dioxide gas mixtures diluted by inert gases. Initial testing activities are using clean soils that have been artificially contaminated with hexavalent chromium, uranium, and other selected metals or radionuclides. Clean soils from several DOE sites are being used in this testing phase to verify that the approach is applicable to a variety of soil types, and to better evaluate the impact of gas concentrations and residence time on performance (see Figure 3.3).

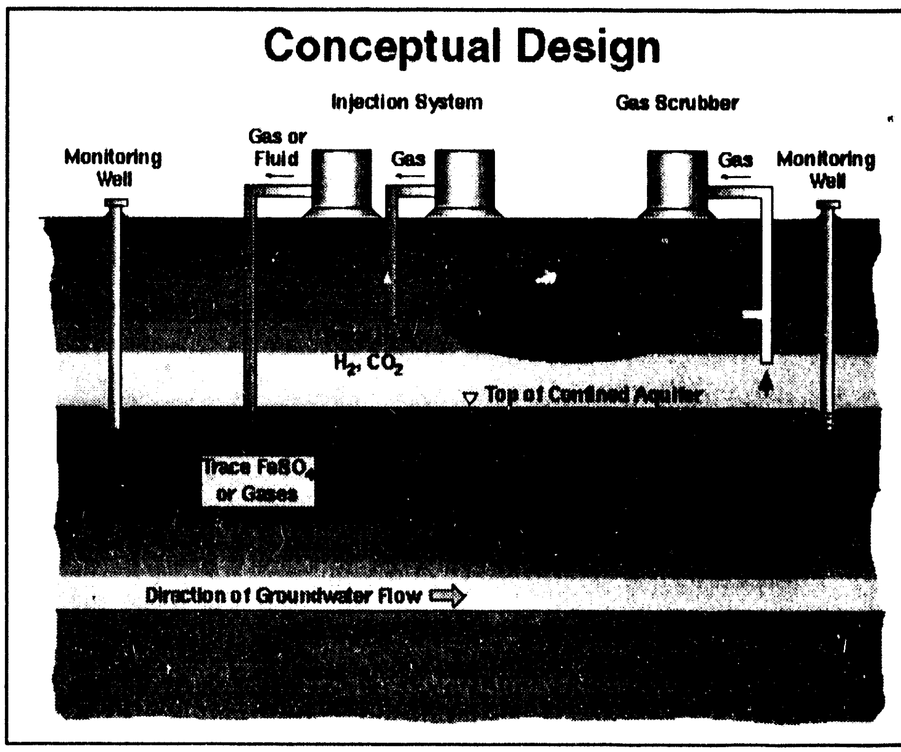

Figure 3.3. In Situ Chemical Treatment Conceptual Design.

Tests will also be conducted using solutions of ferrous sulfate and sodium sulfide, which have demonstrated considerable potential for reduction and precipitation of hexavalent chromium and uranium, and for precipitation of a variety of other heavy metals. An objective of this activity will be to elucidate the chemical interaction between groundwater solutions, aquifer sediments, contaminants, and treatment agents.

Specific tests in this project include bench-scale testing using clean soil artifically contaminated with hexavalent chromium, uranium and other metals. Following the clean soil testing, actual contaminated soil from DOE sites will be tested to optimize treatment procedures, determine treatment costs, and develop approaches for ensuring the control of the reactive gases and homogeneous treatment of large masses of contaminated geomedia.

TECHNOLOGY NEEDS

Although the chemical principles are well established, few data are available to assess the potential of the in situ chemical treatment approach. In particular, the interaction of potential treatment agents with soils or groundwater has not been sufficiently evaluated. Initial proof-of-concept experiments have been conducted to better establish the approach. This testing directed towards the treatment of solutions containing hexavalent chromium and soil spiked with hexavalent chromium indicated that significant immobilization is possible. Further testing is needed to quantify the amount and concentrations of treatment agents needed and to evaluate the potential for treatment and immobilization of a variety of metals and radionuclides. Testing will be conducted with actual contaminated soils and groundwater from DOE facilities to fully establish the validity of the technology.

ACCOMPLISHMENTS

Bench-scale tests using clean soil artificially contaminated with hexavalent chromium, uranium, and nitrate will be completed in FY93. Results to date indicate that about 90% of the chromate added to soils is immobilized following chemical treatment. Gas mixtures containing as little as 100 ppm hydrogen sulfide in nitrogen are effective for use in treatment. These tests included three different soil types, suggesting that soil composition is not a limiting factor. Additional analysis will assess the potential for treatment of uranium and nitrate in soils.

Bench-scale gas treatment and leaching studies will be continued in early FY94 with contaminated soils from DOE work sites. Pilot-scale tests and system design activities will also commence in FY94.

COLLABORATION/ TECHNOLOGY TRANSFER

Potential sites for DT&E of this technology include Hanford, Fernald, and Sandia National Laboratories. Collaboration has been initiated with the sites. Soils from the 100-BC area of the Hanford Site, an acid pit at Idaho National Engineering Laboratory, a calcium chromate disposal site at Sandia National Laboratory, and uranium contaminated sites at Fernald are being tested.

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

TASK DESCRIPTION

A critical question in site remediation is how to manage and optimize the long-term groundwater remediation process. The locations and rates of pumping for each groundwater remediation well, which may change with time, must be selected carefully, as well as 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 of typically 30 to 100 years.

This project focuses on the development of a methodology and associated tools for the management and optimization of groundwater contamination in both unsaturated and saturated systems.

More efficient tools will be investigated for the optimization of large-scale, three dimensional groundwater systems that are hydrodynamically constrained. Despite recent advances in optimal design techniques, a number of problems remain, including, for example, the effects of "clay caps," "cutoff walls," and "horizontal drains" on the optimization schemes.

Specific tasks include the development of three-dimensional groundwater simulators coupled with optimization based on hydrodynamic and solute transport constraints. These codes will allow optimal design of both saturated and unsaturated systems, and will be coupled with a realistic economic model and user-friendly graphical interfaces.

Research on more robust and efficient optimization methods, such as the outer approximation method, will address non-linear optimization of solute transport in groundwater systems. This research is directly applicable to other important subsurface contamination problems, such as multi-phase flow and the use of subsurface chemical treatments. Work will also be performed on the development of more realistic 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.

Graphical interfaces will be developed for a variety of computers. These graphical interfaces will not only increase the potential for technical transfer, but will also provide an important tool for the exploration of data, proposed solutions, and other "what-if" scenarios that involve large amounts of numerical information.

TECHNOLOGY NEEDS

The need for optimization procedures during the evaluation, selection, and implementation of biological and non-biological in situ treatments has been identified by many sites. Sites performing environmental restoration must make informed decisions with respect to the location and pumping rate of groundwater remediation wells, the location of monitor wells, and the use of drains, caps, or cutoff walls.

To make these decisions, calibrated groundwater modeling of contaminant flow and transport must provide realistic simulations of flow and transport through saturated and unsaturated porous media. The results of this modeling must be coupled with economic and risk evaluation models to determine the optimal remediation that minimizes risk and cost and addresses the needs of the stakeholders in the decisionmaking process. The need to communicate the risk and cost impact of potential remedial alternatives to non-technical decisionmakers is a critical element in the optimization process.

ACCOMPLISHMENTS

The contract with the University of Vermont, the major developer of the software for this task, has been completed. Interface parameters (i.e., menus, model result processing, and point-and-click parameters) have been established for software development.

A three-dimensional groundwater simulator coupled with optimization based on hydrodynamic constraints will be delivered in September 1993. A three-dimensional groundwater simulator coupled with optimization based on solute transport constraints will be delivered in September 1994. The simulators will include coupled transport in the unsaturated zone, a realistic economic model, and user-friendly interfaces for the field application of the saturated and unsaturated zone models.

COLLABORATION/ TECHNOLOGY TRANSFER

This work is being performed in collaboration with Dr. George Pinder, Research Center for Groundwater Remediation Design at the University of Vermont. Additional participants include David E. Dougherty of the University of Vermont, and David P. Ahlfield of the University of Connecticut. The tasks in this project are being performed primarily by the University of Vermont. Investigators at Lawrence Livermore National Laboratory ensure that unnecessary overlap with related research projects is avoided and that the research provided by the University of Vermont is relevant to the Department of Energy.

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3.5 IN SITU REDOX MANIPULATION: ENHANCEMENT OF CONTAMINANT DESTRUCTION AND IMMOBILIZATION

TASK DESCRIPTION

This project will develop, test, and evaluate an in situ method for immobilizing inorganics (metals, ions, and radionuclides) and destroying organics (primarily chlorinated hydrocarbons) using chemical or microbiological reduction of both the groundwater and the solid materials within the aquifer to form a permeable treatment barrier. The great majority of the chemically reactive mass in the subsurface system resides in the solid phases, rather than in the groundwater. Therefore, to have a substantial influence on the chemistry of the system, the solid phases should be involved. If changes are made only to the aqueous component, it will quickly reequilibrate with the solid phases.

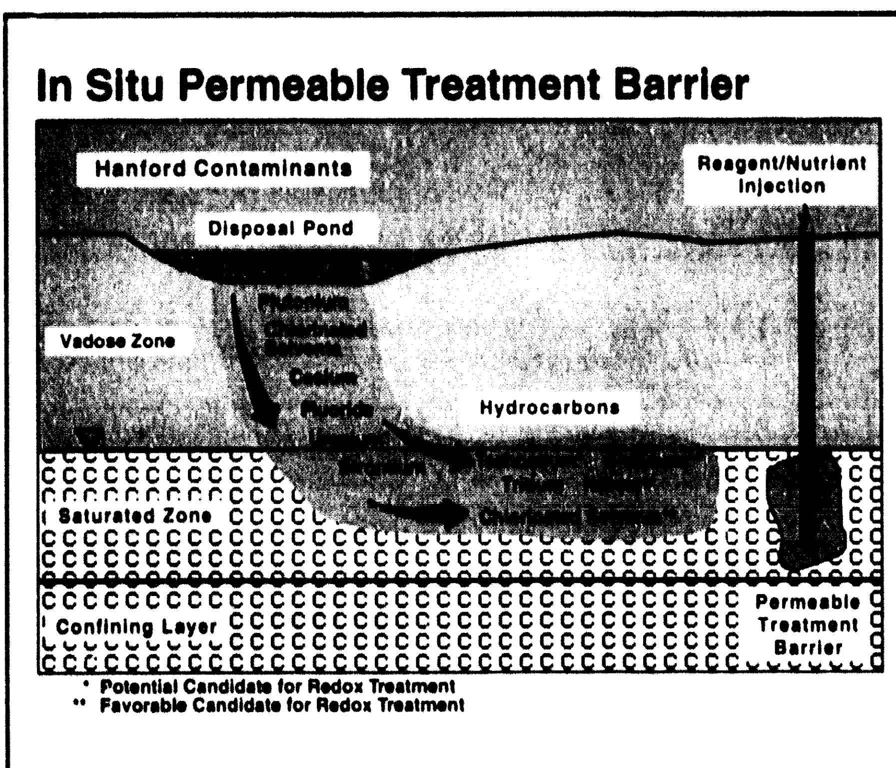

Figure 3.5. Permeable Treatment Barrier Concept.

A series of experiments is planned to test the different reagents or microbial nutrients on the redox potential of an unconfined aquifer. The purpose of redox manipulation is to enhance the biodegradation of organic contaminants and/or immobilize inorganic contaminants. Bench-scale testing will determine the nature of the reactions which occur and the efficiency with which they are induced by the reagent or nutrient. The kinetics of the reduction and subsequent reequilibration of the aquifer will also be determined. The initial experiment will involve reduction through stimulation of indigenous microflora.

There are several ways to approach the addition of reagents or nutrients into the subsurface. Three possible approaches include: (1) direct injection into the contaminant plume, (2) injection ahead of the contaminant plume to form a geochemical barrier by reacting with the solid phases, and (3) use of horizontal drilling technology to introduce a gaseous reagent to the contaminant plume. In the second alternative, a reagent or nutrient is injected ahead of the contaminant plume to form a permeable treatment barrier by reacting with the solid phases. The contaminant plume then reacts with the permeable treatment barrier. The second alternative will be used in this project (Figure 3.5). The basic approach involves a forced gradient, single-well, reactive tracer test. The reagent is pumped into the aquifer in a circle approximately 60 to 100 feet in diameter, allowed to react for 10 to 60 days, and then water containing the reaction by-products and any remaining reagent is pumped back out.

TECHNOLOGY NEEDS

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

ACCOMPLISHMENTS

Iron-reducing bacteria have been cultured under a variety of dissolved oxygen tensions in batch and continuous cultures. Cells cultured under low dissolved oxygen tensions (less than 5% of air saturation) enzymatically reduced iron, uranium, and cobalt-EDTA in anaerobic assays. Cells cultured with higher dissolved oxygen tensions (50-100%) did not exhibit metal reductase activity.

Sodium dithionite was found to reduce structural ferric iron in clays in Hanford soils. Laboratory experiments indicate that the half-life of the dithionite ion will be of the order of two or three days under ambient conditions in the Hanford confined aquifier. This half-life should allow enough time for reduction of solids in the aquifier, while ensuring that dithionite does not remain as a contaminant in the groundwater for extended periods of time.

Laboratory bench-scale testing will be completed in FY93. Activities during FY94 involve the complete characterization of modeling of heterogeneities in the field site. The field demonstration will be initiated at the end of FY94.

COLLABORATION/ TECHNOLOGY TRANSFER

A potential site for DT&E of this technology is the Arid Soils VOC Integrated Demonstration (Hanford). Collaboration has been initiated with the site.

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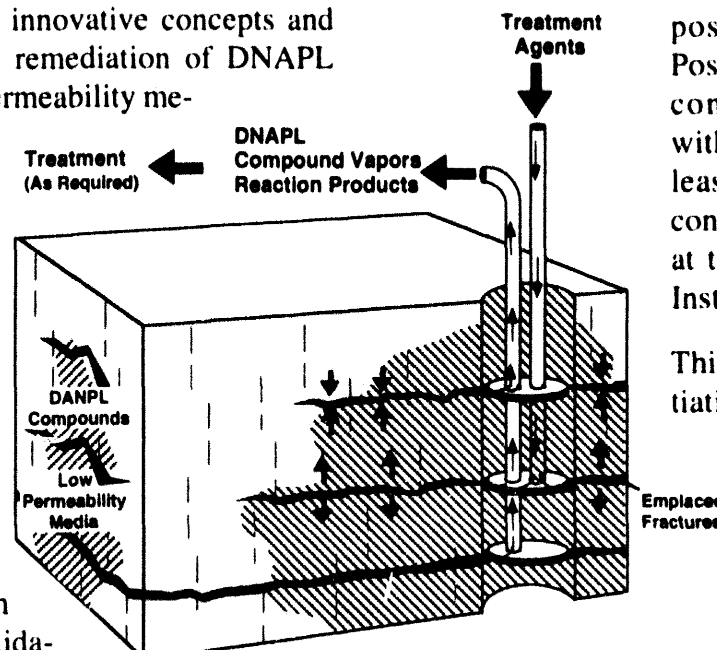
3.6 REMEDIATION OF DNAPL COMPOUNDS IN LOW PERMEABILITY MEDIA

A Joint Initiative of The Department of Energy and The American Petroleum Institute

TASK DESCRIPTION

Appropriate in situ remediation technologies for both source control and mass removal of Denser-than-water Non-Aqueous Phase Liquid (DNAPL) compounds in low permeability media will be tested and evaluated. Activities will be conducted to first identify and assess appropriate emerging and innovative concepts and technologies for the remediation of DNAPL compounds in low permeability media, and then recommend the most promising technologies for testing and evaluation. Technologies contemplated for study include separation and transfer processes, such as vapor extraction and subsurface mobilization, and destruction processes such as oxidation/reduction and bioremediation. Enabling technologies such as hydraulic and pneumatic fracturing, and mixing will also be considered.



Other aspects of the project will be directed to understanding the mechanisms that influence DNAPL migration in the subsurface, and to assessing the effectiveness and performance of the remediation technologies that will be tested under this project.

Investigations will focus on chlorinated solvents such as TCE and PCE. Contamination in the vadose and saturated zones, on low permeability, massive, naturally fractured media, and stratified deposits with inter-bedded clay lenses will be considered. Pilot scale testing will be carried out at the Sarnia, Ontario, site with a controlled release, and eventually at a long-term contaminated site such as Portsmouth sites X-231A, X-231B and X-701B, with controlled remediation and detailed post characterization. Possibilities also exist to conduct experiments with a contaminant release under controlled conditions in large cells at the Oregon Graduate Institute (OGI).

This project is a joint initiative of the Department of Energy (DOE) and the American Petroleum Institute (API). The broad objectives of the DOE/API project are to assess the effectiveness of innovative and emerging in situ remediation technologies and to develop new technologies for the remediation of DNAPL compounds. This undertaking will also help initiate research and development collaboration for environmental restoration and waste management between DOE and API.

TECHNOLOGY NEEDS

DNAPLs such as chlorinated solvents, PCB oils, and other organics constitute a major environmental problem across the DOE complex and the industrialized world. In addition, contaminated low permeability soil and geologic media represent site conditions that are common and very problematic for environmental restoration. However, these conditions have been generally overlooked in the past in terms of remediation technology development.

Following their release and migration into the subsurface, DNAPLs distribute themselves to form isolated "blobs" and "ganglia" known as "residuals," as well as connected DNAPL distributions known as pools. Both pools and residual DNAPLs contribute extremely small amounts of contaminants by dissolution into flowing groundwater over extended periods of time. DNAPLs in the unsaturated zone also contribute vaporized DNAPLs to the surrounding air, or undergo slow dissolution into percolating water.

Conventional remediation technologies have been tried without much success. Pump and treat approaches have been extensively used. Although this technology provides control of dissolved phase contamination, it has little effect on removing or controlling DNAPLs in the non-aqueous phase. In addition, there is increasing concern that the use of improper technologies to locate or remediate DNAPLs can worsen the problem by drawing contaminants into areas not previously affected.

Technologies are needed that will remove the sources of DNAPL contamination rather than merely treat DNAPLs dissolved in groundwater at extremely low concentrations. Removing DNAPLs as they dissolve in water will prove to be very lengthy and very costly.

ACCOMPLISHMENTS

A Memorandum of Understanding (MOU) between DOE Office of Technology Development and API is under preparation to provide the framework for DOE and API to work together in a wide range of subject areas.

The DNAPL work is expected to merge with an existing effort by API which focuses on remediation of light nonaqueous phase liquids (LNAPLs) in low permeability soils. The LNAPL project is ongoing, and deals with remediation of petroleum hydrocarbons. Results from the LNAPL effort will be made available and will be used to address the DNAPL question whenever applicable. The API project started in September 1992, and has accomplished several background technical reviews as well as planning activities. A gasoline spill was produced at the Sarnia site last September and instrumentation has been installed to monitor the migration and fate of the petroleum mixture BTEX used in the spill. Soil vapor extraction will be tested during the summer of 1993, with enhancement by hydraulic fracturing.

The DNAPL project is in the planning phase which began in July 1993. As currently planned, a series of technology focus papers will be authored by selected experts and completed in January 1994. These papers will lead to the selection of in situ remediation technologies to be evaluated. The technical viability of fracturing at the Sarnia test site will be studied during late summer 1993. A controlled release of TCE and/or PCE in one or more test cells at Sarnia is planned for FY94. Laboratory and field experiments will be conducted to evaluate selected in situ remediation technologies at the Sarnia site. Companion experiments will be conducted to address one or more long-term contaminated DOE sites if deemed feasible.

COLLABORATION/ TECHNOLOGY TRANSFER

This project will initiate cooperation between API and its members (about 250 corporations in the petroleum and allied industries), and DOE National Labs, in the environmental and waste management area. BP America is currently managing the API project and is expected to co-manage the combined DNAPL/LNAPL project with Oak Ridge National Laboratory. The combined project will expand the current API team and the consortium will include universities, DOE National Laboratories, oil companies, private industry and members of the solvent-in-groundwater Research Consortium organized by the University of Waterloo, Canada.

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EM-54

Technology Development
In Situ Remediation
Integrated Program

Subprograms

Section 4.0

Manipulation

4.0 SUBSURFACE MANIPULATION SUBPROGRAM

If contaminants are to be removed from soil in situ, effective methods for moving the contaminants through the soil to collection points must be developed. Clays and "tight" soils offer the greatest challenge; hydraulic flow through fine pores will be nearly zero, making these soils non-responsive to traditional soil washing. Electrokinetics is an attractive process for moving water and ionic materials through fine soils, because both electroosmosis and electrolyte migration are transport processes that are independent of pore size. For this reason, electrokinetic technologies are a major focus of this subprogram.

EM-50 has identified the following needs for technology development:

- Fundamentals of electrokinetic process control (pH, Eh, speciation, etc.);
- Contaminant recovery processes for electrokinetics; and
- Field demonstration of electrokinetic process for specific contaminants, e.g., uranium.

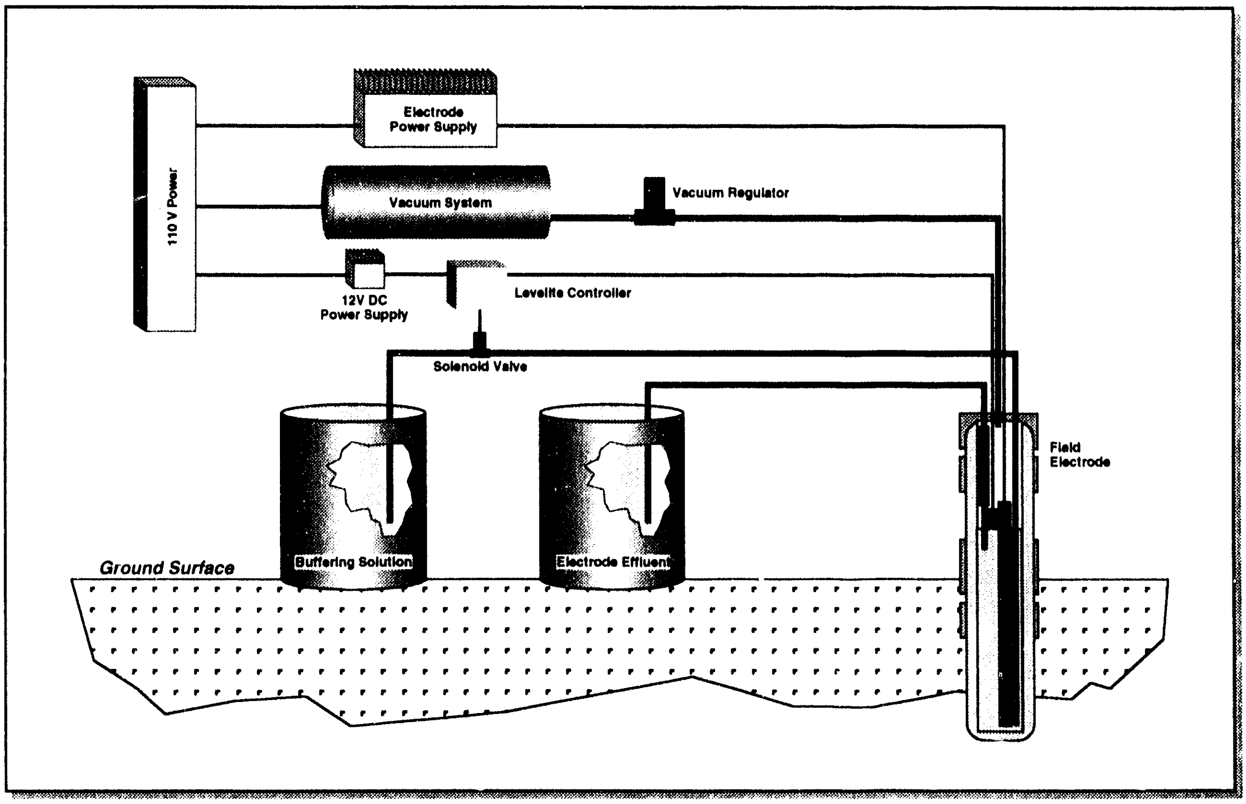

Figure 4.0. Electrokinetic Migration Technology (Sandia).

4.1 FIELD DEMONSTRATION OF ELECTROKINETIC MIGRATION TECHNOLOGY AT OLD TNX BASIN

TASK DESCRIPTION

The primary goal of this work is to demonstrate the electrokinetic remediation of mercury-contaminated unsaturated soil. The field work will be based on extensive laboratory tests of the process on soil samples from the field site, Old TNX Basin at DOE's Savannah River, South Carolina, site. The project will determine the nature and extent of information needed for design of a successful field remediation using electrokinetics.

TECHNOLOGY NEEDS

Many sites throughout the DOE complex have soils that have been contaminated with mercury or other toxic metals. The baseline technology for remediation of such soils is excavation and disposal of the contaminated soil, followed by replacement with fresh, clean soil. A process that would remove the contaminates in situ, thereby cleaning the soil in place, would be a desirable alternative. Electrokinetic migration technology is being evaluated for this task.

Old TNX Basin has been contaminated with mercuric nitrate, and groundwater near the basin has recently shown elevated (5 ppb) mercury levels, presumably due to leaching from the basin soil. If the source mercury can be removed, groundwater contamination should subside to acceptable levels. A field demonstration by Isotron Corporation will be conducted on a small portion of contaminated soil in the basin to determine viability of the electrokinetic technology.

ACCOMPLISHMENTS

Isotron Corporation is completing a lab-scale, one-dimensional study of mercury removal from Old TNX Basin soils at the Savannah River Site using its proprietary Electrosorb process. That study has shown that mercury in those soils can be moved by application of an electric field, and that the mercury can be trapped in Isotron's Isolock polymer at the electrodes. (The soils are primarily sand and kaolinite and contain 10-20% water by weight). The polymer can contain ion exchange resins to sorb the mercury ions before they reach the electrodes. Impregnating the polymer with buffers can control pH excursions in the pore water caused by electrolysis reactions. Selection of operating parameters for a field demonstration will be made from these laboratory data.

COLLABORATION/ TECHNOLOGY TRANSFER

This contract provides Isotron Corporation an opportunity to demonstrate their proprietary technology under carefully controlled conditions, with DOE site personnel assessing the validity of laboratory and field tests. The extent and cost of removal of mercury will be the ultimate measures of success.

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4.2 ELECTROKINETIC REMOVAL OF HEAVY METALS AND MIXED WASTES FROM PARTIALLY AND FULLY SATURATED 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 of specific waste sites. A theoretical and experimental investigation will be conducted to provide the information required to refine a numerical model of the electrokinetic remediation process. The experiments will study process response to a number of changes that can be expected to occur during remediation, e.g., changing pH and its effects on complex-forming metals and on non-ionic species; variations in soil permeability and water content on process kinetics, etc. Several tests will be conducted in a large, 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 incompletely understood because of the complexity of parameters and their interactions that occur when one applies a direct current between buried electrodes in contaminated soil. Contaminants can move through the soil by three different processes induced by the applied field: electroosmosis, electrophoresis, and electromigration. Electrolysis reactions that occur at the electrodes induce pH changes that can affect contaminant speciation and solubility. Contaminant mobility can also be influenced by soil permeability and the degree of water saturation. A mathematical model of all of these effects operating simultaneously will necessarily be complicated, and effects of parameters measured in isolation may not be the same as when changes occur together.

ACCOMPLISHMENTS

The Principal Investigator has analyzed those parameters that are most important to remediation success, and a recent review article nicely summarizes progress to date (SCIENCE, Vol. 260, pp. 498-503, April 23, 1993). Experiments in one-dimensional cells demonstrate that electrode chemistry plays an important role in transporting contaminants to electrode wells for removal. Reagents can be introduced at the electrodes to enhance contaminant removal rates. High degrees of removal have been observed, but propagation of sharp acid and base wave fronts from the electrodes can give rise to a "focusing" effect by which metals accumulate in certain regions of the soil. Simple procedures, including positive ion removal from the cathode region, can eliminate focusing. The ability to make quantitative predictions of expected contaminant removal and costs at an actual hazardous waste site is at an early stage of development.

COLLABORATION/ TECHNOLOGY TRANSFER

Close cooperation between this investigator and others at DOE sites who are attempting practical application of electrokinetic remediation will be maintained. General understanding of process fundamentals will be key to applying the technology in an intelligent and cost-effective manner.

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4.3 ELECTROKINETIC REMEDIATION OF HEAVY METAL CONTAMINATED UNSATURATED SOIL

TASK DESCRIPTION

The ultimate goal of this project is to develop an in situ electrokinetic process for removing chromate contamination from unsaturated soil. After the technology is developed and tested at bench and pilot scale in FY93, a field test in clean soil will be run in FY94 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 FY95 as part of the Mixed Waste Landfill Integrated Demonstration.

TECHNOLOGY NEEDS

A large portion of DOE's contaminated soil is unsaturated with water, especially in 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. There currently are no viable in situ methods for remediating heavy metal contamination from these unsaturated soils. 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 immediately 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 feet. Other DOE sites contaminated with mobile anions (e.g., MoO_4^{2-}, SeO_4^{2-}, $HAsO_4^{2-}$, $UO_2(CO_3)_3^{4-}$) should be treatable with this technology; anions are highly mobile in soil because they typically do not adsorb strongly on the soil surface.

ACCOMPLISHMENTS

Preliminary experiments at Sandia National Laboratories have 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 is presently under review by the Sandia patent office.

COLLABORATION/ TECHNOLOGY TRANSFER

Characterization of Sandia soils for fundamental electrokinetic properties will be performed at the University of Washington. All potential additions to the subsurface will be identified and discussed with the New Mexico Environmental Department to ensure compliance with all applicable regulations. An industrial partner having prior field experience with electrokinetics, ElectroPetroleum, Inc., will assist with design review, installation, and operation of the field demonstration.

For more information, please contact:

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4.4 IN SITU REMEDIATION BY ELECTROKINETICS

TASK DESCRIPTION

Pilot-scale demonstration of electrokinetic removal of uranium from contaminated soil will be accomplished in this project. Site selection and treatability studies will precede the pilot test, and a full-scale field test at a site to be determined is envisioned following evaluation of the pilot scale results. Removal efficiency, control of added fluids, contaminant recovery and disposal, power consumption, mass balance, and control of soil pH must all be evaluated to assure that 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 be such as to allow easy permitting for testing, be representative of the uranium problems throughout the DOE, and be accessible to industry, regulatory agencies, and academia.

TECHNOLOGY NEEDS

Remediation of uranium-contaminated soil is one of the major cleanup tasks facing DOE, and in situ methods are needed that can remove enough uranium to reduce contaminant concentrations to acceptable levels and allow the soil to return to productive use. Electrokinetic methods are being evaluated for this purpose, and applicability to uranium removal from saturated and partially saturated soils needs to be documented.

Soils from the K-311-1 and the K-1300 sites at the K-25 facility in Oak Ridge are being analyzed for treatability by electrokinetics, with results contrasted to previous characterizations made at the Drum Storage Area at the Fernald Site. The latter site has shown good response to carbonate leaching if electrokinetics can be used to move the solubilized uranium through the silty clay soil. Other Oak Ridge sites may also be identified for treatability analysis.

ACCOMPLISHMENTS

A report has been prepared by HAZWRAP and K-25 personnel summarizing initial site selection sampling activities. Regulatory and criticality issues are being investigated by K-25 personnel. Initial soil characterization studies involving disturbed soil samples will be finished shortly and plans for acquiring undisturbed samples are underway.

A suitable site for electrokinetic remediation will be selected on the basis of the treatability data and the site requirements for cleanup. A qualified industrial partner will be selected to conduct the pilot test in FY94.

COLLABORATION/ TECHNOLOGY TRANSFER

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

For more information, please contact:

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How To Get Involved

Technology Development In Situ Remediation Integrated Program

Section 5.0

5.0 HOW TO GET INVOLVED

WORKING WITH THE DOE OFFICE OF ENVIRONMENTAL RESTORATION AND WASTE MANAGEMENT

The Department of Energy (DOE) provides a range of programs and services to assist organizations and individuals once they have identified a potential environmental cleanup business or research opportunity. These programs and services include an Environmental Restoration and Waste Management (EM) Small Business Technology Integration Program (SB-TIP), phased procurements, and licensing of intellectual property. DOE also offers Cooperative Research and Development Agreements (CRADAs), technical personnel exchange assignments, consulting arrangements, and has an Office of Research and Technology Applications (ORTAs) in each major DOE Research and Development laboratory to facilitate industry access.

DOE EM Small Business Technology Integration Program

The EM Small Business Technology Integration Program seeks the participation of small businesses in the EM Research, Development, Demonstration, Testing and Evaluation (RDDT&E) 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.

CONTACT

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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 Research Opportunity Announcement (ROA). Through the use of the ROA, funding is provided to support a phased program of research and development for EM.

The objective of Phase I is to demonstrate the technical feasibility and potential merit of a given concept. The objective of Phase II is to determine the design and performance aspects of a technology relative to its intended use. The EM SB-TIP will work closely with private industry and

DOE EM programs to support full implementation and commercialization of promising technologies. The ROA and associated activities are summarized in Table 1.

TABLE 1. Research Opportunity Announcement and Implementation Phases.

Programmatic Information	Phase I	Phase II	Phase III
Objective	Concept Evaluation	Testing	Implementation
Duration	6-12 Months	12-24 Months	Case-by Case
Funding	Up to $100,000	Up to $500,000	Case-by-Case

Solicitation of Private Sector Technologies - Phased Procurements

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

Most EM Technology Development private sector technology is obtained through R&D contracts solicited through ROAs and PRDAs. EM Technology Development uses ROAs to solicit proposals for R&D projects and PRDAs for proposals for its DT&E projects.

EM uses ROAs to solicit industry and academic proposals for potential contracts in applied research. Proposals are subsequently peer-reviewed. Typically, ROAs are published annually in the Federal Register and the Commerce Business Daily, and multiple awards are made.

PRDAs are program announcements used to solicit a broad mix of R&D and DT&E proposals. A PRDA is used to solicit proposals for projects in areas where R&D or DT&E is required within broadly defined areas of interest, but where it is difficult to describe the work in detail. PRDAs may be used to solicit proposals for contracts, grants, or cooperative agreements. Multiple awards, which may have dissimilar approaches or concepts, are generally made. Numerous PRDAs may be issued each year.

Solicitation of Technologies Developed for Public Purpose

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

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

EM Central Point of Contact

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

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

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

Cooperative Research and Development Agreements

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

Limited Data Withholding

DOE EM has a 3-year limited withholding provision in place to encourage commercialization of DOE-funded technology. This provision is designed to assure that if industry participants provide at least a 20 percent cost share, to the extent permitted, EM will withhold from public release for 3 years commercially valuable information resulting from that work.

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 understand better the differing operating cultures, and are an ideal mechanism for transferring technical skills and knowledge.

Consulting Arrangements

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

Office of Research and Technology Applications (ORTAs)

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

For more information about these programs and services, please contact:

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EM-54

Technology Development
In Situ Remediation
Integrated Program

Section 6.0

Acronyms

ACRONYM LISTING

API	-	American Petroleum Institute
BNL	-	Brookhaven National Laboratory
BTEX	-	benzene, toluene, ethylbenzene, xylene
CRADA	-	Cooperative Research and Development Agreement
DNAPL	-	Denser-than-water Non-Aqueous Phase Liquid
DOD	-	Department of Defense
DOE	-	Department of Energy
DT&E	-	Demonstration, Testing & Evaluation
EM-50	-	Office of Technology Development
EPA	-	Environmental Protection Agency
FST	-	Ukrainian Fractionation Separation Technology
GE	-	General Electric Corporation
INEL	-	Idaho National Engineering Laboratory
ISR IP	-	In Situ Remediation Integrated Program
ITEP	-	International Technology Exchange Program
LLNL	-	Lawrence Livermore National Laboratory
LNAPL	-	Light Non-Aqueous Phase Liquid
MOU	-	Memorandum of Understanding
NAPL	-	Nonaqueous Phase Liquids
OGI	-	Oregon Graduate Institute
ORNL	-	Oak Ridge National Laboratory
PB	-	polybutenes
PCBs	-	polychlorinated biphenyls
PIB	-	polyisobutylenes
PRDA	-	Program Research and Development Announcement
ROA	-	Research Opportunity Announcement
sMMO	-	soluble methane monooxygenase
SNL	-	Sandia National Laboratory
TCE	-	trichloroethylene
TRU	-	transuranic
UMTRA	-	Uranium Mill Tailings Radiation Control Act (UMTRA) of 1978
UST	-	underground storage tank
VOC	-	volatile organic compound
WBS	-	Work Breakdown Structure

DATE FILMED

4/28/94

END