REMEDIATION OF SOIL AND GROUNDWATER CONTAMINATED WITH VOLATILE ORGANIC COMPOUNDS

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ABSTRACT

Contamination of groundwater by volatile organic chemicals (VOCs) is widespread at U.S. Department of Energy (DOE) sites. This problem is also encountered at other Federal sites listed in the U.S. Environmental Protection Agency (EPA) National Priority List (NPL), and private sector sites. These sites represent a variety of geologic, geophysical, climatic, and water-quality conditions. Since DOE sites are scattered across the country, dissimilarity in climatic conditions, such as aridity, becomes significant.

The remediation of these sites by conventional pump-and-treat techniques based on extraction of contaminants through vertical wells or boreholes, is a costly and time consuming process. Although a number of technologies for remediation of subsurface contamination are available, it was found that more efficient and cost-effective technologies are needed to address the widespread problem of contamination of groundwater by VOCs.

INTRODUCTION

Two Integrated Demonstrations have been established by DOE to address various remediation technologies applicable to arid and non-arid sites.An Integrated Demonstration (ID) is a cost-effective mechanism that assembles a group of related technologies and evaluates their performance, both individually, and as part of a complete system, to address waste management and environmental problems. An ID is crafted to meet certain established criteria for success. These criteria include:

- Responsiveness to DOE's Office of Environmental Restoration and Waste Management (ER&WM) Short-Term Needs
- Accomplishing Transfer of Technology to ER&WM and others
- Showing Acceptable and Expedient Regulatory Process for Future Use
- Showing Regulatory Compliance
- Showing Permanency
- Saving Money through Expediency and Efficiency
- Minimizing Generation of More Waste, and
- Showing Social Acceptance

DESCRIPTION OF THE INTEGRATED DEMONSTRATIONS

The DOE Office of Technology Development (OTD) established two IDs to address groundwater contamination of arid and non-arid sites. An ID is being conducted at the Savannah River Site (SRS) to address groundwater contamination by VOCs at non-arid sites, and another is in place at Richland, Washington to address similar problems at arid sites. Activities under the purview of these two IDs are described here.

INTEGRATED DEMONSTRATION FOR REMEDIATION OF GROUNDWATER CONTAMINATED BY VOCS AT NON-ARID SITE (SAVANNAH RIVER)

At the Savannah River Site (SRS), trichlorethylene (TCE) and tetrachloroethylene (PCE) were used as metal degreasing solvents for a number of years. A groundwater plume containing elevated levels of these compounds exists over an area greater than one square mile. A traditional groundwater extraction and treatment system has been in operation since 1984, and has removed approximately 230,000 pounds of solvents from the groundwater. However, additional solvents have continued to leach into the groundwater from the vadose zone.

GENERAL SITE GEOLOGY AND HYDROLOGY

SRS is located on the upper Atlantic Coastal Plain. The site is underlain by a thick wedge (approximately 1000 feet) of unconsolidated Tertiary and Cretaceous sediments that overlay the basement, consisting of pre-Cambrian and Paleozoic metamorphic rocks and consolidated Triassic sediments (siltstones and sandstones). The Cretaceous and younger sedimentary section consists predominantly of sands, clayey sands, and sandy clays.

Groundwater flow at the site is controlled by hydrologic boundaries. Flow at and immediately below the water table is to local tributaries. Flow in the lower Tertiary aquifer is to the Savannah River. Flow in the shallow aquifers in the immediate vicinity of the test site is highly influenced by the eleven-well pump-and-treat recovery network. The test site is located within the large VOC plume in the M-Area of the SRS.

TECHNICAL APPROACH

Innovative environmental technologies, including in situ technologies developed by DOE for the cleanup of groundwater and soils contaminated with chlorinated solvents, are being demonstrated at SRS. These technologies have great potential for providing a high level of environmental protection at the site, and allowing restoration activities to proceed in the most efficient manner possible. This is the first DOE Integrated Demonstration, involving scientists from various DOE laboratories and other federal agencies, working in collaboration at one site to demonstrate and evaluate new environmental restoration technologies.

The ID is being conducted in two phases. The first operational phase of the demonstration involved evaluation of the in situ air stripping process to remediate soils and groundwater contaminated with trichloroethylene (TCE) and tetrachloroethylene (PCE). The system purged volatile contaminants from the groundwater by injecting air through a horizontal well installed below the contaminated aquifer, and extracting the contaminants from another horizontal well installed in the unsaturated (vadose) zone above the water table.

During the period of July 27 through December 13, 1990, over 15,000 pounds of solvents were removed from the subsurface. After 60 days, TCE and PCE contamination concentrations in the groundwater were significantly reduced to levels approaching Clean Water Act standards in most of the monitoring wells installed at the site. Horizontal wells were installed to deliver and extract fluids from the subsurface because this geometry can maximize the efficiency of the remediation process, reduce treatment costs by as much as two-thirds, and can be applied in areas where contamination is present below existing facilities.

The in situ air stripping process using horizontal wells has demonstrated a more efficient way to remediate groundwater and soils contaminated with chlorinated solvents. Innovative monitoring technologies, geophysical tomography, and fluid flow sensors have demonstrated the effects of the air injection during remediation, and offer efficient and cost-effective options during remedial activities.

The second operational phase of the demonstration will involve demonstration of in situ bioremediation using the original two horizontal wells for delivery and extraction. Methane will be injected to provide nutrients to stimulate the indigenous microorganisms. Laboratory tests have shown that microorganisms naturally present in SRS soils can be stimulated to degrade TCE. Additional technologies to be tested during this phase of the project will include a number of gas-phase effluent treatment systems, fiberoptic sensors, and innovative sampling devices.

The integrated approach to demonstration of environmental restoration activities provides for the evaluation of an array of new technologies at a reduced cost, due to the synergism developed by working at one location. Technologies to be considered in the SRS ID are briefly described in the following paragraphs.

Cone Penetrometer - Soil Properties Test, and Cone Penetrometer - Sensor Test (with U.S. Army Corps of Engineers)

The U.S. Army Corps of Engineers (COE) successfully demonstrated their new Site Characterization and Analysis Penetrometer System (SCAPS) system at the integrated demonstration site. Real-time geological, geophysical, and geochemical data were collected using a system that costs approximately one-fourth that of traditional methods.

Hydropunch Test

Depth sampling of groundwater without wells was successfully completed at the demonstration site. It is the first time such samples were collected at these depths using a mud rotary drilling rig. A three-dimensional picture to better characterize the contaminant plume has been created using these data.

Vertical Depth Sampling of Core Tests Lawrence Livermore National Laboratory (LLNL)

Depth sampling of cores was conducted to produce a detailed three-dimensional picture of the contaminant plume. See Hydropunch test above.

Geophysical Tomography - Seismic Test Sandia National Laboratory (SNL), Electromagnetic Test (LLNL), and Electrical Impedance Test (LLNL)

Geophysical tomography has demonstrated the effectiveness of the air injection process. Three geophysical techniques have been tested using cross-hole methods to produce a two-dimensional picture of the subsurface during the remediation.

In Situ Fluid Flow Sensor Test (SNL)

In situ flow sensors have been utilized to monitor the progress of the in situ air stripping test. During air injection, groundwater has been measured moving upwards, whereas during periods of non-injection the gradient is downward.

In Situ Air Stripping Test (SRS)

Two horizontal wells were installed at SRS to test the feasibility of horizontal drilling technologies in unconsolidated sediments and to evaluate the effectiveness of in-situ air stripping of VOCs from the groundwater and unsaturated soils. The system purged volatile contaminants from the groundwater by injecting air through a horizontal well installed below the contaminated aquifer and extracting the contaminants from another horizontal well installed in the unsaturated (vadose) zone above the water table. Three injection rates and two temperatures were evaluated. The VOC removal was equivalent to an 11 well 500 gpm pump and treat system at the same site.

Nucleic Acid Probes (SRS)

This new technology represents a rapid, cost-effective method to characterize the microbes naturally present in the subsurface.

Bioremediation Characterization (SRS), Oak Ridge National Laboratory (ORNL)

Microorganisms indigenous to Savannah River Site soils had been characterized before the start of the in situ air stripping test. During the demonstration, the activity of the microorganisms was monitored. The number of microorganisms increased twofold during the air injection and decreased after the air injection was discontinued.

Helium Tracer Test (SRS)

Helium gas was injected with the air to provide information about fluid flow in the subsurface, i.e., the connection between the two wells. Gas flowing between the two wells was dispersed as it flowed through fine-grained zones. Over one month, approximately 37% of the injected helium was recovered by the extraction well.

Directional Drilling (SRS)

Two horizontal wells were successfully installed to demonstrate new environmental restoration technologies. This is the first time this technology, borrowed from the petroleum production industry, has been applied in the environmental arena.

Modeling and Analysis for System Designing and Control (LLNL)

Two dimensional flow modeling was completed to aid in the design of the air injection/vacuum extraction test. Refinement of this model will be completed using the results from the actual demonstration.

INTEGRATED DEMONSTRATION FOR REMEDIATION OF GROUNDWATER CONTAMINATED WITH VOCS AT ARID SITES (RICHLAND)

OTD established another ID at Richland, Washington to address the VOC-contaminated groundwater in arid areas. The VOC-Arid ID will focus on the development and comparison of technologies for characterization, removal, destruction, and monitoring of VOCs and associated contaminants at arid sites. Specifically, the ID will address vadose zone and groundwater contamination from carbon tetrachloride (CCl_4) and associated contaminants at the Hanford Site. The focus of this ID will be on the demonstration of technologies with applicability to VOC contamination at all of DOE's arid sites, and environments with large vadose zones.

Over 40 years of defense production operations at Hanford, it is estimated that more than 250 metric tons of CCl_4 was disposed to the soil column in the 200-West Area. Although direct soil column discharge of hazardous chemicals is no longer permitted, past operations have resulted in severe contamination of the vadose zone and a groundwater contaminant plume *extending* over more than seven square miles. Remediation of a site of this magnitude requires the development and demonstration of technologies encompassing all phases of a remedial action, from site characterization and assessment, through remediation, to evaluation of effectiveness and monitoring. Characterization technologies will be needed to locate and identify contaminated zones. Performance assessment and perspective capabilities will be needed to provide a scientific basis for decision-making. Remedial technologies will be needed to remove and/or destroy contaminants within the vadose zone and groundwater, and monitoring technologies will be needed to assess the overall effectiveness of the remedial technologies.

Bioremediation of Groundwater

Cost effective methods for surface treatment of extracted groundwater and in situ treatment of contaminated aquifers will be required for the VOC-Arid ID and for complete environmental restoration of the 200-West Area CCl_4 plume. Bioremediation processes for above-ground and in-situ treatment of CCl_4 and nitrates (NO_3) in groundwater are being developed in collaboration with researchers at the University of Washington (UW), Washington State University (WSU), and the University of Idaho (UI). Laboratory, bench, and pilot-scale testing has shown that CCl_4 and NO_3 can be simultaneously destroyed by indigenous (native) microorganisms.

The objectives of this research and development (R&D) effort are to develop and test cost effective surface treatment methods for extracted groundwater, and to develop and test in situ methods for stimulating the indigenous microflora to destroy the groundwater contaminants. Therefore, this activity is comprised of two primary approaches; above-ground biological treatment testing, and in situ bioremediation development.

In collaboration with ORNL researchers, a pilot-scale, above-ground biological treatment process was developed and tested with simulated groundwater. Recent activities have focused on the development of in situ bioremediation methods. Testing of the pilot-scale system will resume in the near future. The pilot-scale process and accompanying facility is permitted as a RCRA treatment facility; therefore, intermediate-scale testing will be possible without completing a lengthy regulatory permitting cycle. The facility will also allow other biological, physical, and chemical remediation technologies (or combinations of these technologies) to be tested with actual groundwater. Pilot-scale testing with actual groundwater will be coordinated with other R&D activities planning groundwater treatment testing to ensure that facility and regulatory permits are utilized to their fullest extent.

The goal of the in situ bioremediation development activity is to develop and test a remediation system that stimulates natural microorganisms to degrade CCl_4 and NO_3. The approach is to: 1) characterize a test site in the 200-West Area selected for field evaluation; 2) conduct laboratory feasibility studies to evaluate transport and degradation processes, using aquifer samples from the field site; 3) conduct intermediate-scale tests in flow-columns and controlled field-lysimeters to evaluate microbe stimulation techniques, transport, co-contaminant mobility, and model predictions; and 4) conduct small-scale, controlled field-testing at the 200-West Area site to evaluate the success of microbial stimulation techniques in an actual contaminated aquifer. Flow-through column testing and lysimeter testing with saturated sediments would allow for confirmation of laboratory results and validation of predictive models at approximately 1/15 scale of field testing.

Following the small-scale field testing, an R&D Technology Status Report will be prepared to provide a basis for determining whether the technology should move to demonstration, testing and evaluation (DT&E). Field testing at the DT&E phase would likely involve the use of horizontal wells and would be coordinated with the other DT&E activities comprising the VOC-Arid ID.

In Situ Heating

The first objective of this undertaking is to demonstrate electrical soil-heating as an inexpensive method for generating steam in situ to flush organic contaminants from impermeable soils as an enhancement to conventional soil-venting and washing methods. In FY 1990, combined in situ soil venting and heating was successfully demonstrated on a pilot-scale, using electrode/vents connected to a 480-volt six-phase power to provide extremely uniform soils drying without requiring any additives to maintain electrical conduction at such low voltages. Analytical and computer-based models for electrical soil heating and venting were developed and validated using the pilot-scale test data.

The major focus in the near future will be directed towards bringing ohmic soil heating near the point where a full-scale system can be designed for implementation at one or more of the site VOC IDs. This is scheduled to begin in FY 1992. The first target application for ohmic soil heating will be to thermally enhance the removal of VOCs from two impermeable clay layers located near a soil-gas extraction well at the SRS ID. A detailed conceptual design of a full-scale soil-heating system will be prepared as a basis for estimating costs and assessing overall practicality.

The second objective is to develop a cost-effective in-situ soils-treatment process based on in situ partial electrical discharges (high-energy corona). The process would be capable of rapidly destroying hazardous organic compounds in situ, obviating the need for excavation, pumping, stripping or above-surface treatment. Such a process would be ideal for destroying contaminant plumes in the vadose zone, particularly when nonvolatile contaminants and/or impermeable soils like clays and silts are involved. To date, laboratory-scale studies have demonstrated the capability of partial electrical discharges to destroy organic compounds in liquid, gas and solid form, as well as compounds absorbed on soils particles under water-saturated and bone-dry conditions. Destruction occurs without the need for additives other than ambient air at ambient pressures.

Preliminary bench-scale tests showed that partial discharges tend to occur at wet/dry interfaces in soils, but can also be initiated in dry bulk soil, and at unexpectedly low applied voltages. Initial data suggests that a 500-eV plasma is generated in the soil discharges, versus 2-3 eV in plasmas generated by RF- or microwave discharges. The high-energy soil discharges are expected to be capable of completely oxidizing organic waste compounds with the expected decomposition products being only water, carbon dioxide and halide salts.

Additional work planned towards this objective will be to test key hypotheses relating to simultaneous soil-heating and soils ionization, the two main phenomena that are believed to govern the in situ soil-treatment process.

Supported Liquid Membrane Treatment

Coupled transport (CT), an emerging membrane process that utilizes a supported-liquid membrane (SLM), is particularly attractive when compared to other technologies (i.e., reverse osmosis (RO), ion exchange, or evaporation) that are capable of removing the toxic ionic components down to acceptable levels. The principle advantage of the SLM process is that, unlike the other technologies, it can remove the toxic components selectively, leaving the nonhazardous components behind. The technology has application to any contaminated aqueous streams (i.e., groundwater, decontamination solutions, byproduct streams, condensates). Supported liquid membranes remove radioactive and hazardous contaminants while producing a small amount of secondary waste. Activities will involve the design, construction, and operation of a small to moderate-scale SLM system for pilot-scale field application to the cleanup of contaminated groundwaters.

Current activities include:

- Fiber optimization to identify the optimum (preferred) fiber for coupled transport of chromium (Cr), uranium (U), and nitrate. A selected fiber must have strength, high flux, and high bubble point.
- Identification of suitable chemistry for uranium- and nitrate-coupled transport to identify preferred complexing agent and solvent and preferred strip-solution composition for U-, and NO_3, -coupled transport.
- Chromium, uranium, and nitrate CT design studies to determine the performance of CT modules for Cr and U separation under a range of conditions and integrated uranium and chromium CT design studies.

The goal of the short-term activities is to design and construct a combined reverse-osmosis/coupled transport (RO/CT) system for the removal of Cr(VI), U(VI), technetium, and nitrate from a selected groundwater at the Hanford site. The RO would produce purified water and the RO raffinate would be fed to the CT unit to remove the contaminants in the form of a concentrated stream. An advantage of the combined RO/CT system is that it requires minimal CT membrane area. CT membranes are more expensive than RO membranes. Specific FY 1992 activities include; design, fabrication, and shakedown testing of the pilot scale system. The facility in which the field testing will be conducted will be identified and the necessary permits obtained shortly.

The in-field testing of the SLM process will be conducted in FY 1993 using actual contaminated groundwater. The field testing will demonstrate the volume of secondary waste achievable, the reliability, the efficiency of the process, and the operating parameters of importance. The demonstration results will be documented in an R&D Technology Status Report.

Drilling Technology Development

The purpose of this effort is to investigate, demonstrate, test and evaluate new and innovative drilling technologies to improve the access to subsurface soil and rock strata and groundwater for characterization, monitoring, and remediation. The immediate activities are devoted primarily to planning the program to meet the needs of the Department of Energy Sites which have drilling technology development needs, and/or a desire to participate in the VOC-Arid ID.

A Drilling Technology Development Plan which supports the needs of the VOC-Arid ID has been prepared. The plan will also address the other drilling technology development needs for site characterization, installation of monitoring wells, application of remedial cleanup technologies, and providing access to contaminated soil columns for in situ sensors and monitors and the use of geophysical logging techniques. The drilling technology subtask will be moved to the DT&E task in FY 1992 as transfer of horizontal well drilling technology proceeds.

Many DT&E technologies are ready for demonstration in one or more phases of remedial action (i.e., characterization, remediation, etc.). The VOC-Arid ID planning task will identify those technologies to be implemented in the early phases of the ID. Many more technologies require additional R&D before a sound technical decision can be made on whether they should be moved to the DT&E phase for this ID. These R&D technologies are being developed because they may provide a much more effective means of remediating the site at reduced cost.

Currently, the R&D activities associated with the VOC-Arid ID include technologies for in situ and above-ground destruction of CCl_4 and NO_3 groundwater contaminants, in situ volatilization and destruction of CCl_4 in off-gas streams, above-ground separation of metals, radionuclides, and NO_3 from groundwater or wastewater streams, and drilling enhancements to safely and effectively support the characterization, remediation, and monitoring phases of the ID. During planning of the VOC-arid ID, additional R&D tasks will be identified that support the overall objectives of the program. Many of these R&D tasks will be selected from applicable ongoing tasks within OTD across the DOE Sites.

TECHNOLOGY TRANSFER

Both NASA and EPA are interested in transferring the in situ air stripping technology for use at NASA sites contaminated with volatile organics. NASA and EPA both participated in a review of operations and a tour of the demonstration site. Although DOE has patented their process, three companies already hold licenses for this technology.

CONCLUSIONS

Remediation of groundwater contaminated by volatile organic chemicals using conventional pump-and-treat techniques is costly and time-consuming. More efficient, cost-effective technologies are needed to address the wide-spread problem of VOCs in groundwater. Integrated Demonstrations at an arid site and a non-arid site are exploring multiple in situ technologies.

DOE identified directional drilling as a potentially important technique for characterization and remediation of subsurface contamination. The horizontal in situ air stripping process extracted an average 110 pounds per day of VOCs during the extraction-only phase, as compared to approximately 25 pounds per day in one vertical well using a vapor extraction technique. The extraction rate was increased by approximately 20% with the addition of air injection below the water table. Further, indigenous microorganisms increased two-fold during the air-injection phase. In situ sensors and helium tracer testing were used to monitor fluid flow in the subsurface.

A pilot scale biological treatment process was developed and tested. In situ biological treatment methods are being developed. In situ electric soil heating and venting has been successfully demonstrated on a pilot scale. Analytical and computer models were developed and validated based on the pilot test data. Bench scale testing of high energy coronas can be initiated in dry and wet soils.

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The information in this article was developed during the course of work under contract No.DE-AC01-90DP48063 with the U.S. Department of Energy. Portions of the following have been referenced by the author.

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ACKNOWLEDGEMENTS

The authors gratefully acknowledge the assistance provided by D.S. Kaback and B.B. Looney, Westinghouse Savannah River Company, and by Steven Stein, Pacific Northwest Laboratory, in the preparation of this paper.