International Program for Technology Identification, Evaluation, Demonstration and Deployment: Technology Development & Deployment at Florida State University

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Introduction

Throughout the United States, as well as other industrialized nations, the problems associated with the cleanup of contaminated soils and groundwater represent significant human health and economic impacts on government agencies, industry and private citizens. Of particular concern is groundwater contaminated with dense non-aqueous phase liquids (DNAPLs). DNAPLs pose serious, long-term groundwater contamination problems due to their toxicity, limited solubility in groundwater; and significant migration potential in the vadose zone, groundwater, and/or as separate phase liquids. In 1998, the Interagency DNAPL Consortium (IDC) was organized by the U.S. Department of Energy/Office of Environmental Management and the Department of Defense, through the Air Force Research Laboratory, in an effort to develop a pre-deployment testing regime for mature DNAPL treatment technologies. The U.S. Air Force's 45th Space Wing, the National Aeronautics and Space Administration and the U.S. Environmental Protection Agency have joined the effort with the selection of Launch Complex 34 as the demonstration site. The IDC is currently conducting side-by-side demonstrations in Cape Canaveral, Florida of three promising DNAPL remediation technologies. Also of concern to DOE is the contamination of soils with heavy metals (e.g., lead-contaminated soils).

Another example of work that is also underway at Florida State University involves the development and deployment of bioremediation and phytoextraction technologies in cooperation with the Institute for Ecology of Industrial Areas (Katowice, Poland) with the ultimate goal of deployment at DOE sites. These technologies address both organic contaminants and heavy metals contamination of soils at sites similar to those within the DOE Complex.

This paper describes the working relationship among the various U.S. federal agencies involved with the DNAPL REmediation project as well as the on-going work conducted cooperatively with the Institute for Ecology of Industrial Areas in Katowice, Poland. The contact at Florida State University for this project is Dr. J. Michael Kuperberg (tel: 850-644-5524; fax: 850-574-6704; e-mail: mkupe@mailer.fsu.edu

Problems/Objectives

The problems addressed in this paper relate to subsurface contamination of soils and groundwater. Dense Non-Aqueous Phase Liquids (DNAPLs) pose serious, long-term groundwater contamination problems due to their toxicity; limited solubility in groundwater; and significant migration potential in soil gas, groundwater, and/or as separate phase liquids.

DNAPL chemicals, particularly chlorinated solvents, are among the most common of environmental contamination problems in the United States as well as for most industrialized countries. There are thousands of DNAPL-contaminated sites in the United States, often at contaminant volumes that are difficult to detect, but in quantities that can represent significant sources of groundwater contamination. Many agency and private-sector sites have DNAPL contamination problems, including federal, state and local government agencies. The Office of Management and Budget estimates that the federal government alone will spend billions of dollars for environmental clean-up of DNAPL contamination problems.

While various DNAPL remediation, characterization and monitoring technologies have been demonstrated in the past, it is difficult, if not impossible, to make meaningful comparisons of either performance or cost among these technologies because of the variable conditions at the demonstration sites. As a result, "problem holders" and regulatory officials have been reluctant to deploy these technologies for site clean up. In order to expedite the regulatory acceptance and use of these innovative remedial technologies, comparative cost and performance data must be collected. This project was designed to obtain those data for one selected site.

An important step in reducing technology risk and increasing user and regulatory acceptance of DNAPL remediation, characterization and monitoring technologies involves conducting concurrent, "side-by-side" field demonstrations. These side-by-side demonstrations result in comparative cost and performance data collected under the same field conditions. Through appropriate documentation, the resulting cost and performance data can be evaluated for site-specific applications. Side-by-side demonstrations help to fill an important "gap" in the process of technology development and deployment and will accelerate technology privatization.

This paper also addresses the problem of removal of heavy metals from relatively large areas of soils (phytoremediation) and the bioremediation of petroleum hydrocarbons from soils. Specifically these two projects implemented in southern Poland will be addressed and discussed in this paper. Each of these three technologies (for DNAPLS, heavy metals and petroleum hydrocarbons) will be discussed in the context of applications within the DOE Complex.

Approaches

In early 1998, a multiagency consortium (Interagency DNAPL Consortium – IDC) was organized by the United States Department of Energy/Office of Environmental Management (DOE/EM) and the Department of Defense (DOD) through the Air Force Research Laboratory (AFRL) and the 45th Space Wing in cooperation with the National Aeronautics and Space Administration (NASA) and the United States Environmental Protection Agency (EPA) to demonstrate innovative DNAPL remediation and characterization technologies at a NASA remediation site on Cape Canaveral Air Station, Cape Canaveral, FL. TheIDC was formed to:

- address a serious, widespread and shared environmental problem adversely affecting many U.S. federal agencies (e.g., DOE, EPA, DOD, NASA, Department of Interior, Department of Agriculture);

- cost-share the demonstration and comparison of these remediation and monitoring system technologies;

- accelerate both the demonstration and deployment of DNAPL remediation, characterization and monitoring technologies for the purpose of reducing the perceived technology risk associated with these technologies;

- increase regulatory and user acceptance of these technologies by providing documented, cost and performance data; and

- provide increased opportunities to test new sensors designed to support *in situ* remediation of DNAPL contamination problems in addition to *ex situ* treatment and disposal.

In order to conduct this side-by-side demonstration, a Core Management Team was organized consisting of representatives from the partnering agencies. The Team is a collaborative decision-making body that draws upon the strengths of each agency to solve problems associated with the project. The Team utilizes a Technical Advisory Group (TAG) for support in making decisions that concern individual evaluation of remediation systems. The TAG is comprised of experts from industry, academia and federal agencies with broad experience in DNAPL remediation technologies. With the support of the TAG, the Team selected three of the most promising remediation technology groups as suitable for the site and solicited proposals from the private sector. *(in situ* oxidation, *in situ* flushing, and *in situ* heating).

The approach used to implement the two projects (bioremediastion and phytoextraction) in southern Poland involves the use of the Joint Coordinating Committee for Environmental Systems (JCCES) which consists of representatives from DOE-EM (including the SCFA) and the Institute for Ecology of Industrial Areas (IETU) in Katowice, Poland. The JCCES members evaluate various proposed projects for testing and select the technologies to be evaluated. Teams consisting of IETU scientists, Florida State University scientists, experts from Westinghouse Savannah River Company and the Technical University of Budapest were formed to develop and demonstrate these two technologies in southern Poland.

Project(s) Description

Project Description: DNAPL Remediation Technologies

Six Phase Soil Heating

The Six Phase Soil Heating Technology removes contaminants from soil and groundwater by passing an electrical current through the soil matrix. The passage of current generates heat due to electrical resistance within the soil. This is the same process used in any electrically heated device (e.g., clothes iron, heater, stove). Heat is generated throughout the soil in the remediation area and the temperature of the soil is increased to the boiling point of water. Soil moisture becomes steam that is captured by vapor recovery wells for removal. Soil contaminants are vaporized concurrently and are captured for *ex situ* treatment.

Chemical Oxidation with Permanganate

In situ oxidation using potassium permanganate is a potentially fast and low cost solution for the destruction of chlorinated ethylenes (TCE, PCE, etc), BTEX (benzene, toluene, ethylbenzene, and xylene) and simple polycyclic aromatic hydrocarbons. In particular, potassium permanganate reacts effectively with the double bonds in chlorinated ethylenes such as trichloroethylene, perchloroethylene, dichloroethylene isomers, and vinyl chloride. It is effective for the remediation of DNAPL, adsorbed phase and dissolved phase contaminants and produces innocuous breakdown products such as carbon dioxide, chloride ions and manganese dioxide. The permanganate solution typically is applied at concentrations of one to three percent solution via injection wells. This solution is easily handled, mixed and injected and is non-toxic and non-hazardous.

Bench scale laboratory tests of potassium permanganate with trichloroethylene have resulted in up to a 90% reduction of trichloroethylene in four hours of treatment. The effectiveness of the *in situ* injection of permanganate is a function of the reaction kinetics, the transport and contact between potassium permanganate and the contaminant, as well as competitive reactions with other oxidizable species (e.g., iron, natural organics). The effective use of this remedial technology requires an engineered approach for maximizing the contact between potassium permanganate and the target contaminant. As with many technologies, low permeability and heterogeneity of soils present a challenge and require a carefully designed application system.

Thermal Remediation (Steam Injection)

Thermal remediation by steam injection and recovery uses Dynamic Underground Stripping, Steam Enhanced Extraction, Hydrous Pyrolysis/Oxidation, and Electrical Resistance Tomography. Combining these technologies the Dynamic Underground Stripping System uses boilers to generate steam which is then pumped into injection wells that surround the contaminants. The steam front volatilizes and mobilizes the contaminants as it pushes the resulting steam front toward a central network extraction well where it is vacuumed to the surface. Direct electrical heating of soils, clay and fine-grained sediments causes trapped water and contaminants to vaporize and forces them into steam zones where vacuum extraction removes them. Electrical Resistance Tomography is used as a process control method to measure electric resistance and temperatures in the subsurface that allow for real-time control of the heating process.

Sensor Technology Evaluations

In addition to DNAPL remediation technology demonstrations, the project provides the opportunity to evaluate innovative characterization technologies for locating DNAPL, *in situ* lithologic mapping, *in situ* vadose zone and saturated zone sampling and *in situ* hydraulic conductivity measurements. These technologies were deployed using the DOE and EPA Site Characterization and Analysis Penetrometer System (SCAPS) trucks. In addition to sensor technology evaluation, the SCAPS trucks have been used for data collection essential to conceptual model design and strategic location of critical lithologic units, sediment sampling and monitoring well placement. The following cone penetrometer (CPT) based sensors and sampling tools have been deployed at the Site.

Project Description: Bioremediation Technology

The US Department of Energy and the Institute for Ecology of Industrial Areas (IETU), Katowice, Poland have been cooperating in the development and implementation of innovative environmental remediation technologies since 1995. A major focus of this program has been the demonstration of bioremediation techniques to cleanup the soil and sediment associated with a waste lagoon at the Czechowice Oil Refinery (CZOR) in southern Poland. After an expedited site characterization (ESC), treatability study, and risk assessment study, a remediation system was designed that took advantage of local materials to minimize cost and maximize treatment efficiency. U.S. experts worked in tandem with counterparts from the IETU and CZOR to design, implement and monitor the bioremediation system. Passive and active gas injection using DOE-patented technologies were compared and contrasted with fertilizer, leachate recirculation, and surfactant addition to stimulate bioremediation of this low pH, PAH contaminated soil..

This is a multi-year project that began at a 100-year old oil refinery in Czechowice, Poland. The initial phases of the project used a biopile approach to decontaminate "aged" hydrocarbon contaminated soils. The approach used for the biopile involved the use of a combined aeration/leachate collection system to provide oxygen and steam to the biolpile. This technology proved to be highly successful in degrading the hydrocarbons at the site, particularly in soils that were at relativelky low pH as a result of the technology used to refine the crude oil at this refinery (acid-cracking technology). The indigenous microbial strains isolated at the site, the dual aeration/collection system and the potential to adapt this system to a mobile bioreactor have been the primary accomplishments of this project.

Project Description: Phytoextraction Technology

Since 1995, the US Department of Energy and the Institute for Ecology of Industrial Areas (IETU), Katowice, Poland have been cooperating in the identification, evaluation and deployment of international environmental remediation technologies that have a potential for application at U.S. Department of Energy sites. This includes remediation technologies that are being developed in Central & Eastern Europe, or other technologies that could benefit from evaluation/demonstration in Poland. One technology currently being evaluated by this program is the use of plants to remove heavy metals such as lead and cadmium from soil and sediment - Phytoextraction. The goal of this effort is to demonstrate phytoextraction of lead and cadmium at field scale, to minimize cost and maximize treatment efficiency. U.S. experts are work in tandem with counterparts from Poland to design, implement and monitor the phytoextraction process.

This project involves the large-scale application of selected plants to remove lead and cadmium from surficial soils at a site proximate to older metal smelting operations in southern Poland. The site selected is a cooperative farm that provided an opportunity to utilize conventional agricultural practices to implement this engineered phytoremediation technology. In addition to the use of selected plant species, special soil amendments were utilized to mobilize metals and stimulate plant uptake of these available metals. Other interesting advances of this technology involve the use of two instruments and associated software to optimize the technology and to minimize the cost of the technology. One of the most expensive components of this technology involves the purchase and application of the soil amendments. Scientists at the IETU developed a computerized application system, using site characterization data and a geographic information system that only applies amendments to areas of the site that exceed targeted soil concentrations. The result is an "on/off" sprayer that only applies amendments to contaminated soils. The application system is affixed to a conventional tractor-driven sprayer. The result is the reduction in the overall project cost of 21% or \$1.64 USD m^2. The other significant advance of this technology involves the use of a specialized chlorophyll fluorometer that evaluates plant "stress". This instrument allows the operator to monitor the plants as they reach maximum maturity and as amendments are introduced to the plants. The instrument indicates the optimal harvest time of the plants so as to harvest them after their maximum uptake of metals has occurred.

Results/Accomplishments

The accomplishments of the DNAPL technology demonstrations at Launch Complex 34 have resulted in comparable ("side-by-side") demonstrations of three remediation technologies. The results of these demonstrations include cost and performance data on each technology, plus the "lessons learned" associated with the use of these technologies. An additional important accomplishment of this project has been the formation of an overall approach for multi-agency projects involving environmental problems common to DOE, EPA, DOD, NASA and other federal agencies.

The primary accomplishments of the bioremediation project in southern Poland include the identification/isolation of the indigenous microbial (acidophylic) strains isolated at the site, the development and use of the dual aeration/collection system used at the site and, most importantly, the potential to adapt this overall system to a mobile bioreactor for use at DOE sites with low pH soils.

Both the ESC and risk assessment components of the bioremediation project represented "firsts" for the application of these procedures in Poland. These activities identified VOCs and BTEX as primary contributors to risks posed to present and future site workers at the refinery. Remedial goals for the cleanup of soils and sediments contaminated by lagoon sludge were established to guide the remedial activities. The innovative biopile design used a combination of passive and active aeration in conjunction with injection of nutrients and surfactants to increase biodegradation of the very acidic soil containing high concentrations of polynuclear aromatic hydrocarbons (PAHs). Simultaneous lab studies using soil columns were used to optimize treatment techniques and verify field observations under more controlled conditions.

This full-scale bioremediation demonstration showed that, with minimal cost, the total mass of petroleum hydrocarbons could be reduced by more than 81% (120 metric tons) over the 20 month project. During this time, the most toxic compounds were reduced to levels acceptable for multiuse resource activities. Though a variety of biodegradation monitoring methods were used, measures of microbial number and activity (i.e., direct fluorochrome counts and dehydrogenase activity) were found to be best correlated with rates of biodegradation in the biopile. In addition, our data indicate that passive aeration could reach the same end point as active aeration, it would just take longer. Rates of biodegradation were comparable to other prepared bed studies of petroleum contaminated soil, i.e., 121 mg/kg soil/day (82 mg/kg soil/day in the passive side). However, given that this material was highly weathered and very acidic these rates are much higher than expected. Much of this increase can probably be attributed to the sawdust added as a bulking agent, surfactant addition and to the aeration process.

The finding that microbial counts and dehydrogenase measurements accurately reflect biodegradation rates suggests that these direct measurements can be used to provide real-time control of biopile operation to maximize biodegradation rates under a variety of conditions. The cost savings from passive aeration may provide an advantage over active aeration when clean-up time is not a primary consideration. This demonstration also emphasized that biodegradation is initially quite rapid, but in less than 12 months requires additional stimulation via nutrient or surfactant addition. The remediation strategies that have been applied at the CZOR waste lagoon were designed, managed and implemented under the direction of the Savannah River Technology Center/IETU team in cooperation with the CZOR and Florida State University, for the United States Department of Energy. This collaboration between DOE, IETU and its partners, provides the basis for international technology transfer of new and innovative remediation technologies which can be applied to DOE sites, in Poland and at other locations worldwide.

The primary accomplishments of the phytoextraction project in southern Poland include the multi-hectare scale of the project (this is the largest scale phytoremediation known to exist), the development of the computerized system, adapted to a tractor-driven spray applicator for soil amendments and the development and integration of the specialized chlorophyll fluorometer for optimizing the timing of plant harvesting.

Based on initial results, research has focused on those factors which control cost and restrict performance. A significant factor in the cost of phytoextraction is the use of soil amendments. These amendments, primarily chelating agents, are used to increase the solubility of heavy metals in soil. The application rate for these amendments is based on soil properties, plant species and pollutant concentration. The issue of concern is the cost of amendments, which constitute the major part of the phytoextraction project budget (approximately 70%). The project sought to improve the accuracy of amendment application to the soil. Standard agricultural dispenser sprayed the soil amendments from above the plant canopy. This resulted in damage to the plants, losses of amendment through deposition on the plants and uncontrolled dispersion by the wind. This problem was addressed by developing a system that more carefully controlled the rate and location of amendment application (previously discussed). The improved version, equipped with downriggers and soil-level distribution nozzles, applied the amendments directly to the soil, close to the plant stems. This resulted in a reduction in the amount (and so, the cost) of amendments and eliminated the adverse effects of soil amendments on plants.

In the case of anthropogenic soil pollution, pollutants typically are not distributed evenly across a site. A system was developed to control the distribution of amendments so that areas of high contamination received high doses of amendments while areas of low or no contamination received little or no amendment. The resulting amendment control system utilizes digital site characterization data for pollutant concentrations across the site. The device controls the distribution of amendments so that the amount of amendment applied corresponds to the concentration of the target metal in soil. The unit is mounted on a tractor and controls valves that meter the flow of soil amendment. It is simple to operate and is controlled by the tractor driver from inside the tractor cabin. A field portable chlorophyll fluorometer developed by

Central European Advanced Technologies (Budapest, Hungary) is being applied in this project to evaluate the level of physiological stress experienced by plants as a result of the phytoextraction process. Many local plant species have been screened under greenhouse conditions for the ability to concentrate heavy metals in the above ground biomass. There is a generally recognized need for such screening activities to broaden the applicability of phytoextraction. Promising local plant species are included in subsequent field evaluations. The disposal of contaminated plant biomass resulting from phytoextraction is an important component of this technology. This project has evaluated the production rates and contaminant levels for several different plant species. The potential for composting and incineration for contaminated biomass has also been investigated. Finally, the project has developed initial data showing no adverse effects of soil amendments on soil microbial communities. Potential adverse effects are a concern for regulators. Further investigations are planned to address this question more broadly.

This phytoremediation project has implemented the largest scale application of phytoextraction documented to date. The cost and performance data obtained as well as the advances resulting from innovative modifications to the technology should provide needed support for a large scale deployment of phytoextraction at a DOE site in the US. The savings resulting from reduced use of soil amendments could be as much as 35% of the total cost of phytextraction. This reduction in cost, coupled with the experience and documentation gained from this project provide the Department of Energy with necessary information and a basis for further applications of this technology to the cleanup of contaminated soils in the United States and worldwide.

Application/Benefits

Each of these three projects have resulted in data and technologies which have direct application to DOE sites and other sites in the United States. The DNAPL remediation technology project will provide comparable cost and performance data for evaluating the technologies at DOE and other sites. The project to develop a mobile bioreactor based on the bioremediation project would result of device that could be used to treat secondary organic waste contaminants that result from e.g., bore-hole drilling, well drilling, sample collection and other aspects of site remediation. DOE sites also have surficial contamination of soils that could benefit from the phytoextraction technology developed in Poland.

Future Activities

The planned FY01 activities for the DNAPL remediation project at Cape Canaveral include the following:

- Post Demonstration Coring (soil sampling) in the Six-Phase Heating Cell;
- Demobilization of the Six-Phase equipment;
- 6-Month Monitoring Coring in the Oxidation Cell and Associated Groundwater Sampling;

- Pre Demonstration Coring in the Steam Cell;
- Construction of the Steam Injection Technology;
- Operation and Maintenance of the Steam Injection Technology;
- Demobilization of the Steam Injection Equipment;
- Post Demonstration Coring in the Steam Injection Cell;
- Preparation of Cost and Performance Data Documents for all 3 Technology Demonstrations.
- Groundwater sampling will occur according to project schedule throughout the year as well as peripheral project work such as biological sampling and monitoring.

The planned FY01 activities for the Bioremediation and Phytoremediation Technology projects include the following:

- Petroleum-Contaminated Soils Bioreactor Optimization and Enhancement Project;
- Use of the Bioreactor to Treat Chlorinated Solvent/Nitroaromatic-Contaminated Soils;
- Monitoring of Assisted Natural Attenuation at the Refinery Biolpile in Poland;
- Completion of the Comprehensive, Multi-Year Phytoremediation Project Report;
- Phytoremediation: Treatability Studies for DOE;
- Innovative Approaches to Mercury Contamination in Soil.

Related Publications

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Tien, A. J., A Worsztynowicz, K. Zacharz, D J. Altman, T C. Hazen. 1998. Technology Development and Transfer for Environmental Remediation, Sigma Xi Forum on International Cooperation in Science and Technology. Vancouver, B. C. 12-13 November 1998.

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Contract Information

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