DEVELOPING INNOVATIVE ENVIRONMENTAL TECHNOLOGIES FOR DOE NEEDS*  

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To be presented at  
30th Intersociety Energy Conversion Engineering Conference  
Orlando, FL  
July 31-August 4, 1995  

*Work supported by the Office of Technology Development within the U.S. Department of Energy's Office of Environmental Management under contract W-31-109-ENG-38.
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ABSTRACT

Environmental restoration and waste management activities at U.S. Department of Energy (DOE) facilities are diverse and complex. Contamination at DOE sites and facilities includes radionuclides, chlorinated hydrocarbons, volatile organic compounds, non-aqueous phase liquids, and heavy metals, among others. Soil and groundwater contamination are major areas of concern and DOE has focused very significant efforts in these areas. Relevant technology development activities are being conducted at DOE's own national laboratories, as well as through collaborative efforts with other federal agencies and the private sector. These activities span research and development (R&D) of new concepts and techniques to demonstration and commercialization of mature technologies. Since 1990, DOE has also supported R&D of innovative technologies through interagency agreements with U.S. Environmental Protection Agency (EPA), U.S. Department of Defense, the National Science Foundation, and others.

This paper summarizes DOE's environmental technology development efforts through participation in EPA's Hazardous Substances Research Center (HSRC) Program. It examines the R&D progress to date and discusses the status of the promising innovative technologies and their applicability to environmental remediation problems.

EM PROGRAM AND TECHNOLOGY DEVELOPMENT NEEDS

Contamination at the U.S. Department of Energy (DOE) sites is a legacy of past nuclear weapons research and production activities and includes radioactive, hazardous, and mixed contaminants. DOE has approximately 4,000 contaminated sites and facilities that need remediation. In addition, Department facilities are generating large quantities of waste from existing programs and cleanup efforts, (in 1992, for example, DOE generated approximately 140,000 m³ of radioactive waste and 125,000 tons of non-radioactive waste), even though large reductions in the amounts of waste generated have been achieved in the recent years.

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The wastes at DOE facilities include high-level radioactive waste, low-level radioactive waste, transuranic waste, hazardous waste, mixed waste, sanitary waste, and uranium mill tailings.

Soil and groundwater contamination are major problems at contaminated DOE sites and are of specific interest in terms of DOE needs for developing remediation technologies. Surveys of soil/sediment and groundwater contamination at several DOE facilities and waste sites have shown that chlorinated solvents, heavy metals, and radionuclides are the primary contaminants.

In 1989, DOE consolidated its environmental restoration and waste management activities in one office. Currently, designated as Environmental Management (EM) program, it is headed by a DOE Assistant Secretary. The EM organization's main technical components include: Office of Waste Management (EM-30), Office of Environmental Restoration (EM-40), Office of Technology Development (OTD, EM-50), and Office of Nuclear Materials and Facility Stabilization (EM-60).

The mission of OTD is to develop new, innovative, and effective technologies, and make them available or transfer them to the users in the DOE system. New technologies are sought to meet legal and regulatory requirements; to reduce risks, operating costs, and operating time; and to minimize the generation of new waste. Five focus areas have been defined for the program: high-level waste tank remediation; contaminant plume containment and remediation; mixed waste; landfill stabilization; and facility deactivation, decommissioning, and material disposition. The OTD acts in the role of program sponsor to identify, develop, and exploit new technologies for EM needs.

Early on in the EM Program, DOE recognized the importance of resources available in various sectors and elicited board participation from national laboratories, DOE facilities, universities, research organizations, other federal agencies, and the private sector in developing technologies that will allow environmental restoration efforts to proceed at optimum levels of safety and efficiency.

A number of mechanisms are being used for innovative research and development, and demonstration of the technologies. These mechanisms include Cooperative Research and Development Agreements (CRADAs) between federal and private sectors, and procurement mechanisms such as Research Opportunity Announcements (ROAs) and Program Research and Development Announcements (PRDAs). The procurement activities are currently being coordinated by DOE's Morgantown Energy Technology Center. An example of the first private sector procurement activity by DOE in 1990, and managed by Argonne National Laboratory is available in DOE/CH-9303 report.

Another mechanism being used effectively is the Interagency Agreement (IAG), which provides DOE an opportunity to leverage its funds in the research and development (R&D) phase of technology development through co-sponsoring projects with U.S. Environmental Protection Agency (EPA), the National Science Foundation (NSF), U.S. Department of Defense (DOD), and others. Under the IAG with EPA, DOE participates in two major programs, Hazardous Substances Research Centers (HSRC) Program, and the Superfund Innovative Technology Evaluation (SITE) Program. The first program focuses on R&D, and concept demonstration, while the latter focuses on demonstration of technologies prior to commercialization and application.
HAZARDOUS SUBSTANCES RESEARCH CENTERS PROGRAM

The HSRC Program was set up by EPA in response to the 1986 amendments to the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA, also commonly known as the "Superfund" law), when U.S. Congress authorized $25 million in funding for the first five year life of the program. The Center's program was renewed for another five year period and a number of other programs have been added to the Center's mission in addition to their original mission of conducting R&D to develop technologies for the Superfund Program. The additional programs include the Minority Academic Institution Program (MAI), and the Research and Re-education for the Department of Defense (R2D2) program.

The HSRC Program established five centers, geographically distributed across the country and each center covering two federal EPA regions. Each center is located at a main participant university but consists of a consortium of several universities in the region. These centers are the Northeast (NE) HSRC, Great Lakes and Mid-Atlantic (GLMA) HSRC, South/Southwest (S/SW) HSRC, the Great Plains/Rocky Mountain (GPRM) HSRC, and the Western Region (WR) HSRC. Currently, 23 universities participate in the program. The basic mission of the HSRCs is to study all aspects of managing hazardous substances and waste. Currently, the main focus of the program is the R&D related to remediation of contaminated sites.

The research focus at individual centers represents the regional environmental needs and the key expertise of its consortium members. The focus of the research at NE Center, based at New Jersey Institute of Technology, is incineration/thermal destruction technologies and physical/chemical/biological methods for remediation. The GLMA Center, based at the University of Michigan, is focused on bioremediation research. The S/SW Center, based at Louisiana State University, is focused on contaminant characterization and transport in sediments and dredged materials. The focus of the GPRM Center, based at Kansas State University, is on soils and groundwater remediation. The WR Center, based at Stanford University, is focused on in-situ bioremediation methods and heavy metals remediation.

DOE PARTICIPATION IN THE HSRC PROGRAM

DOE signed a Memorandum of Understanding (MOU) with EPA that was issued on January 2, 1990. Under this MOU, the DOE agreed to co-fund research (and technology transfer and training activities) relevant to DOE's needs and interests in the environmental restoration and waste management areas through EPA's HSRC Program. The MOU was later incorporated into a master IAG with EPA.

Participation in an existing EPA program allows DOE to leverage its funds to develop innovative technologies that are of particular interest for use at existing DOE sites. It has two major benefits: avoiding duplicate efforts with federal dollars, and directing scarce innovative technology development funds to focused research for EM needs. The HSRC program also offers DOE a very cost-effective way of tapping into the vast research expertise at many of the nation's top universities. An independent targeted program could cost DOE many times more. The DOE funds for this activity are highly leveraged to derive maximum benefit and payback to DOE. Several DOE-sponsored projects in the HSRC Program have led to development of innovative technologies that have been demonstrated and are ready for field application.
Typical DOE participation in the past has been to co-fund projects in this program at a level of about three quarters of a million dollars per year with direct access to a million and a half or more dollars worth of research. In 1993, the DOE fully supported three additional projects at quarter of a million dollars each for a total program investment of 1.5 million dollars that year. However, the total research conducted at these five centers is typically 10 million dollars or more annually, double the base EPA grant of 5 million dollars a year because of the addition and funding of other programs such as the MAI and R2D2 programs, and because of other sources of funding such as state, private industry, other federal sources, and university matching funds. This is the major value-added feature of the program that participation in the program allows DOE access to vast amounts of research and specific technologies of interest can be transferred through various mechanisms for DOE’s use.

R&D FOR INNOVATIVE TECHNOLOGIES

The DOE has co-sponsored projects in the HSRC Program since 1990. A list of DOE co-sponsored recent projects is shown in Table 1.

The ongoing projects involve the following research areas: microbial degradation of contaminants, use of a radon-222 method for locating non-aqueous phase liquids (NAPLs) in the subsurface, modeling of contaminant plumes in the subsurface, electrochemical sensor development for heavy metals, use of electric purging of heavy metal from soil, immobilizing heavy metals in a ceramic matrix, development of hollow-fiber membranes for metal recovery in waste, and development of nano-scale metal oxides as reagents for destruction of hazardous substances.

The most notable examples of successful projects include: pneumatic fracturing to enhance removal of volatile organic compounds (VOCs), in-situ bioremediation of contaminated aquifers, and field applicable gas chromatograph-mass spectrometer (GC-MS), which have been completed; the mercury-coated iridium ultramicroelectrode (Hg/IrUME) sensor for heavy metals in groundwater, and destruction of hazardous substances through the use of nano-scale metal oxides, which are close to a demonstration stage.

HSRC TECHNOLOGY DEVELOPMENT HIGHLIGHTS

In the remainder of this paper, four DOE co-funded projects, (1) through (4), are discussed (for details see publications in the Bibliography). In the first two projects described here, innovative technologies have already been developed and demonstrated and are ready for field application. In the latter two projects, promising technologies are nearing completion.

(1) The first project involves application of pneumatic fracturing. The DOE, along with the EPA, supported the development of the pneumatic fracturing technology in the research stages through the NE HSRC. The project was based at the New Jersey Institute of Technology (NJIT, John Schuring, Principal Investigator).
Table 1: RECENT HSRC PROJECTS*

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<td>Phase Equilibria and Transport Properties of Surfactant Systems of Interest to Soil Remediation</td>
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<td>WR</td>
<td>Degradation of Chlorinated Aliphatic Compounds by Autotrophic Nitrifying Bacteria</td>
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<td>Radon-222 Method for Locating and Quantifying Contamination by Residual NAPLS in the Subsurface</td>
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<td>Heavy Metals in Ceramic Matrix: Heavy Metal/Clay Interactions in Ceramic Processing</td>
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<td>In-Situ Bioremediation of Chlorinated Aliphatic Compounds Phenol Utilizing Bacteria</td>
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<td>Enhancement of Biodegradation through the Use of Substituted Porphyrins to Treat Groundwater Contaminated with Halogenated Aliphatics**</td>
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<td>NE</td>
<td>Electrochemical Sensor for Heavy Metals in Groundwater: Phase II - Instrument Development and Field Demonstration</td>
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<td>Individual Metal Removal/Recovery by a Novel Hollow Fiber Membrane</td>
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<td>Three-Dimensional Characterization of Subsurface Contamination: Before and During Remediation</td>
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<td>Competitive and Mass Transfer Effects on the Sorption and Desorption of Contaminants in Soil</td>
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<td>Use of Pneumatic Fracturing to Enhance Removal of VOCs from Clay Formations**</td>
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<td>Electrical Purging of Heavy Metals and Mixed Hazardous Wastes from Partially and Fully Saturated Soils**</td>
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<td>GPRM</td>
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<td>Innovative Treatment and Bank Stabilization of Metals-Contaminated Soils and Tailing along Whitewood Creek, South Dakota</td>
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<td>Modeling the Use of Plants in the Remediation of Soil and Groundwater Contaminated by Hazardous Organic Substances</td>
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<td>Nano-Scale Metal Oxide Particles as Reagents for Destruction and Immobilization of Hazardous Substances</td>
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* During 1994, 9 of 21 DOE co-funded HSRC projects were completed.  
**Special projects.
Pneumatic fracturing has been demonstrated to be highly effective in enhancing the removal of VOCs from clay, siltstone, and sandstone formations. Solvent contamination in low-permeability formations is an especially difficult problem where conventional remedial approaches have generally failed. Here again, the pneumatic fracturing technology has been demonstrated to enhance VOC removal even though the efficiencies are somewhat lower.

Field demonstrations of the technology have been completed at the following sites: Frelinghuysen Township, NJ; AT&T Richmond Works, Richmond, VA; NJIT Campus, Newark, NJ; ECRA Site, Roseland, NJ; ECRA Site, Hillsborough, NJ; and the ECRA Site, Newark, NJ. Accutech Remedial Systems of New Jersey is commercializing the technology. Enhanced removal of trichloroethylene (TCE) has been demonstrated at a number of these sites. TCE is also a major contaminant at several DOE sites.

In 1993, a demonstration on pneumatic fracturing was funded by DOE as a special HSRC project at the Tinker Air Force Base (AFB) in Oklahoma. The project objectives were three-fold: (1) to enhance recovery of fuel oil (from leaking underground storage tanks) from the saturated zone, (2) to enhance recovery of BTEX and chlorinated solvents from the unsaturated zone, and (3) to assist in technology transfer. All of these objectives were achieved. The demonstration at Tinker AFB in Oklahoma also provided a look at potential cost savings. The Air Force pumped 2,100 gallons of fuel oil in 25 months prior to pneumatic fracturing; post-fracturing, they recovered 2,900 gallons in two months.

The potential cost savings will vary for contaminated sites because of the number of variables involved. However, cost analysis for the Tinker AFB site has clearly demonstrated that significant savings can be achieved in remediation of the sites contaminated with VOCs if this technology can be applied. In general, the extraction wells required in the post-fracture environment are reduced to about one-fourth the number in the pre-fracture environment, which leads to savings in equipment and operational costs. Also, from the EPA demonstration data on this technology, it was observed that the air flow rate in the post-fracture environment was enhanced by a factor of almost 80 and the TCE removal was enhanced by a factor of 6. It is clear that application of pneumatic fracturing technology in conjunction with VOC extraction technology can provide significant cost savings.

For remediation purposes, the technology can be used in concert with other technologies, for example, pneumatic fracturing/hot-gas injection, or pneumatic fracturing/in-situ-bioremediation. The technology is currently being considered for application at DOE's Hanford site.

(2) At the WR Center, development work has been carried out on in-situ bioremediation. The goal of this project, based at Stanford University (P. McCarty, Principal Investigator), has been to evaluate in the field the rate and extent of degradation of chlorinated aliphatic compounds using microorganisms. Chlorinated aliphatic compounds are a major contaminant of groundwater at many DOE and EPA sites requiring remediation.

Cometabolism using phenol as a primary substrate has been studied. Earlier research at Stanford has indicated that microorganisms containing the toluene monoxygenase (TMO) or toluene dioxygenase (TDO) enzyme can oxidize chlorinated aliphatic compounds such as TCE by cometabolism, similar to biodegradation by methanotrophs with methane monoxygenase.
(MMO). The toluene oxygenases can be induced by several primary substrates, including phenol. In order to obtain a comparison between the relative advantages and disadvantages of the TMO or TDO systems and the MMO enzyme system, an evaluation was conducted at the field site at Moffett Field Naval Air Station in California where a four-year evaluation of the MMO system had earlier been completed.

Phenol and oxygen were dissolved in recycled groundwater, along with TCE, dichloroethylene, and vinyl chloride for introduction into a confined aquifer about 4 m below the surface. The growth of the native phenol-degrading population, and the rate and extent to which the introduced chlorinated compounds were removed, were continuously monitored by automatic extraction of groundwater from monitoring wells and on-site analysis. The extent of transformation was evaluated through comparison of concentration decreases with conservative tracers.

Field and laboratory studies at Stanford University have helped develop a basic understanding of the processes involved in methanotrophic treatment of chlorinated aliphatic compounds as well as with phenol utilizing bacteria, and through cometabolism with toluene-oxygenase microorganisms. Thus, research at Stanford has provided data to engineer in-situ bioremediation systems for field application. It has also shown that bioremediation of groundwater offers great promise because it results in the destruction of key contaminants of concern, such as TCE.

A field demonstration of in-situ bioremediation of chlorinated aliphatics is being conducted at the St. Joseph's Superfund Site in Michigan. In-situ bioremediation based on methane insertion is also being applied at DOE's Savannah River Site.

(3) This project at the NE HSRC involves development of a an electrochemical sensor for real-time in-situ measurement of environmentally significant heavy metals in surface or groundwater. The ability to obtain real-time, in-situ, high-quality data is crucial for screening of groundwater at purported hazardous waste sites. Analytical data turnaround for state, federal, and commercial laboratories typically exceeds several months, resulting in increased costs and delayed decisions. Electrochemical techniques, because of their remarkable sensitivity and ease of use in aquatic media, offer the promise of being versatile and efficient approaches for in-situ measurement of metal-ion species.

The project is led by Tufts University (S. Kounaves, Principal Investigator), a consortium member of the NE HSRC, with collaboration from the Center for Integrated Systems at Stanford University and the EG&G Instruments of Princeton, NJ.

In the first phase of this project, researchers successfully constructed and tested the electroanalytical component of the sensor, the Hg/IrUME. It is capable of measuring heavy metal ions such as Pb and Cd, from low-ppb to high-ppm levels, in various model and natural water systems. In the second phase, the researchers have tested a unique prototype, integrated-circuit-based, multi-element-array version of the Hg/IrUME with increased sensitivity, reproducibility, and stability.

The aim is to incorporate a final version of this unique microarray sensor into a custom-made portable instrument. The researchers want to ensure that the final version of the sensor could be easily and cheaply fabricated to facilitate eventual technology transfer and commercialization.
This led researchers to consider photolithographic and microelectronic processes for fabricating the iridium array for the sensor.

Field demonstration of the technology is planned and it is expected that the technology will be commercialized in near future.

(4) In this project based at Kansas State University (K. Klabunde, Principal Investigator) through the GPRM HSRC, research is in progress on nano-scale metal oxide particles as reagents for destruction of hazardous substances. This innovative technology is based on ultrahigh surface area metal oxides with reactive surfaces that behave as "destructive adsorbents" and the purpose is to accomplish one-step destruction of hazardous substances, including chlorocarbons, chlorofluorocarbons, organophosphorus, nitrogen, and sulfur compounds.

Results of the research so far indicate that for metal oxides to be effective destructive adsorbents for chlorocarbons (which are of specific interest to DOE), three parameters are critical: high surface area; surface basicity; and favorable thermodynamics. Thus, products and rough material balances have been determined for CCl₄, CHCl₃, and C₂Cl₄.

The chemical reactions occur in the 300-600°C temperature range. The metal oxides being tested in the laboratory include CaO and MgO. Because the reaction takes place only on the surface of the metal oxides, the metal oxide must have a very large surface area for the reaction to be efficient; hence, ultrafine, nanoscale metal oxide particles are required.

Until very recently, nanoscale CaO was the best destructive adsorbent. However, researchers have now prepared ultrahigh surface area Fe₂O₃ on MgO, and have found that this combination surpasses all the numerous others tested before. The high capacity of Fe₂O₃/MgO for destructive adsorption of CCl₄ is apparently due to a "spillover" catalytic effect as yet unknown in the literature. It appears that Cl/O exchange takes place on Fe₂O₃ and Cl spills over onto MgO where another Cl/O exchange takes place. In this way, much more MgO is converted to MgCl₂. This discovery of "catalyst enhanced" destructive adsorption is significant, and further studies are continuing.

Experiments on the destruction of carbon tetrachloride have been highly successful; however, for TCE the efficiencies were lower. Further studies are continuing with nonactivated and autoclave- prepared CaO and under different parametric conditions. The researchers are also studying destruction of some "model" toxic chemicals such as dimethyl methylphosphonate (DMMP), a nontoxic mimic of a military nerve agent, on nano-scale MgO particles. It is anticipated that these studies will lead to a cost-effective technology for destruction of stockpiles of nerve agents.

The researchers have constructed a laboratory-scale semi-continuous reactor that can be utilized to better understand the bulk behavior of the particles and optimize the operation parameters like temperature, pressure, particle size, etc. This reactor system may serve as a scale-up model for the advanced reactor system that is currently being planned.
CONCLUSION

For its complex remediation needs, DOE is fostering development of innovative environmental technologies through a variety of mechanisms. Participation in the EPA HSRC Program is one such mechanism through which DOE has co-sponsored research and development projects since 1990. A number of technologies developed under the program have been demonstrated and are being commercialized. Examples include field-applicable GC-MS, pneumatic fracturing, and in-situ bioremediation. Technologies that are currently very close to the demonstration stage include electrochemical sensor for measuring heavy metals contamination in groundwater and nanoscale metal oxides for the destruction of hazardous wastes.

Participation in the HSRC program has allowed DOE to highly leverage its investment in the R&D phase of the technology development process, when the risks are high. The innovative technologies developed through the program are a testimony to its success.

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