HARVESTING EMSP RESEARCH RESULTS FOR WASTE CLEANUP

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ABSTRACT

The extent of environmental contamination created by the nuclear weapons legacy combined with expensive, ineffective waste cleanup strategies at many U.S. Department of Energy (DOE) sites prompted Congress to pass the *FY96 Energy and Water Development Appropriations Act*, which directed the DOE to:

> "provide sufficient attention and resources to longer-term basic science research, which needs to be done to ultimately reduce cleanup costs…"
> "develop a program that takes advantage of laboratory and university expertise, and…"
> "seek new and innovative cleanup methods to replace current conventional approaches which are often costly and ineffective."

In response, the DOE initiated the Environmental Management Science Program (EMSP)—a targeted, long-term research program intended to produce solutions to DOE's most pressing environmental problems. EMSP funds basic research to lower cleanup cost and reduce risk to workers, the public, and the environment; direct the nation's scientific infrastructure towards cleanup of contaminated waste sites; and bridge the gap between fundamental research and technology development activities. EMSP research projects are competitively awarded based on the project's scientific, merit coupled with relevance to addressing DOE site needs.

This paper describes selected EMSP research projects with long, mid, and short-term deployment potential and discusses the impacts, focus, and results of the research. Results of EMSP research are intended to accelerate cleanup schedules, reduce cost or risk for current baselines, provide alternatives for contingency planning, or provide solutions to problems where no solutions exist.

INTRODUCTION

The natural progression of research is from basic science to applied science and technology development to demonstrations to deployments. Basic research is the fundamental building block that may unfold new and creative solutions to high priority needs, enabling DOE to meet cleanup milestones. In some cases, EMSP research quickly provides processes or technologies that are ready for immediate use, as seen by the completed deployments. Still other EMSP projects require little additional work to be incorporated into cleanup activities, and deployments are imminent. Some EMSP projects have been transitioned to applied research or technology development programs for further development or field testing. Results may take the form of increased scientific understanding or the development of new tools or processes.

The projects highlighted in this paper are divided into three categories based on technology maturity:

Field transfers technologies that have been successfully demonstrated or deployed in the field at a DOE site

Emerging science projects that will result in technologies that may be ready for deployment within two years with the support of a site champion to take the research to the next step

Core science projects in the conceptual phase and expected to yield results in greater than two years.

The EMSP is currently in its seventh year, and promising new results for DOE's cleanup program are emerging. Although the program is relatively young, EMSP research has been instrumental in five deployments to field operations. Research by one EMSP project supported the technical basis for amending the Record of Decision for groundwater treatment at the Test Area North location at the Idaho National Engineering and Environmental Laboratory (INEEL). The new remedy, which uses monitored natural attenuation and in situ bioremediation, in combination with the originally selected pump and treat technology, will accelerate removal (by a factor of two) of trichloroethylene contamination to within 15 years and save taxpayers $23 million in life-cycle costs (1). When the plugging of an evaporator at the Savannah River Site caused premature shutdown of the Defense Waste Processing Facility (DWPF) in October 1999, an EMSP researcher studying the formation of aluminosilicates developed a thermodynamic model to predict solids formation and establish a safe operating envelope for evaporator composition (2). Also at the DWPF, severe foam problems occurred that hindered processing. EMSP research on the fundamental understanding of the physical mechanisms that produce foaming in the DOE high-level waste and low-activity radioactive waste separations processes led to the development of a radiation-resistant anti-foam agent for the DWPF (3). In another project, a radon thoron detector developed by New York University has been deployed around radon silos at the Fernald site. It has also been deployed to detect radon in water at fish hatcheries in Pennsylvania and for various monitoring activities in China, Finland, Canada, Thailand, and Japan (4). In yet another project, an electromagnetic survey of Pit 9 at the INEEL created maps of buried waste, which when coupled with the information obtained from other surveys and shipping records enabled DOE to safely emplace stainless steel tubes for neutron logging and chose a preferred excavation site to demonstrate remediation capabilities. Construction began four months ahead of schedule, and a $1 million fine was avoided.

Projects highlighted in this paper are just a sampling of some of the successful EMSP projects. At least ten technologies resulting from EMSP research have already been commercialized. In addition to these quantifiable benefits, EMSP research has increased the scientific knowledge base in areas directly needed to achieve DOE's cleanup mission. Scientific concepts developed by EMSP researchers have already shown promise in fields unrelated to DOE cleanup, and may be useful in both the public and private sector, similar to technologies developed by the space program. Countries, such as the former Soviet Union, are using the advances from EMSP research for cleanup or monitoring of contaminated nuclear sites.

EMSP FIELD TRANSFERS

The following five EMSP projects have been deployed. The number of projects deployed is a significant accomplishment for a basic research program since the transition from basic research to application normally takes several years to occur.

Control of Biologically Active Degradation Zones by Vertical Heterogeneity: Applications in Fractured Media (Project #55416)

Fig. 1. Aseptic sampling of fractured rock.

Many DOE sites have contaminants that are difficult to access due to depth and complex geology and are challenging to remediate using conventional methods. Fundamental, field-based research is required to understand what is needed to address complex cleanup issues, such as the cleanup of dense non-aqueous phase liquids (DNAPLs) in fracture flow environments.

The key objective of this project was to determine the distribution of biologically active contaminant degradation zones in a fractured, subsurface medium. The research was performed at the Test Area North (TAN) site at the Idaho National Engineering and Environmental Laboratory (INEEL) where a dissolved trichloroethylene (TCE) plume is migrating in the Snake River Plain Aquifer (SRPA). INEEL scientists provided technical assistance to develop a technology to verify that enhanced microbial degradation of TCE is occurring in the subsurface as a result of lactate introduction. This effort resulted in an amendment to the Record of Decision at TAN, which promoted enhanced bioremediation near the injection well and natural attenuation in the distal plume, resulting in $23 million in life-cycle savings. Additionally, the effort reduced the expected time required for remediation by one-half. Technologies developed and deployed for sampling the subsurface at TAN through this EMSP research were also transferred to scientists at the Idaho Water Resources Research Institute (1).

Precipitation and Deposition of Aluminum-Containing Phases on Tank Wastes (Projects #65411 and 81887)

When high-level wastes (HLW) are transported through pipes, deposits develop that can clog the pipes. Of all tank waste constituents, aluminum-species have the greatest potential for clogging pipes and transfer lines, fouling highly radioactive components, such as ion exchangers, and forcing the shutdown of processing operations. In October 1999, an evaporator at the DOE Savannah River Site (SRS) clogged, causing shutdown of the Defense Waste Processing Facility (DWPF) and resulting in additional cost and delays during waste treatment.

The researchers are working with SRS to verify the thermodynamic stability of aluminosilicate compounds under tank waste conditions in an attempt to solve the deposition and clogging problems. The primary objectives of this study are to (a) understand the major factors controlling precipitation, heterogeneous nucleation, and growth phenomena of relatively insoluble aluminosilicates, (b) determine the role of organics for inhibiting aluminosilicate formation, and (c) develop a predictive tool to control precipitation, scale formation, and cementation under tank waste processing conditions.

The results of this work will provide essential information to develop effective technologies for processing sludges and supernatants prior to vitrification and establish a safe operating envelope for evaporator composition (2).

Foaming and Antifoaming in Radioactive Waste Pretreatment and Immobilization Processes (Projects #60143 and 81867)

The SRS is responsible for the safe storage, processing, and immobilization of the HLW currently stored in approximately fifty million-gallon underground storage tanks. Foaming occurs in many areas of HLW processing, including chemical processing, evaporation, and cesium decontamination. The presence of foam during chemical processing and evaporation steps leads to slower production rates in the HLW evaporators and in the DWPF waste pretreatment, and may lead to higher capital costs or slower production in cesium decontamination. Excessive foam also causes radioactive contamination of the condensate and equipment.

The primary focus of this project was to better understand the mechanics of foam generation and stability, identify key parameters that aggravate foaming, and identify effective ways to eliminate or mitigate foaming. The commercial antifoaming agent in use at the start of the project was found to be ineffective in the aggressive physical and chemical environment in the DWPF sludge chemical processing. Based on the understanding of foam generation and stability, the results of this research led to the successful development, demonstration, and deployment of new, improved antifoaming agents in DWPF that were found to be more effective than the commercial product in minimizing foam generation. Reduced foaming in HLW processing enables higher waste production rates, lower capital costs, and reduced radioactive contamination.

Two additional deployment opportunities using the lessons learned and the techniques developed in this research are being applied to develop advanced antifoaming/defoaming agents for use in the Hanford River Protection Waste Processing project and the SRS Alternative Salt Disposition project (3).

Measurement of Radon, Thoron, Isotopic Uranium and Thorium to Determine Occupational Environmental Exposure at U.S. DOE Fernald (Projects #59882 and 74050)

This research is directed at developing state-of-the-art personal and environmental exposure assessment capabilities for inhaled radionuclides by understanding how the particle size and movement of inhaled radon, thoron, and thorium isotopes impacts human health. A deployment has been conducted at the DOE Fernald site where the specific nuclides of interest are radon (Rn-222) and thoron (Rn-220) emission from the silos and thorium-230, 232 airborne aerosol particles from the waste pits. The detector has also been deployed in:

China – A project with the Beijing University to study high thoron areas in China
Finland – A short-term study in Rovanemi (top of the world) to measure outdoor radon

Canada – Two studies: one to measure around radium-bearing tailings piles and the other to measure inside fish hatcheries, where millions of gallons of water are used and radon can reach high concentrations
Thailand – The detectors are continuously at a monazite (thorium ore) processing facility, where high thoron concentrations are present.
Japan – An intercalibration study
Pennsylvania – A Department of Environmental Protection study at fish hatcheries.

An inexpensive sampler probe is being fabricated commercially for general use at DOE sites. The sampler can be used for any particulate airborne material by changing the detection method. Ultra-low alpha-particle detectors are used to measure radioactivity. The inhaled particle size distribution data will be used in a bronchial lung dose model to realistically calculate the occupational or offsite dose at Fernald to individuals subsequent to the remediation.

Two new instruments developed as a result of this research have been in use at Fernald for about 2 years. Together they permit the air concentrations of the gas and the particle size distribution of airborne particulates to be measured on a continuous basis. The first instrument is a radon-thoron passive alpha track detector that can be worn or used as an area detector to obtain research quality measurements for modeling or personal exposure assessment. Measurements at Fernald with simultaneous measurements at research homes in the New York/New Jersey area show that essentially all radon measurements contain a fraction of thoron. Four detection chambers, rather than three, enable duplicate, simultaneous measurements of radon and thoron.

The second instrument is a particle size analyzer. Although the inhaled particle size is the major determinant of bronchial dose, Fernald is the only site attempting to do particle size distribution measurements. Prior to the development of this instrument, the labor intensive effort needed, as well as the cost, precluded the measurement. The particle size analyzer presently supplies airborne particulate concentration and size data at the waste pits, the soil dryer, and at buildings being removed. A wider network of analyzers is being deployed to study resuspension and transport of particles. The new instruments can have wide application at other DOE sites, with the potential to increase overall worker health and safety (4).

Enhancements to and Characterization of the Very Early Time Electromagnetic (VETEM) Prototype Instrument and Applications to Shallow Subsurface Imaging at Sites in the DOE Complex (Project #60162)

DOE has a legacy of large quantities of radioactive, chemical, and other wastes. In some cases, past disposal practices for hazardous wastes have been inadequate to ensure the health and safety of DOE workers and the public. Accurate subsurface imaging—whether by seismic, electromagnetic, magnetic, radiometric, resistivity, or other techniques—can help ensure public health and safety and may save hundreds of thousands of dollars by pinpointing the location and characterizing the physical nature of subsurface wastes through non-intrusive means. Possible applications of subsurface imaging within the DOE complex include:

Confirming waste pit and trench location
Characterizing the contents of pits and trenches
Assuring the thickness and conformance to construction standards of waste pit caps
Periodic imaging of pit caps to assess long-term integrity
Assessing shallow grout injections
Monitoring dense non-aqueous phase liquid (DNAPL) and light non-aqueous phase liquid

(LNAPL) spills and cleanup
Characterizing the vadose zone by mapping electrical conductivity contrasts (in geologic structures) that may be related to differences in hydraulic conductivity.

Research in this project has developed and incorporated software/hardware into the VETEM prototype instrument to produce high-resolution electromagnetic images of the shallow (0 to 5 m) subsurface when the electrical conductivity of the earth is too high for ground penetrating radar to be effective, such as in the clay capping material covering the waste pits. Physical modeling experiments, numerical forward and inverse modeling, and field demonstrations were also performed.

The VETEM system was deployed at Pits 4, 9, and 10 in the Subsurface Disposal Area at the Radioactive Waste Management Complex at the INEEL to obtain geophysical images of the location and estimated depths of waste in the pits. VETEM outperformed other techniques, both in sensitivity to buried materials and in resolution of the 2D and 3D images of the subsurface, and the information obtained was used to support remediation operations. VETEM, along with accompanying algorithms, is a flexible and highly effective system for electromagnetic imaging that offers significant new 3D electromagnetic imaging capabilities for the shallow subsurface (5).

EMSP EMERGING SCIENCE

The following projects are expected to be available for deployment within two years.

Ion Recognition Approach to Volume Reduction of Alkaline Tank Waste By Separation of Sodium Salts (Projects #65339 and 81935)

Disposal of HLW is horrendously expensive, in large part because the actual radioactive matter in underground waste tanks at various DOE sites has been diluted over 10,000-fold by ordinary inorganic chemicals. To vitrify the entire mass of the HLW would be prohibitively expensive. Accordingly, an urgent need has arisen for technologies to remove radionuclides such as ^{137}Cs from the HLW so that the bulk of it may be diverted to cheaper, low-level waste (LLW) forms and cheaper storage.

Chemical research at Oak Ridge National Laboratory (ORNL) is seeking a fundamental understanding and major improvement in cesium separation from HLW by focusing on cesium-selective calixcrown extractants, molecules that combine a crown ether with a calixarene. The overall objective is a significant advance in the predictability and efficiency of cesium extraction from HLW in support of potential implementation at DOE sites. In July 2001, the DOE selected Caustic-Side Solvent Extraction as the preferred alternative for improved cesium removal at the DWPF, a $1 billion facility at the Savannah River Site. Subsequent tests with real waste at Savannah River Technology Center achieved decontamination factors exceeding requirements to meet the salt processing waste acceptance criteria (6).

Millimeter-Wave Measurements of High-Level and Low-Activity Glass Melts (Projects #65435 and 81897)

Vitrification and long-term storage of HLW and LLW represents one of the major challenges of EM’s effort to clean up nuclear waste sites. Present nuclear waste melters, such as the DWPF, and planned melters for the Hanford site lack sophisticated diagnostics due to the hot, corrosive, and radioactive environments of these melters. New, robust diagnostics that can operate on-line and reliably measure glass characteristics in the high-temperature and chemically corrosive environment of nuclear waste glass melters are needed.

Molten glass characteristics of temperature, resistivity, and viscosity can be reliably monitored in the high-temperature and chemically corrosive environment of nuclear waste glass melters using millimeter-wave sensor technology. Millimeter-waves are ideally suited for such measurements because they are long enough to penetrate optically unclear atmospheres, but short enough for spatially resolved measurements. Real-time monitoring of glass melt, cold cap, and plenum off-gas temperature profiles and of molten glass conductivity, density, resistivity, and viscosity will improve vitirification process controls and ultimately result in increased glass manufacturing efficiencies, reduced storage volumes through increased waste loading, reduced storage risk by ensuring the long-term stability of the poured glass product, and significant cost savings.

Collaborations with other laboratories are being exploited to field test the research accomplished by this project. For example, a field test was carried out at the Clemson Environmental Technology Laboratory (CETL) in August 2000 on a pilot-scale melt test of an INEEL glass surrogate. An open invitation exists from CETL for additional joint experiments.

The cross fertilization of research partners on this project led to the recognition of the Millimeter-Wave Measurement technology as an R&D 100 award winner. In addition, there may be significant commercial spin-off applications to the glass manufacturing and metals refining industries (7).

Phytoremediation of Ionic and Methyl Mercury Pollution (Projects #54837, 70054, and 86608)

Mercury contamination of soil and water persists across the United States and in many other parts of the world due to ineffective clean-up of mining, manufacturing, agricultural, and nuclear processes from both government and industry. Once mercury escapes to the environment, it circulates in and out of the atmosphere until it ends up in the bottoms of lakes and oceans. Bacteria and chemical reactions in lakes and wetlands change the mercury into a much more toxic form known as methylmercury. Fish become contaminated with methylmercury by eating plankton and smaller fish that have absorbed mercury. Low doses of methylmercury are concentrated into much higher doses as the toxin moves up the food chain. Fish and carnivorous animals can have a million to a hundred million times more methylmercury in them than originally found in the soil.

Fig. 2. Transgenic merA9 tobacco efficiently removes mercury from hydroponic media.

Pregnant women, women who may become pregnant within the next several years, children less than six years old, and people that consume large quantities of fish may be harmed by mercury. Mercury can damage human health because it is toxic to the nervous system. The developing brain and spinal cord of a fetus or young child are especially vulnerable.

For the most part, plants just sit there in the sunshine—taking in nutrients from the soil, transmitting the nutrients through their plant tissues to be metabolized, and eliminating the byproducts into the air through their leaves. But aided by a couple of genes from bacteria, plants may eventually be employed to clean up toxic metals in soils, marshes and rivers. These researchers have engineered an assortment of flowering plants, including yellow poplar and tobacco, to extract toxic mercury compounds from contaminated soils and convert them into less toxic forms that are either expired into the air or sequestered in their leaves. The long-term objective of this project is to apply scientific strategies and technologies from a rapidly developing field called phytoremediation to enable highly productive plant species to extract, resist, detoxify, and/or sequester toxic organic and heavy metal pollutants.

Plants engineered to hyperaccumulate or volatilize mercury can also be applied to the remediation of other heavy metal pollutants (e.g., arsenic, cesium, cadmium, chromium, lead, strontium, technetium, uranium) at a lower cost than current methods of remediation. Field-testing and deployment of these bio-engineered plants at Oak Ridge are currently being negotiated (8).

Improved Radiation Dosimetry Risk Estimates to Facilitate Environmental Management of Plutonium Contaminated Sites (Projects #59918 and 73942)

For years, there has been concern about possible harm to the general public from plutonium (Pu) contamination at DOE's Rocky Flats Environmental Technology Site (RFETS). DOE standards require evaluating non-cancer-producing radiological doses to the immediate worker to determine intake level that corresponds to serious injury or prompt death. Historically, however, only criticality prompt doses have been calculated and characterized as high, moderate, or low. Doses associated with inhalation intakes have not been adequately evaluated; rather, they have only been subjectively indicated as high, moderate, or low with little scientific justification. Radionuclide soil action levels (RSALs) based on inadequate analyses and/or compounding of overly conservative assumptions could lead to wasting millions or more dollars on cleanup of Pu-contaminated sites. Improved integrated-risk-assessment capability will facilitate obtaining improved RSALs for sites such as Rocky Flats.

RFETS scientists are faced with evaluating intakes of Pu aerosols that would be associated with serious radiation deterministic effects (e.g., respiratory dysfunction, death from radiation pneumonitis), following a Pu accident involving inhalation exposure. Such accidents could arise during decontamination and decommissioning/deactivitation (D&D) operations related to Pu-contaminated facilities. Modeling and epidemiological research is being conducted related to evaluating the validity of the linear, no-threshold (LNT) model for radiation-induced stochastic (random) effects. Present results indicate that mg quantities of Pu need to be inhaled in order to cause serious deterministic effects, such as radiation pneumonitis and impaired lung function. This project reviewed an original draft white paper related to selecting appropriate respiratory devices and pointed out major shortcomings related to protecting DOE D&D workers. This project will continue to assist DOE in preparing a more credible plan for protecting workers and in preparing an associated white paper (9).

Field Portable Microchip Analyzer for Airborne and Surface Toxic Metal Contaminants (Projects #64982 and 82749)

During D&D and other field operations, samples are frequently taken to determine the isotope and level of contamination. Sample collection increases worker risk and exposure, and is costly and time-consuming. Samples are then sent for laboratory analysis, thus increasing expense and delaying the project for months until results are available. A real-time, in-situ detection device is needed to improve safety, reduce cost, and accelerate schedule. In addition, real-time analysis results would help distinguish contaminated from non-contaminated items and help evaluate the effectiveness of decontamination techniques in the field. The "lab-on-a-chip" being developed by this project will provide an inexpensive, quick way to detect hazardous waste metal ions in real-time, allowing key decision making to be done in the field and avoiding costly and time-consuming laboratory analysis.

The "lab-on-a-chip" technology uses small microchannels etched onto a glass slide to allow capillary electrophoretic separations to be performed on a microscale. The research team has proven the concept by identifying low ppb levels of uranium (VI), Co, V, Ni, Cu, Fe, Mn, and Cd. The researchers are now extending the capability to other waste metal ions including Be^{2+}, Cr^{6+}, Hg^{2+}, Pb^{2+}, Co^{2+}, Ni^{2+}, Cs^{+}, and

Sr^{2+} and developing a multi-channel chip to measure multiple metal ions simultaneously. Researchers are also examining how samples can be retrieved from various surfaces and be applied to the microchip platform. The researcher team is working with the Nevada field office to address their need for uranium detection in soils and groundwater, since no baseline technology exists. This work will result in a field-portable microchip sensor capable of identifying numerous radioactive and hazardous waste metal ions simultaneously. The results of this research can be applied to all D&D facilities across the DOE complex, including Nevada, Hanford, SRS, INEEL, RFETS, Los Alamos National Laboratory (LANL), Fernald, Mound, and ORNL (10).

Atmospheric-Pressure Plasma Cleaning of Contaminated Surfaces (Projects #54914 and 73835)

Decontamination of equipment contaminated with transuranic (TRU) elements is challenging and expensive, because the contamination is easily aerosolized and inhaled, greatly endangering the worker. In addition, workers can receive high radiation doses just by their proximity if radiation levels are high. Routine decontamination of components, such as gloveboxes and hoods, that are still in use is required to keep radiation levels low and reduce worker risk. Equipment that is being removed during D&D poses the same risks, with the added factor that TRU waste is much more expensive to dispose of than LLW. Baseline technologies, such as acid baths, are expensive and dangerous. A safer method is needed to remove TRU contamination from gloveboxes, hoods, and other equipment, both during routine cleaning and D&D.

This project is developing an atmospheric-pressure plasma etching system that will fill this need. The system uses fluorine atoms carried in a plasma to attract and bond to actinides, volatilizing the actinides and allowing them to be collected by a vacuum system with HEPA filters. The plasma system can remove the TRU elements from HLW with little secondary waste; the waste can then be classified as LLW and disposed of at a much lower cost. Atmospheric-pressure plasma operates at low temperatures and can be used to routinely decontaminate TRU contaminated gloveboxes and hoods to reduce the radiation exposure to workers using the equipment. A prototype system has been built and successfully tested using fluorine to etch tantalum, a surrogate for plutonium, and on depleted uranium.

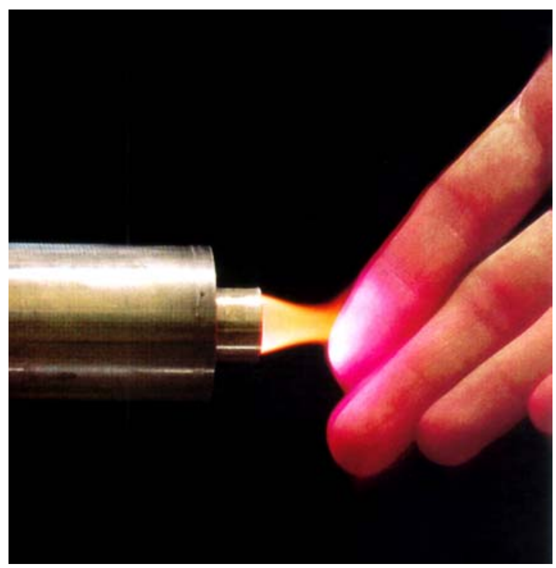

Fig. 3. Low temperature, low pressure plasma jet

This low-energy, low-temperature, low-pressure, mobile process can be taken into the field for decontamination of TRU-contaminated equipment, or for routine decontamination of TRU-contaminated gloveboxes and hoods to reduce the radiation exposure to workers using this equipment (11).

Spectroelectrochemical Sensor for Technetium Applicable to the Vadose Zone (Projects #54674 and 70010)

Within the DOE system, over 300 underground nuclear waste storage tanks and numerous buried waste sites have potentially contaminated the vadose zone and subsurface water. Technetium (Tc) contamination at the Hanford site is of particular concern because of its long half-life and fast migration in soils. A sensor that provides more specificity for Tc is needed for analysis of the complex chemical mixtures found at Hanford and other DOE sties nationwide.

This project is developing a novel spectroelectrochemical sensor that combines three levels of selectivity in one device: selective portioning into a film, electrochemical excitation signal, and optical response signal. The research has many facets, including the development of selective coatings for the sensor, instrumentation, and theory to describe the spectroelectrochemical behavior. A small portable sensor unit consisting of a virtual interface, control electronics, and optics is being developed is currently undergoing testing using In-Farm and U-Plant Hanford simulated wastes. Practical application of the sensor has been demonstrated with the determination of ferrocyanide in Hanford waste tank simulant solution (U-Plant-2). The present goal is to develop sensor for a soluble form of technetium (TcO4-) that is applicable to characterizing and monitoring the vadose zone and associated subsurface water at the Hanford site. The key to adapting this generic sensor to detect TcO4- lies in the development of unique chemistry within the chemically selective film to provide a modulated optical response. The sensor will have the capability for on-site monitoring, either by immersion in subsurface water for continuous monitoring or for the immediate analysis of collected samples (12).

Novel Optical Detection Schemes for In-Situ Mapping of Volatile Organochlorides in the Vadose Zone (Project #70050)

DOE spends approximately $330 million per year to clean sites contaminated with chlorinated hydrocarbons. Cost effective, field-deployable sensors are needed to enable real-time, in situ characterization and monitoring for DOE site clean-up and waste processing operations and to lower sampling and analysis costs. However, there is currently no method for measuring low levels (ppb) of organic vapors in the vadose zone. The research being conducted under this project uses resonance-enhanced multi-photon ionization (REMPI) in combination with Raman spectroscopy to measure volatile organic solvents in a soil matrix over a wide range of concentrations. The sensor can be used to quantify contaminant levels in soil and groundwater to characterize and identify sources of contamination; this information is necessary for selecting remedial alternatives and verifying remediation strategies.

The approach taken here differs from current approaches in that a visible laser, rather than a UV laser, is used for excitation to reduce cost and complexity and improve robustness and reliability. Visible wavelengths are more compatible with existing fiber-optic probes and enable the use of long fiber cables. The sensor has been used in the laboratory to measure benzene, toluene, xylenes, TCE and Perchloroethylene (PCE) and is ready for field-testing. The project team can be ready for a field demo within 3-4 months of receiving technology development funding, which would be used for a transportable laser system, purchase of a cabled optical fiber, and configuration of the sensor into a package that is suitable for the test area (13).

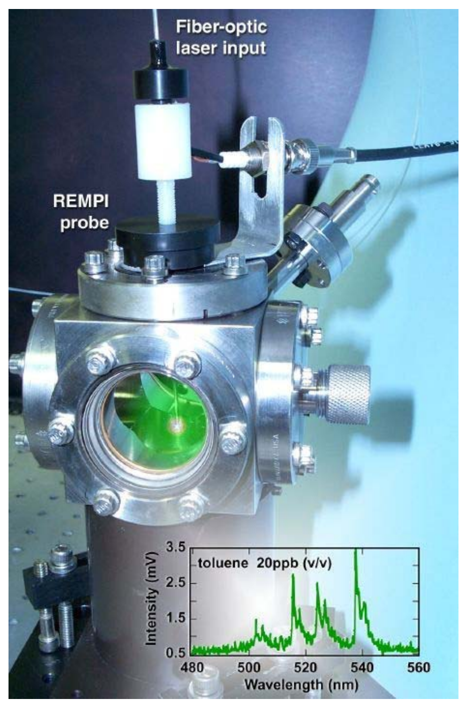

Fig. 4. REMPI probe in test cell

EMSP CORE SCIENCE

The following projects are expected to yield significant benefits in the long-term.

Mechanism Involved in Trichloroethylene-Induced Liver Cancer: Importance to Environmental Cleanup (Project #54684)

TCE is a common contaminant of groundwater resulting from past disposal practices. As a consequence, this solvent is the focus of many hazardous waste sites clean-up operations. The finding that TCE induces liver cancer in mice has been a primary driver for current environmental regulations of this contaminant. Under proposed cancer risk guidelines of the Environmental Protection Agency (EPA), identifying the dose-response behavior of key events involved in carcinogenic responses can be used for developing alternative risk assessments, which ultimately impact environmental standards and remediation costs. Reducing cleanup standards for TCE would lead to millions of dollars in cost savings at many DOE locations throughout the country.

A critical issue in addressing the mechanism by which TCE induces liver cancer is to identify the metabolites produced by TCE that contribute to the tumor response. It has been proposed that dichloroacetate (DCA) and trichloroacetate (TCA) are potential metabolites that have been produced from TCE, and both metabolites are carcinogenic in mice. Classically, TCA was considered the active metabolite in inducing liver cancer from TCE exposure. TCA falls into a broad category of chemicals known as "peroxisome proliferators," which utilize a mechanism of tumor induction that is thought to be specific to rodents. In contrast, DCA induces tumors in multiple species through mechanisms that are distinct from TCA. Therefore, understanding the relative contributions of TCA and DCA in TCE-induced liver cancer is an important variable when considering the potential risk to humans.

The EPA is using the data generated by this project and a paper describing the mode of action for induction of liver tumors to revise their risk assessment on TCE. EPA continues to track the published results as this decision process reaches its conclusions. A separate step will be actions taken under the Office of Water to revise drinking water standards or the Comprehensive Environmental Response, Compensation, and Liability Act to modify clean-up standards that are derived from the revised risk assessments (14).

Design and Sensor-Based Control for Hyper-Redundant Mechanisms (Project #82873)

Nuclear facilities often contain contaminated areas with complex, tightly packed piping and equipment. Access is required to characterize, decontaminate, and dismantle these facilities, but both the contamination and geometry limit access. A small, versatile robot that can enter these areas and collect visual and physical samples is needed.

This project, begun in October 2001, is developing a multi-degree-of-freedom "snake" robot that can thread through tightly packed volumes, inspect pipes, and enter small spaces. This articulated probe, or hyper-redundant mechanism, will have the strength to lift its own weight by one joint, so it can maneuver in three-dimensional space. The project tasks include mechanism design, path planning and control, and sensor integration. In the first year, the researchers have designed, built, and tested a six-joint mechanism that is fixed at one end. Tests show one joint has the strength to "cantilever lift" all six joints. The research team plans to develop control algorithms that allow the robot to navigate in unknown three-dimensional spaces with control modes that range from tele-operation to full autonomy. The tele-operation mode will use a joystick to direct the "head" of the snake, and a path planner to coordinate the internal degrees of freedom of the snake to allow the forward motion. This research will result in a much needed and useful inspection and characterization tool that can collect samples and take still and video photos in areas too small or too hazardous for human entry.

The multi-degree-of-freedom "snake" robot can be used in many D&D applications across the DOE complex, including Hanford, SRS, INEEL, RFETS, LANL, Fernald, Mound, and ORNL. The INEEL has a need for this technology to collect samples, smears, and take video and still pictures during the upcoming Experimental Breeder Reactor-II decommissioning effort. In addition, it can be used for homeland security to assess the presence of biological or radioactive contamination in areas that have possibly been contaminated by terrorist attack. This fast-track project is expected to produce a working, table-mounted prototype within the three-year research grant (15).

Contaminant-Organic Complexes: Their Structure and Energetics in Surface Decontamination Processes (Projects #64947 and 82773)

Throughout the DOE complex, large volumes of contaminated metal require D&D, either so facilities can be reused, or so the metal can be disposed of and reused. Contaminants trapped within an oxide layer (or rust) on the metal and possible migration of contaminants into cracks and pores often make decontamination difficult and prohibit reuse of this metal. A method to safely and effectively remove the oxide layer and remove contaminants from cracks is needed to allow decontamination and reuse of this metal.

This project is developing a method to remove actinide surface contamination from oxidized steel or iron and solubilize the associated contaminants using microbially produced chelates (siderophores). These siderophores, which are less corrosive than the acids commonly used, remove contaminants from under oxidation layers, as well as from corrosion pits and cracks. Siderophores have a high binding affinity to iron and actinides, so contaminants are bound to the cleaning agent, reducing secondary contamination. Initial data shows that thorium is rapidly removed from a hematite surface at a rate equal to that of iron solubilization. Tests on oxidized samples aged over one year have shown that the ability of these chelates to solubilize and remove actinides is not affected by aging. Researchers are studying the structure and bonding of siderophores and their functional moieties and how these change with chemical environment, and are developing a molecular modeling system to select the optimum siderophore structure. This method can be used to decontaminate surfaces of steel and iron with minimal secondary waste, allowing reuse of the metal or re-classification to LLW with the corresponding lower disposal costs.

SUMMARY

The EMSP has existed as a research program for only seven years, yet has already made a difference in DOE cleanup operations. This paper has highlighted five projects that have already accomplished field transfers, eight emerging research projects with field transfers imminent, and three groundbreaking core science projects. The reason for the number of success stories coming out of the program can be attributed to the marriage of good science with relevance to actual site problems.

Information exchange between EMSP researchers and other researchers, program personnel, and site problem holders is necessary to produce a product useful to DOE. The EMSP Idaho technical integration staff facilitates interaction between researchers and end users throughout the research process to create avenues to more effectively apply science to address problems. Each staff member, or technical liaison, focuses on a specific environmental management problem area and works to integrate EMSP projects into cleanup operations. Collaborations with site end users are actively sought to produce science-based, engineered solutions that will reduce cost, schedule, and/or risk. Dissemination of research results is provided via the EMSP website and through a number of publications, conference presentations, and peer-reviewed journal articles.

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