VOC-ARID INTEGRATED DEMONSTRATION: PROGRAM AND MONITORING TECHNOLOGY SUCCESSES

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ABSTRACT

The U.S. Department of Energy's (DOE's) Office of Technology Development has provided two important mechanisms for the development and deployment of innovative technologies via the Integrated Program and the Integrated Demonstration. These two programs have provided the infrastructure to solicit, develop, evaluate, and deploy technologies in a cost-effective manner in the shortest time frame possible. Through use of the Integrated Demonstration program, new monitoring technologies have been successfully demonstrated at host sites in less than 18 months from inception. The Volatile Organic Compounds-Arid sites-Integrated Demonstration (VOC-Arid-ID) is meeting the environmental restoration challenges remaining from the nuclear deterrent era through the use of innovative concepts, infrastructure, and inter-laboratory cooperation on a large scale. In forming partnerships with industry and inter-agency leveraging of funding, the VOC-Arid-ID has positioned itself to respond to environmental cleanup challenges well into the future. Innovative and emerging commercial technologies can be demonstrated at DOE host sites on time scales designed to integrate closely with the needs of the Environmental Restoration and the Waste Management programs at DOE cleanup sites.

INTRODUCTION

Historical activities at U.S. DOE facilities around the United States during World War II including development of a nuclear deterrent, resulted in the discharge of chemical and radioactive materials to the environment. The DOE has now focused a major technical effort on the mitigation of the effects of those discharges through an environmental restoration program. In many cases, the particular chemical species involved and the circumstances surrounding the discharges would lead to prohibitive costs if conventional technology were applied for remedial action. The Office of Technology Development (OTD) has launched a major initiative to develop and demonstrate more cost-effective and safer means of restoring contaminated environmental matrices. This initiative integrates available conventional technologies and innovative and/or emerging technologies with on-going environmental restoration activities.

The ultimate goal of the OTD initiative is to have demonstrated technologies available for commercial application when they are needed at DOE sites. Key elements of the initiative are divided between Integrated Programs (IPs) and Integrated Demonstrations (IDs). Integrated Programs provide a vehicle for the conduct of applied research and development of new technical approaches to environmental restoration and waste management challenges. In many respects, the IPs act as incubators for the IDs in that they develop promising new ideas to the point where they are ready for full-scale demonstration. Integrated Demonstrations provide the necessary framework for demonstrating, testing, and evaluating technologies (from industry, university, DOE laboratories, and other federal agencies) during full-scale field activities. The IDs also allow for the evaluation of alternative technologies in parallel and within a context that embraces all factors that affect successful demonstration and implementation.

INTEGRATED DEMONSTRATIONS PROGRAM SCOPE

The three aspects of the ID program are operational, technology filtering, and technology integration. Operational aspects include the integration of all elements of successful environmental restoration including characterization, assessment, remediation, and monitoring. Technology filtering addresses the selection of technologies for demonstration with the greatest potential for meeting current needs in a short time frame. Technology integration provides for the early and continued interaction with interested states, federal regulatory bodies, host communities, and other stakeholders to expedite public and regulatory acceptance. As a consequence, an essential part of the program scope also includes technology transfer to industry for producing the required technologies that will have value in meeting the environmental restoration needs of DOE. Technology transfer is effected through formation of partnerships with industry and through partnerships and leveraging with resources with other DOE components, Environmental Restoration (EM-40) or Waste Management (EM-30).

THE VOC-ARID-ID

The OTD initiative contains several IDs that have been formed to address the needs of DOE sites that have similar characteristics and remediation requirements. The Volatile Organic Compounds-Arid sites-Integrated Demonstration, or VOC-Arid-ID, was initiated at the Hanford Site in southeastern Washington State in March 1991 to address all phases of remediation of volatile organic compounds (VOCs) in soils and ground water at DOE sites. Initially, the VOC-Arid-ID activities have focused primarily on carbon tetrachloride and associated contaminants found in the 200 West Area of the Hanford Site. At the 200 West area, beginning in 1955, an estimated 637 metric tons of carbon tetrachloride were released to the subsurface along with co-contaminants to three liquid waste disposal facilities. Co-contaminants and/or degradation products include chloroform, mono-, di-, and tributylphosphates, dibutylbutylphosphonate, lard oil (a com-

plex mixture of triglycerides), cadmium, nitrates, hydroxides, fluorides, sulfates, and various radionuclides, primarily plutonium and americium.

The VOC-Arid-ID consists of an integrated set of technology activities targeted at addressing the characterization, remediation, and monitoring of the VOC contaminants at the arid host sites. To date, three successful monitoring demonstrations involving national collaboration have been completed at the Hanford Site. Technologies demonstrated were a Portable Acoustic Wave Sensor (PAWS), a fiber optic spectrochemical emission sensor (HaloSnif), and a fiber optic sensor system based on solvatochromic dyes. Conduct of the demonstrations relied on successful cooperation among Westinghouse Hanford Company, Pacific Northwest Laboratory, Sandia National Laboratory, Lawrence Livermore National Laboratory, and several industrial partners. It was through the use of the ID program that these technologies were successfully funded and field demonstrated in less than 18 months. Commercialization efforts are under way for these technologies and their subsequent availability from industry will further expedite their future use in environmental restoration activities. Each technology is discussed in more detail below.

PORTABLE ACOUSTIC WAVE SENSOR (PAWS)

The PAWS instrument was designed to measure both the wave velocity and wave attenuation of a surface acoustic wave (SAW) based on distortions that occur to a chemically sorbed coating. From these measurements the PAWS instrument can determine the identity of an isolated chemical species as well as its concentration in the vapor phase in the range of 50 ppm to more than 100,000 ppm. The PAWS instrument and associated downhole sensor system represents significant advancements for in situ VOC vapor phase sensing.

This instrument consists of two parts: 1) a downhole sensor and electronic assembly, and 2) a surface signal processing unit with computer interface. The downhole sensor, which is approximately 3 inches in diameter by 30 inches long, can be tethered to a winch assembly for lowering into existing boreholes of 4-inch-diameter or larger to conduct in situ measurements of VOCs (e.g., carbon tetrachloride). The downhole sensor is constructed with two SAW devices which are coated with identically sorptive polymer materials. These two devices are physically separated, allowing one to become a reference device isolated from the environment and the other the sensing device which is challenged by a gaseous phase to detect the desired species. Sensing of contaminants is a result of specific species sorbing into the polymer coating, causing its mass to increase and soften. These physical changes in the polymer result in changes in the wave velocity and wave attenuation, which are detected by the electronics. Prior calibration, using known concentrations of the target species and using the temperature correction and performance of the reference SAW device, allows identification of the target species as well as measurement of its concentration.

At the surface, signal cables from the downhole sensor enter a data acquisition and control system which processes and acquires the relevant sensor data and activates several gas valves in the probe. The gas valves of the PAWS instrument work in parallel with a pump, which purges the borehole at a screened interval with an upper and lower packer in place. The borehole has screened intervals at various depths that allow for soil gas sampling at these intervals when packers are deployed. Packers consist of inflatable components that are part of the downhole probe and which provide a seal above and below the sensor elements for in situ measurements. A computer provides for data storage, reduction, and analysis using sensor baseline data, calibration data, and real-time measurements. Concentrations are then calculated from these data based on signals from the SAW devices and known performance characteristics of the system.

This technology was developed by Sandia National Laboratory under an OTD program which sought to produce sensors with sufficient sensitivity to monitor the relatively high concentrations of VOC vapor underground. Initial testing was performed at a non-arid ID and was used for some borehole investigations during sensor development. Further development led to a 1991 patent on the technology and its incorporation into a dual output device for use in the VOC-Arid-ID. In June 1992, the PAWS instrument was brought to the Hanford Site and demonstrated at the 200 West area in the off-gas stream of a vapor extraction system. The instrument was successfully demonstrated again in July 1992 in the field with the cone penetrometer, a soil probe used to collect soil gas samples. Sandia is currently working with fabrication vendors on the commercialization of the technology and marketing for widespread use.

FIBER OPTIC SPECTROCHEMICAL EMISSION SENSOR (HALOSNIF)

The HaloSnif instrument was designed to detect chlorine-containing compounds in a gaseous phase by passing the suspect gas through a plasma chamber where the excited chlorine atom would exhibit optical emissions whose intensity was proportional to concentration. This instrument measures carbon tetrachloride concentrations in off-gas streams in the range of 10 ppm to 10,000 ppm in a continuous real-time monitoring mode. The instrument overcomes the limited range and slow response times of currently available instrumentation.

The HaloSnif instrument uses a radio frequency power supply to provide a high-power, high-frequency signal to electrodes that surround a ceramic plasma tube chamber. The suspect VOC stream is mixed with helium and fed through the plasma chamber, where the high energy plasma excites the chlorine atoms. The emission is carried by the fiber optic link to a spectral filter and detector. The technology offers a low detection limit and wide dynamic range, making it suitable for use in off-gas process streams or for real-time monitoring of vapor concentrations from bore holes or other soil sampling probes.

In 1988, a proof-of-concept sensor was developed at Pacific Northwest Laboratory that was specific for measuring the concentration of VOCs containing chlorine. With funding obtained in late 1991, a prototype instrument was constructed for field testing at the Hanford Site VOC-Arid-ID. Additional support for the technology came from the U.S. Air Force at Tinker Air Force Base and from the Savannah River Site. This technology was demonstrated in off-gas and in a vadose zone well stream in September 1992 at the VOC-Arid-ID and is scheduled for further demonstration in 1993. A commercial partner is working with Pacific Northwest Laboratory on the development of the radio frequency power supply and is considering future manufacturing and marketing of the entire instrument.

FIBER OPTIC SENSOR SYSTEMS BASED ON SOLVATOCHROMATIC DYES

Solvatochromic dyes have been used with success in silicone polymer matrices for constructing reversible gasoline and methylene chloride sensors. Nile Red and Reichardts's dyes were used in developing carbon tetrachloride selective reversible fiber-optic-based sensors, and detection limits have been observed in the 100 ppb range. Additional developments included sensors that can detect trichloroethylene with a linear working range of 10 ppb to 1000 ppb. A project currently funded within the IP is currently focused on incorporating these developments into a sensor to measure carbon tetrachloride. This approach serves as an example of an innovative technology going through the IP development process for subsequent field demonstration in the VOC-Arid-ID.

Lawrence Livermore National Laboratory has been a pioneer in the development of fiber-optic chemical sensors (optrodes) and in their application to field measurements of environmental contaminants. Optrodes have been designed for many different types of compounds. Recently Lawrence Livermore developed a successful integrating-type optrode for the Hazardous Waste Remedial Action Program that measures trichloroethylene and chloroform. Funding was approved by the IP for continued development and deployment of this sensor technology in 1992 and 1993 for detection of carbon tetrachloride. The Lawrence Livermore sensor was demonstrated in September 1992 at the Hanford Site in the laboratory as proof of principle in detection of carbon tetrachloride for the VOC-Arid-ID. This technology is scheduled for demonstration at Hanford when development is completed as part of the IP.

OTHER MONITORING DEMONSTRATIONS

The VOC-Arid-ID conducted another demonstration in monitoring technology called the Limited Demonstration of Portable Gas Monitoring *Equipment.* The VOC-Arid ID sponsored this demonstration to evaluate performance of commercially available, portable gas monitoring equipment as alternatives to innovative technologies. During the last two weeks of October 1992, nine commercial vendors came to the Hanford Site and demonstrated eleven instruments in a controlled situation for performance evaluation.

A series of bottled gases, including calibration standards and unknown concentrations, were analyzed by each of the vendors with their instruments. Each instrument, as appropriate, conducted analyses on unknown quantities of: 1) benzene, toluene, xylenes (BTEX) compounds, 1-20 ppm; 2) carbon tetrachloride, 1-25 and 100-550 ppm; 3) alkanes, 1-20 ppm; 4) chlorinated solvents 1-20 ppm; and 5) ketones, 1-20 ppm. In general, all instruments performed well in the areas for which they were designed.

A performance evaluation report, based on collected data, is under way for all the instruments demonstrated. This report will include a statistical analysis of the accuracy and precision of each instrument as well as an evaluation of each instrument's portability, durability, and ease of use. Ongoing evaluation and demonstrations of off-the-shelf commercial equipment are essential elements of the ID program as it strives to maintain current status with state-of-the-art instrumentation. Evaluations of commercial equipment continue to provide baseline performance specifications for use in the ID and IP decision making processes.

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