Environmental Management Technology Demonstration and Commercialization

Christina Behr-Andres, PhD, PE (cbandres@undeerc.org 701-777-5133)
Melanie Hetland (mhetland@undeerc.org 701-777-5155)
Dan Daly (ddaly@undeerc.org 701-777-2822)
Energy & Environmental Research Center
University of North Dakota
15 North 23rd Street
Grand Forks, ND 58203

Introduction

The Energy & Environmental Research Center (EERC) is a nonprofit research, development, demonstration, and commercialization unit of the University of North Dakota. For the last six years, the EERC has participated in a cooperative agreement with the U.S. Department of Energy (DOE) National Energy Technology Laboratory (NETL) in which the EERC has provided technical expertise, systems engineering and analysis, and brokering between DOE, Environmental Management (EM) sites, and companies with technologies applicable to EM needs.

NETL–EERC EM Cooperative Agreement Concept

Commercialization of detection and cleanup technologies can be limited for many reasons, including a lack of testing and demonstration capabilities, the resolution of technical issues outside the traditional focus of the technology developer, limited capital, and only rudimentary knowledge of DOE and EM site needs. Deployment of a technology in the highly competitive EM marketplace requires sound field test data that clearly demonstrate the technology's superior capabilities, knowledge of personnel and site cleanup plans, and the potential to incorporate the technology into the ongoing site cleanup activities with minimal disruption.

Under the NETL–EERC EM cooperative agreement, the EERC contributes technical expertise and facilities as well as familiarity with the EM program to speed up the development, commercialization, and deployment of various innovative monitoring and cleanup technologies. The synergism offered by this arrangement benefits all parties. The various inventor companies receive research and development (R&D) assistance; exposure of both their technolog(ies) and their company to DOE, other governmental agencies (such as the U.S. Environmental Protection Agency [EPA] and Department of Defense [DOD]), and potential private-sector partners; and assistance with demonstrating their technology at an EM site. At the same time, DOE can expedite cleanup of the EM sites through the more rapid deployment of cutting-edge technologies that have been identified and/or developed with the EERC's assistance. Each company's competitive advantage is protected through proven confidentiality agreements.

Innovations in sensor technologies and treatment processes that are cost-effective, efficient, and safe are needed for DOE to realize its goals in the EM program. The work of the EERC, in partnership with a variety of environmental technology companies, facilitated by the NETL–EERC EM cooperative agreement, is helping DOE to meet these goals. The following project descriptions are examples of the EERC's efforts in the cooperative agreement.

Cone Penetrometer for Subsurface Metal Detection

The EERC has worked with Science & Engineering Associates, Inc., of Albuquerque, New Mexico, during the development of its fiber optic laser-induced breakdown spectroscopy (LIBS) cone penetrometer system for the real-time, in situ characterization of heavy metal contamination of soil. The technique can be applied to both subsurface metal surveying and surface mapping. The EERC:

- Developed a novel calibration technique that uses the entire LIBS spectrum.
- Evaluated potential LIBS calibration techniques for lead and chromium using 81 field samples.
- Developed a LIBS data reduction procedure and provided technical/data reduction support to a field demonstration of the unit at Sandia National Laboratory.
- Developed a method to produce suites of soil and air filter samples for calibrating field and laboratory instruments.
- Compared LIBS analytical methods to conventional laboratory techniques.

The applicability of the technique is being expanded to new areas as the EERC explores the ability of LIBS to detect lead in paint, characterize metal alloys, detect beryllium in air-sampling media, and provide real-time characterization and confirmation of site cleanup. The LIBS technique will be of value during characterization, decommissioning, and decontamination activities at any of the EM sites.

Remediation of High Explosives-Contaminated Soil

The EERC is developing a portable field technology that uses hot, liquid (i.e., subcritical) water for ex situ soil cleaning. The technology can be used to remove organic compounds ranging from polychlorinated biphenyls and polycyclic aromatic hydrocarbons (PAHs) to pesticides and high explosives. The soil remaining after treatment is nontoxic and supports plant growth. The technique offers several practical advantages over other cleanup techniques, such as degradation efficiencies of greater than 99.9%, even with initial contaminant levels as high as 12 wt%; low-severity operating conditions; simplicity of equipment design; the benefits of a closed-loop system; it requires no chemical reagents other than pure water; and it does not oxidize the contaminants, so nitroso-derivatives are not formed.

EERC research accomplishments have included the following:

- The removal of PAHs and pesticides from soils has been demonstrated at both the laboratory and pilot (i.e., 8-L) scale, with ending contaminant concentrations at nondetect levels.
- Wastewater cleanup by precipitation of PAHs with naturally occurring organics.
- The removal and degradation of high explosives from contaminated soil.
- Destruction rates of TNT, RDX, and HMX at various water temperatures were determined.
- Publication of the results of the tests with high explosives in *Environmental Science and Technology*.
- Demonstration that the static method (no water flow) for high explosives removal and degradation is simpler and less expensive than the dynamic mode in which water is flowing.
- The 8-L pilot unit was trailer-mounted with a generator for portable, remote operation (the operator will only need to be present to load the vessel).
- Negotiations for an on-site demonstration of the technology at Los Alamos National Laboratory are continuing. The proposed

demonstration is currently undergoing the required health and safety review.

There are currently at least 14 needs for remediation of explosives-contaminated soil and other debris at various DOE sites that the subcritical water remediation technique could address.

Prevention of Chloride Corrosion in High-Temperature Waste Treatment Systems

The EERC has teamed with GTS Duratek of Columbia, Maryland, to continue developing its technology to vitrify radioactive, hazardous, and mixed wastes currently stored in tanks at the DOE Hanford site. The EERC's role is to develop and optimize chloride and sulfate removal technologies for incorporation into the Duratek process. Most Hanford tank wastes contain high levels of chloride and sulfate, both of which are undesirable in vitrification environments, as sulfate floats on top of the vitrification melt and can "short out" the vitrifier electrode and chloride can corrode the vitrifier and emission control system components. Conventional chloride and sulfate removal technologies are unsuitable because the Hanford tank wastes are highly alkaline, extremely nonhomogeneous, and contain anionic complexed radionuclides and high levels of competing anions including hydroxide, nitrate, and nitrite. In response to GTS Duratek's request, the EERC developed technologies for the safe and effective removal of chloride and sulfate from tank wastes.

The EERC developed methods for preparing and using anion-specific exchange resins that remove only chloride and sulfate from solution and leave negatively charged radionuclide complexes and other anions behind. In tests with GTS Duratek-supplied Hanford tank waste simulants, the processes have consistently achieved chloride removals of 99%, sulfate removals of >95%, and have been shown to be 100% regenerable. The processes were configured for column-based operation in which waste treatment occurs as waste solution flows upward and resin regeneration occurs when regeneration solution flows downward. Specific EERC research activities have included:

- Development and optimization of methods for conversion of commercial cation exchange resins to chloride- and sulfate-specific ion-exchange resins.

- Optimization of chloride- and sulfate-specific ion-exchange process operating conditions encompassing pH, resin capacity, exposure time, and physical setting.

- Development and optimization of methods for spent resin regeneration.

- Optimization of total system performance in the column configuration.

The EERC has continually modified the technologies to ensure compatibility with the evolving GTS Duratek Hanford vitrification facility design and has also improved the effectiveness and economics of the technology. The work performed by the EERC on the GTS Duratek vitrification process will help to ensure timely implementation of the GTS Duratek Hanford vitrification facility and also applies to waste at other DOE sites that is similar in alkalinity and composition to the Hanford wastes.

Thermodynamic Modeling of Volatile Hazardous Metal Behavior in the Vortec Vitrification System

Waste from the Paducah Gaseous Diffusion Plant at Paducah, Kentucky, is proposed for vitrification in a facility designed by Vortec Corporation of Collegeville, Pennsylvania. The EERC is assisting Vortec with the optimization of its flue gas-handling and cleaning systems for the vitrification facility by computer modeling of chemical equilibria (e.g., vaporization and condensation of hazardous metals) using a thermochemical equilibria code specifically suited to this complex thermal system. Based on the results, design modifications and operating procedures can be made to minimize metal emissions. Modeling was performed using Version 3.0 of the Facility for the Analysis of Chemical Thermodynamics (FACT) code developed at the Ecole Polytechnique de Montreal. The modeling activities showed that:

- Significant fractions of uranium, plutonium, technetium, and cesium will vaporize from the flame.
- The maximum concentrations present in the flame are hundreds of ppm for uranium, tens of ppm for technetium, tens of ppb for plutonium, and part-per-quadrillion levels for cesium.
- Vaporization of uranium can be dropped by orders of magnitude using a substoichiometric flame, although CO levels will rise.
- Insufficient data exist to model neptunium behavior.
- Most metals will condense at the entrance to the recuperator, although cesium will condense throughout.
- The recuperator should be broadly outfitted with sootblowers and oriented vertically so that deposits fall into the melt.
- During initial tests, deposit formation and composition should be closely monitored within temperature bands in the recuperator.
- Fine-particle formation and composition leaving the recuperator should also be monitored during initial tests.

The EERC's efforts on this project will result in the minimization of metal emissions from the vitrifier, thereby improving the system safety and acceptability.

Development of an In Situ Instrument for Measuring Mercury in a Gas Stream

The EERC is supporting Sensor Research and Development Corporation of Orono, Maine, with the development of a portable prototype for a continuous emissions monitor for the detection of mercury in gas streams. The monitor uses surface acoustic wave (SAW) technology to determine mercury concentrations. The EERC:

- Created a test plan to determine SAW technology effectiveness under a variety of conditions.
- Provided expertise during efforts to improve detection limits.
- Is developing a pretreatment and preconcentrating system that will improve SAW detector performance.
- Conducted preliminary bench-scale tests using a prototype instrument.

A reliable continuous emissions monitor will find extensive use in a wide range of situations, such as at DOE EM sites, in waste-to-energy systems, and in fossil fuel combustion systems.

SpinTek Centrifugal Membrane Filtration

Remediation of liquid mixed-waste streams at the various weapons complex sites will be more cost-effective if their volume is minimized. SpinTek Membrane Systems, Inc., of Huntington Beach, California, owns a novel centrifugal membrane filtration technology that makes use of ultrafiltration and centrifugal force to separate suspended and dissolved solids from liquid waste streams, producing a filtered-liquid stream and a low-volume contaminant–concentrate stream. The EERC assisted SpinTek in the continued development of its process by:

- Demonstrating high solids removals in tests with tank waste surrogates.

- Testing alternate turbulence promoter designs to determine which version provided the greatest increase in flux while decreasing power consumption. A beveled promoter was found to perform the best.

- Testing against other, competing filtration technologies, which showed that the SpinTek process is applicable to a wider variety of liquid waste streams than the other tested technologies.

- Demonstrating that the SpinTek process provided the appropriate prefiltration needed for ion exchange technologies such as might be used in radionuclide removal in mixed waste applications.

The SpinTek ultrafiltration process can be used to greatly reduce the millions of gallons of tank waste that require treatment at EM sites. It can be used to prefilter streams prior to radionuclide ion exchange, remediate contaminated groundwater plumes, treat secondary liquid waste streams from other remediation processes, and filter liquid waste streams generated during decontamination and decommissioning activities.

ADA Mercury Removal

ADA Technologies, Inc., of Englewood, Colorado, has developed a novel mercury sorbent specifically designed to remove low concentrations of mercury from aqueous waste streams. The sorbent relies on the selective sorption of mercury by noble metals. The EERC assisted with ADA's field demonstration of the sorbent's effectiveness by:

- Designing and fabricating a 0.5-L/min sorption unit to evaluate the performance of the ADA sorbent without mechanical or operations interference.

- Transporting the sorption unit to DOE's Oak Ridge, Tennessee, Y-12 reservation, setting it up, and providing on-site engineering for the first six weeks of operation.

Although influent mercury concentrations were nearly 1900 ppt, the system removed mercury to levels of <12 ppt for a throughput of 65,000 bed volumes over a 15-month period.

The ADA proprietary sorbent offers a means of further reducing low mercury levels in groundwater, such as can be encountered at several locations on EM sites.

Deactivation and Decommissioning Focus Area (DDFA) Technical Support

The EERC provides program support to the DDFA in project planning and analyses through the collection and assay of EM data. This effort centers around the development, maintenance, and use of an information system designed to provide fundamental information and data relationships on DDFA technologies, needs, technical responses to needs, and EM Paths to Closure project baseline summary information. One product developed at the EERC for the DDFA team members is the Deactivation and Decommissioning (D&D) Information System (DDIS). This decision-support tool is used to identify and track relationships between DDFA technologies and site needs. The database is housed on the NETL LAN for use by the DDFA team.

The EERC's efforts:

- Improve the D&D of the EM complex by identifying and assessing additional technologies not currently in the EM portfolio.

- Enhance data analysis capabilities and increase the transfer of information between DDFA support team, sites, and vendors by maintaining a database and developing user-friendly tools for interacting with the database.

Acknowledgments

We wish to acknowledge Edgar Klunder, the NETL Contracting Officers' Representative for the EM cooperative agreement.