

APPENDIX B

SELECTED

VISIBLE AND IMPORTANT PROBLEMS

TABLE OF CONTENTS

EMISSIONS MONITORING FOR HIGH-LEVEL WASTE PROCESSING	B.1
ALTERNATIVE HIGH-LEVEL WASTE TANK DISPOSITION	B.2
MONITORING MIXED WASTE TREATMENT PROCESSES AND EFFLUENTS	B.4
LONG-TERM MONITORING OF REMEDIAL MEASURES	B.6
REAL-TIME MONITORING AND CHARACTERIZATION OF SOILS AND GROUNDWATER	B.7
<i>IN SITU</i> DETECTION OF SURFACE CONTAMINATION TO FREE- RELEASE GOALS	B.8
UNDERSTANDING NATURAL PROCESSES AFFECTING CONTAMINANT FATE AND TRANSPORT	B.10
IMPROVED METHODS AND STRATEGIES FOR MANAGING AND INTERPRETING DATA	B.11
SUMMARY OF SOLUTION PATHS AND STRATEGIES	B.13

SELECTED VISIBLE AND IMPORTANT PROBLEMS

In this Appendix we revisit the **Visible and Important Problems (VIPs)** featured previously in this **ROAD MAP**. These are only a small portion of the universe of CMM science and technology development challenges to be faced by DOE-EM. They were selected because they are topics of considerable recent and current concern. The goal of **APPENDIX B** is to describe specific aspects of the selected **VIPs** in detail and to outline solution strategies. The **VIPs** are, on the whole, multi-part challenges that may require several different responses. The approaches presented here may be thought of as brief technical responses to some of the highest priority CMM-related challenges facing DOE-EM at this time.

Most of these selected **VIPs** are currently being addressed by OST with CMST-CP involvement; technical solution paths are reasonably clear, and appropriate technology development is already underway. For these the solution path already selected is presented here. In other cases, although the need may be equally important, the solution path is not so clear at the present time; a solution strategy is proposed for those cases. The solution paths and strategies presented are based on OST's past successes in CMM R&D.



EMISSIONS MONITORING FOR HIGH-LEVEL WASTE PROCESSING

There are many monitoring challenges associated with HLW processing. This one is notable because it is related not only to HLW processing but also to mixed and mixed-TRU waste and nuclear materials stabilization concerns.

Effluent monitoring for NO_x and other constituents during HLW processing

Direct vitrification is one possible treatment of choice for the remaining sodium-bearing liquid wastes (SBW) at INEEL. If this approach is selected, it is anticipated that a vitrification facility will be built that will include an off-gas treatment train as a major system. Regulatory permitting of the off-gas treatment system will require monitoring effluent gases for NO_x (NO, NO₂) and possibly also for CO, NH₃, CO, and/or H₂, depending on the off-gas treatment strategy selected.

Four NO_x removal processes have been considered for the design of a pilot melter facility at INEEL. Two of these processes use NH₃ for the reduction of NO_x; the third involves steam reforming that may produce CO, H₂, and unchanged NO_x as products; and the fourth, a reburner process, may produce CO and unchanged NO_x. If NH₃ processes are used for NO_x level reduction, upstream and downstream NH₃ monitoring will be required for both process control and effluent monitoring. If other processes are selected, off-gas monitors will be needed to determine the efficiency of NO_x removal. Downstream monitoring for CO and H₂ may also be required for the steam reforming and reburner processes.

In addition to the melter facility, other thermal waste process facilities at INEEL and elsewhere will require effluent monitoring for a variety of hazardous constituents including radionuclides, toxic heavy metals, hydrocarbons, halogenated organics, and priority pollutants. Operation of off-gas control systems will be regulated by state agencies and by U.S. EPA in accordance with the Maximum Achievable Control Technology (MACT) rule for incinerators, the Clean Air Act (CAA), the Resource Conservation and Recovery Act (RCRA), and related laws and regulations. On-line monitoring of Hg, CO, NO_x, total hydrocarbons, and other species will facilitate compliant operation and will provide independent verification of process off-gas sample analyses.

Technology development within DOE and beyond

The need to monitor gaseous and particulate emissions extends well beyond DOE concerns to off-gases from thermal processes such as incineration and power generation as well as emissions from petroleum and metal refineries and chemical processing plants. A good deal of technology development has already taken place in response to this wider need, and commercial instrumentation is available for a number of

applications. To expedite the acceptance and use of such instrumentation, U.S. EPA sponsors the Environmental Technology Verification program. This EPA program has already verified the operation of four technologies to monitor HF, NO, NH₃, and other compounds under simulated test conditions. A Phase I test of six commercial mercury monitors has been completed at a pilot scale combustion facility. The most successful mercury monitors will undergo Phase II testing at a commercial test facility.

Supplementing the U.S. EPA program, TMFA has been testing Continuous Emissions Monitoring (CEM) technologies as well. Given the advanced state of development and verification of commercial CEM technologies, an appropriate approach to meeting the INEEL CEM needs is the adaptation of these technologies to site-specific functions, requirements, and conditions. Most relevant in the HLW tank sphere of concern is monitoring volatile off-gases produced by the introduction of HLW and LLW into a melter. Since such measurements are needed to design and qualify melter operations, adaptations of commercial instruments for use with off-gas systems should be given the highest priority.

Meeting the site needs

The first step is for the site, utilizing technical expertise and assistance from the appropriate Core Technology group, and working in concert with regulators and interested stakeholders, to develop function and design (F&D) requirements to specify specific gases and concentrations to be monitored as well as data and engineering requirements. Following documentation of F&D requirements, the site, again assisted by DOE-EM OST as appropriate, will select a commercial monitoring system and identify a technology provider to assist it in the installation and demonstration of the monitoring technology in the planned pilot vitrification facility. To address the need to provide CEM technology for regulatory compliance of thermal processes, OST has taken the lead in the development and deployment of both new and commercial technologies.



ALTERNATIVE HIGH-LEVEL WASTE TANK DISPOSITION

New disposition approaches will present characterization and monitoring challenges.

Alternatives to HLW removal and processing

Removing, pre-processing, stabilizing, and shipping high-level tank wastes to long-term storage repositories present both substantial cost and technical risk. Accordingly, at this time DOE-EM is evaluating alternative scenarios for HLW tank disposition, including addressing the inherent risks associated with waste residuals that may remain following the completion of retrieval operations. Aspects of these closure scenarios include the following.

- ! Inventory remaining in the tanks must be assayed regarding the volume and composition of the wastes.
- ! Inventory remaining in the tanks must be stabilized to minimize the likelihood of leakage.
- ! Tank integrity must be assured before closure and subsequently monitored.
- ! Subsurface barriers may be required to guard against groundwater contamination in the event of tank leakage.
- ! Sensitive leak detection systems must be emplaced to ensure rapid detection of any leaks; contingency plans must be formulated for dealing with any leaks that might occur.

Such closure scenarios include post-closure monitoring to validate the assumptions and performance of the closure approach. Following retrieval operations, any residual waste that may be present is not expected to be uniformly distributed, nor of uniform composition, nor readily accessible with available risers. Information about residual waste is key to concluding retrieval operations as well as developing closure agreements and proceeding with closure operations. Timely sampling and analysis to support the on-going work of crews engaged in these operations is critical. Feedback of sample information in hours is essential to maintaining the productivity of the deployed crew.

Resulting characterization challenges

These challenges are similar to those faced previously, but demand greater refinement in this closure scenario.

- ! Careful estimation of residual waste volumes is needed. The Topographical Mapping System (TechID 130), developed by OST and previously deployed, has potential for this application, although further development appears to be needed. There is also interest in investigating alternative volume estimation methods.
- ! Characterization of the tank residual radionuclide inventory is needed as well. This presents significant technical challenges due to tank waste heterogeneity, difficulties in sampling, and self-absorption. Traditional sampling (where feasible) and radio-chemical analyses are available but costly due to the hostile environment inside the tanks, the risk of exposure, and the need for disposal of secondary waste; even this approach has its uncertainties due to the heterogeneity. Alternatives could involve robotically deployed radiation sensors. A related challenge is to establish the degree of characterization needed to support *in situ* closure scenarios. For example, it may be less important to provide a complete assay of tank contents than to provide a scientifically defensible short list of indicator parameters for subsequent leak detection and monitoring.
- ! Characterization of structural integrity will also be required. The structures involved include both the tanks themselves and subsurface barriers that would be installed to intercept any leaks that might develop.

Resulting monitoring challenges

Similarly, the nature of the objects being monitored will place stringent demands on monitoring systems.

- ! Improvements on current methods for monitoring tank integrity will be needed for both single-shell and double-shell tanks. Currently only a very small proportion of the tank wall is monitored at any given time, as making these measurements is cumbersome and time-consuming. One must anticipate increased monitoring requirements as a prerequisite to *in situ* closure. TFA and CMST-CP have been investigating tank integrity issues during recent years; these investigations will assume greater importance in this scenario.
- ! *In situ* sensor systems will be needed to provide early-warning detection capability for possible releases. These systems would be similar to those deployed in more typical subsurface monitoring scenarios, but would possibly need to be even more sensitive. In this setting one may be able to exploit known properties of the wastes in choosing indicator species or parameters. One interesting possibility would be to artificially incorporate highly mobile indicators into the grout or other materials used to stabilize the wastes.

Strategies

Many of these challenges may be addressed by modifying technologies and strategies previously developed for this and other settings. The Topographical Mapping System (TechID 130) has already been mentioned as a tool for estimating the total volume of residual wastes. Providing an assay of the radionuclide content of residual wastes is more challenging because of the heterogeneity of the wastes and their self-absorption, particularly of alpha particle emissions. One possibility is to modify the Pipe Explorer™ (TechID 74) by inserting the everted membrane, with beta and gamma sensors and alpha scintillators, into slotted tubes that can then be used to probe the sludges and provide a three-dimensional sampling of emissions. For monitoring outside the tanks CMST-CP and others have been developing a variety of cone-penetrator-deployed sensors for radiation and other indicator parameters that may readily be employed in this setting. For subsurface barriers, the SEAtace™ technology (TechIDs 308, 2204) of introducing a non-naturally occurring gas to act as a sentinel may be attractive, although this would involve recurring expendables; the idea of emplacing mobile indicator species on the tank side of the barrier or even embedding them in the grouts in the tanks may also be attractive.

For other challenges the path forward is not yet so clear. In particular, the TFA and CMST-CP studies of tank integrity verification and monitoring have begun to identify approaches, with some promising results. These studies should be continued whether or not the alternative disposition strategies are adopted.



MONITORING MIXED WASTE TREATMENT PROCESSES AND EFFLUENTS

This **VIP** and its solutions involve multiple agencies, developers, and technology users.

Continuous Emission Monitors

Current baseline compliance strategies attempt to control emissions by setting operating parameter limits (OPLs) based on comprehensive trial runs. This methodology alone cannot, however, ensure facility emission compliance during routine operation.

The most direct and perhaps only way to ensure that Mixed Waste treatment facilities are operating properly is to implement continuous emission monitors (CEMs). If acceptable CEMs are used, not only are the regulators and stakeholders more confident that actual emissions are below allowable levels, but also the extent of waste feed characterization and expensive off-line performance testing can be reduced. DOE has undertaken a program of developing and testing CEMs for a range of pollutants including mercury, multiple metals, dioxins and furans (D/F), and particulate matter (PM). CEMs offer the potential to provide a continuous, near real-time record of emissions for a variety of potential pollutants, as well as optimized real-time process control.

Treatment systems are needed for DOE LLW and HLW, mixed waste (MW) and mixed transuranic (MTRU) waste. Thermal treatment systems such as melters, incinerators, and plasma systems have traditionally been used. In the future, other processes are expected to be implemented, including steam reforming, thermal desorption, and chemical oxidation. These will also operate under regulatory permits, which are becoming increasingly stringent. Developing CEMs for alternative treatment technologies is, therefore, a natural extension of current CEM development.

U.S. EPA promulgated its Maximum Achievable Control Technology (MACT) for Hazardous Waste Combustors rule in September 1999. The MACT Rule establishes regulatory requirements for the operation of incinerators and certain kilns. It does not explicitly cover other treatment processes, but permit writers are expected to model many permit provisions after the MACT Rule, particularly those regarding emissions. Moreover, worker safety, public health, and environmental responsibility demand that DOE treatment facilities not emit hazardous pollutants.

Particulate matter

Two primary challenges for PM CEM development are (1) instrument calibration and (2) facilities using high efficiency particulate air (HEPA) filters. EPA has proposed that calibration correlation coefficients should be at least 0.95. Achieving this requires that the CEM be challenged over its entire response range; challenging the high range requires a PM concentration greater than the MACT emission limit. Even though EPA has indicated that this may be allowable during brief calibration periods, this is not an option for DOE facilities if radionuclides are present. TMFA, CMST-CP, Florida International University and Oak Ridge TSCA incinerator investigators recently completed a comparative evaluation of commercial PM CEMs. The better CEMs are expected to satisfy the correlation requirement.

In facilities using HEPA filters in the effluent stream, PM levels downstream of the HEPA filter are orders of magnitude lower than the MACT Rule emission limit (34 mg/dscm). These downstream levels are below the level of detection (LOD) for the current generation of PM CEMs and may be below the LOD for EPA Reference Method 5i, against which PM CEM performance must be judged. An EPA/DOE National Technical Workgroup (NTW) has been established to address this problem. One technical challenge

involves developing a protocol for calibrating the instrument at this low level, which may also require modifying Method 5i for PM levels below 1 mg/dscm. A second technical challenge is to establish a protocol for CEM use for compliance monitoring at MW treatment facilities. It is likely that CEM measurements will be nondetects during normal HEPA filter operation. However, if the HEPA filter were to fail, then the instrument must be able to detect that failure. The NTW study is designed to determine what type and degree of HEPA filter failures can be detected by a PM CEM. EPA and state permit writers are involved in this study, as are DOE-EM personnel including CMST-CP; the major work is taking place at the Mississippi State University's Diagnostic and Instrumentation Analysis Laboratory (DIAL) under DOE-EM support.

Mercury

Mercury is present in many DOE waste streams, although exact quantities and forms are rarely known. Most treatment facilities do not presently have control technology for mercury emissions; hence facility designs and permits assume that all mercury present in the feed is emitted to the atmosphere. The new MACT Rule emission limit for mercury (130 µg/dscm) is two to three times lower than current allowable limits. At the MACT off-gas concentration, and assuming no removal in the treatment process, the maximum waste feed mercury concentration would need to be less than about 10 ppm. Sampling and analyzing waste feed for mercury to that level is very costly and would greatly increase the potential for worker exposure to radionuclides. Reliable CEM technologies are available; DOE could easily offset their cost with savings in waste characterization.

Previous testing of mercury CEMs by DOE and EPA found that systems needed to be made more rugged to withstand the very harsh conditions potentially found in some treatment facility off-gas streams: high PM, moisture, and sulfur dioxide all have caused severe maintenance problems. Additionally, detectability and accuracy need to improve somewhat. TMFA is conducting a long-term evaluation of several mercury CEMs at TSCA. Florida International University (FIU) and DIAL will assist in the test and data analysis. These efforts are being coordinated with the EPA Environmental Technology Verification Program, which conducted a Phase I test of five commercial mercury CEMs in January 2001 at a pilot-scale facility and is now proceeding with Phase II testing at full-scale facilities. Novel mercury monitoring methodologies such as cavity ring down spectroscopy, a high-resolution compact field spectrometer, and a surface acoustic wave sensor are also being developed; these are related to technologies previously developed by DOE-EM OST for use in other settings.

Multiple metals

The MACT Rule multiple metals (MM) include mercury, cadmium, lead, arsenic, beryllium, and chromium. With the exception of mercury, DOE facilities readily meet the MM emission limits; these metals are present mostly in the particulate phase and DOE facilities have extensive PM control for radionuclides. The incentive to deploy MM CEMs comes from stakeholder interests in assuring that hazardous metal emissions are monitored and communicated on a continuous basis, as well as from a desire to minimize waste feed analysis costs. Previous testing found that most of the instruments had difficulty detecting mercury and arsenic with adequate precision and accuracy. Detectability and interferences remain as technical challenges for application at most waste treatment facilities.

Dioxins and furans

Dioxins and furans (D/F) present a unique challenge in that their principal source is formation in the combustion system or the air pollution control system. The mechanisms for this formation are not yet totally understood despite considerable research. Complicating the problem further, the regulatory levels of D/F are extremely low. Individual congeners must be measured down to about 0.005 ng/dscm, or about 5 parts per quadrillion; no "real-time" monitor can achieve these LODs. The current method for measuring D/F involves sampling for two to six hours followed by off-site analysis, which takes four to six weeks. Therefore, studying how D/F formation responds to process conditions is an extremely laborious and costly procedure. To address this problem, a coordinated EPA/INDP program is developing a D/F CEM with high selectivity and sensitivity for individual congeners to aid in the study of the formation and destruction mechanisms for DOE treatment systems. The technical challenge is to understand D/F formation and

destruction sufficiently well that a simple, less expensive monitoring technique, perhaps involving detecting precursors or indicators of the relevant D/F congeners, may be developed. The ability to have data within minutes rather than weeks will allow researchers to generate data much efficiently over a much wider set of experimental conditions.



LONG-TERM MONITORING OF REMEDIAL MEASURES

All major DOE sites require long-term monitoring of passive remedial measures, which include natural processes, containment, reactive barriers, and stabilization operations.

The SCFA three-pronged approach

The SCFA has identified a three-pronged approach to meeting these needs. One approach will address groundwater monitoring needs by developing *in situ* sensors capable of meeting compliance requirements for VOCs, followed by heavy metals and radionuclides. This will be supplemented by employing advanced geophysical tools for monitoring contaminant transport fluxes in the vadose zone, combined with geostatistical sampling techniques to provide ground truth results. Finally, in larger areas, particularly those difficult to access, aerial monitoring platforms will be developed to measure key indicators of contaminant breaching.

Containment and stabilization

In view of the importance of containment as the preferred remedy at DOE sites, the DOE-EM OST has sponsored several technology development projects for verification and monitoring of the caps and covers used with buried waste. These include remote sensing systems development, subsurface barrier validation using the SEAttrace™ monitoring system, a monitor for demonstrating the effectiveness of barrier installation and long-term performance using electrical resistance tomography, and the advanced tensiometer.

In 1996 the OST CMST-CP, working with SCFA, identified areas of needed technology development based on assessment of Technology Development Needs Statements, Site Technology Deployment Plans, and site cleanup schedules and plans. One need identified through this process was for monitoring the emplacement and effectiveness of subsurface barriers. A Program Research and Development Announcement (PRDA) solicitation was commissioned by the National Energy Technology Laboratory (NETL, at that time the Federal Energy Technology Center, FETC). The "Subsurface Barrier Validation with the SEAttrace™ Monitoring System" project was selected competitively for development by industry; the resulting technology is a gaseous tracer-based verification system for use with subsurface containment barrier structures.

Another technology need identified was for improved, preferably real-time, field characterization and monitoring techniques for the remediation of contaminated soils. To address this need, OST leveraged support from the Accelerated Site Technology Deployment (ASTD) program and managed the technical progress of the project, "Radiation Tracking System for Delineating Contamination in Soils." This ASTD project involved the integration and implementation of four existing technologies developed with EMSP and other OST support: (1) mobile radiation tracking system, (2) portable high-purity germanium sensors for *in situ* gamma spectrometry, (3) the Warthog system for 3D, real-time excavation screening support, and (4) software packages of provide data analysis for decision support.

Monitored natural attenuation

DOE-EM will continue to need to develop long-term monitoring solutions for other requirements. The future focus will be on monitoring of post-closure sites and natural and *in situ* remediation processes (such as monitored natural attenuation, bioremediation, and reactive barriers) for meeting regulatory and stakeholder requirements. Monitoring of these processes will also determine their efficacy and help determine measures for their enhancement.

Regulatory acceptance and EMSP research

A requirement for regulatory buy-in for natural attenuation and/or bioremediation for organic contaminants in the subsurface is an ability to demonstrate that actual decontamination is occurring, rather than mere diffusion of the contaminant into a larger volume. Several EMSP projects are exploring potential techniques; the most likely path forward will be to assess the most successful of these projects. One project, for example, involves using ratios of carbon isotopes to determine whether or not biodegradation is occurring; other isotopic ratios have been used to study the exchange between different aquifer layers. Another EMSP project explores the use of precise isotopic ratio measurements of chlorine and carbon to determine the mechanism and extent of in situ bioremediation of chlorinated organic solvents. Several other projects involve genetic engineering approaches to developing microorganisms for bioremediation of chlorinated organics in mixed wastes with high radiation levels as well as of a variety of other contaminants found at DOE sites.

The future challenge for DOE-EM will be to guide these basic and applied research results from EMSP through development to regulatory and stakeholder acceptance and ultimate field implementation.



REAL-TIME MONITORING AND CHARACTERIZATION OF SOILS AND GROUNDWATER

This **VIP** involves building on the long history of OST and CMST-CP sensor technology and integration successes within DOE-EM.

Early advances

Through OST, DOE-EM has followed a progressive approach toward addressing characterization, monitoring, and modeling of groundwater and soil contamination. In the early years the focus was on developing field analytical instruments for meeting site screening characterization needs. The analytical instruments developed have been used for surface soil characterization for VOCs, heavy metals, and radionuclides as well as in conducting well-head analyses of water samples.

Expedited Site Characterization

Later technology development combined these field analytical tools with deployment platforms such as the cone penetrometer and GeoProbe™ to enable subsurface characterization for these contaminants of concern. These field analysis capabilities were coupled with the development of decision support tools such as data fusion and statistically-based sampling techniques, culminating in a streamlined site characterization approach known as Expedited Site Characterization (ESC).

Researchers at Argonne had identified a methodology and procedure for remedial site characterization at Department of Interior and Department of Agriculture sites. A private sector organization had also developed and was practicing a similar approach. OST, through CMST-CP, began funding further developments for DOE sites in February 1993. The ESC process emphasizes the use of a variety of minimally intrusive technologies to optimize sampling locations and thereby minimize monitoring well installation. On-site decisions about subsequent sampling locations are made daily; this is made possible by the use of on-site analytical capabilities. This approach cuts the time necessary for full site characterization from many months or even years to a few weeks.

A parallel OST/CMST-CP project at Ames Laboratory that began in FY94 focused on the use of the ESC methodology as a driver for accelerated transfer of site characterization technologies. This work characterized contaminated sites using state-of-the-practice and new technologies simultaneously to enable quantitative evaluations of the merits of the new technologies. The work of this project is summarized in the OST ITSR *Expedited Site Characterization* (TechID 77). The ESC approach was accepted as an ASTM standard practice (D6235-98a, *Standard Practice for Expedited Site Characterization of Vadose Zone and*

Ground Water Contamination at Hazardous Waste Contaminated Sites) to provide guidance on site characterization. These techniques to characterize the perched aquifer at Pantex and the SRS D-Area Oil Seepage Basin during FY 1995, the Central Nevada Test Area and a Formerly Utilized Sites Remedial Action Program location in Ohio during FY 1997, and numerous other Federal and non-Federal sites.

Electrical Resistance Tomography and Electrical Impedance Tomography

Another set of technologies aimed at improving real-time subsurface monitoring and characterization involves Electrical Resistance Tomography (ERT) and Electrical Impedance Tomography (EIT). OST has sponsored projects involving ERT for subsurface imaging, tank leak detection, and monitoring. ERT has been used as a monitor for demonstrating the effectiveness of barrier installation, subsurface remediation of DNAPLs, and long-term performance of remediation measures including monitored natural attenuation. One of the most challenging and important remaining subsurface characterization needs is to develop reliable methods for locating DNAPLs in the subsurface; EIT has been and is being explored for this purpose. Basic science research supported by EMSP continues to explore fundamental aspects of a variety of electromagnetic methods potentially useful for subsurface imaging.

The new generation of soil and groundwater sensors

DOE sites have continued to express a high priority need for improved field characterization methods; this need has evolved from field screening and characterization applications to final assessment applications. For example, several sites have expressed the need for real-time characterization of soil for radionuclide and heavy metal contamination during excavation to judge when it is appropriate to stop excavating. Such real-time characterization is needed also to perform waste sorting and separation based on contamination by radionuclides and/or heavy metals; effective separation would reduce the volume of contaminated soils to be dealt with and hence the cost of remediation.

DOE-EM should place a priority on the development of improved real-time subsurface characterization and monitoring techniques by FY 2006. The focus during the next few years should involve engineering design, development, and integration of field analytical tools to work with various platforms to provide needed solutions for technology performance gaps identified in **APPENDIX A**. These gaps include real-time subsurface characterization in deep, hard-to-access areas beyond the reach of existing platforms. Also, integration of real-time characterization tools with excavation platforms and conveyor belt operations should be pursued to enable real-time differentiation of soil based on contamination by VOCs, heavy metals, and radionuclides.

Again, an attractive strategy will be to follow the progress of several EMSP projects. Promising sensing techniques under EMSP development include Laser-Induced Breakdown Spectroscopy (LIBS) and electrochemical techniques for subsurface characterization of heavy metals and radionuclides; Micro-Electro-Mechanical Sensors (MEMs) with applicability for all contaminants of concern; and other new schemes for detecting radionuclides and heavy metals; see the "Recent R&D Projects" panels in **APPENDIX A**.



IN SITU DETECTION OF SURFACE CONTAMINATION TO FREE-RELEASE GOALS

This **VIP** involves a collaboration of several OST programs (DDFA, INDP, and CMST-CP), sharing expertise and resources to solve a prominent challenge facing DOE-EM.

Deactivation and Decommissioning safety challenges

The varied nature of facilities undergoing deactivation and decommissioning (D&D) presents a wide range of contaminant types and site-specific characterization challenges, each typically requiring a detector

tailored specifically to the contaminant being measured and its matrix. One such challenge involves the characterization of property and equipment contaminated with beryllium (Be).

During DOE characterization and D&D efforts at the Rocky Flats Environmental Technology Site (RFETS) and elsewhere, workers may come into contact with property and equipment contaminated with Be. RFETS is concerned about the safety of workers from potential exposures to airborne Be re-suspended from surfaces and the potential liability associated with property release. Epidemiologists associated with the Beryllium Health Effects Study have expressed the opinion that with respect to berylliosis no safe exposure level exists for airborne Be. They have also indicated that dermal exposure to Be may result in sensitization, especially if the skin is cut or abraded. A primary site concern is the prevention of Chronic Beryllium Disease (CBD).

A portable surface and air beryllium monitor

DOE would benefit greatly from the implementation of a nearly instantaneous and continuous real-time monitor to measure both surface and airborne Be contamination. This monitor could be utilized to improve worker safety by providing an alarm for airborne Be. As a surface contamination monitor, it will allow for more effective free release of property. It will also aid in the identification of Be-contaminated work areas prior to potential worker exposure. By providing reliable real-time worker safeguards, real-time Be monitoring will increase worker efficiency and accelerate site closure.

Numerous other DOE sites may be able to benefit from real-time surface and/or air Be monitors, since these sites must establish their own Be exposure levels in response to the Chronic Beryllium Disease Prevention Program, promulgated as Title 10, Code of Federal Regulations, Part 850 December 8, 1999 (10 CFR 850).

The development of a real-time monitor for airborne and surface Be contamination has been identified as an OST priority. The monitor will be required to measure all types of Be inhalation hazards, including salts, oxides, and metal, in both air and surface surveys. It must possess sufficient sensitivity, accuracy, and precision to verify meeting or exceeding site action limits and other limits. It will need a lower detection limit of 0.1 micrograms Be per cubic meter for airborne measurements and 0.2 micrograms Be per hundred square centimeters for surface measurements.

The Be monitor is being developed by a commercial firm, Science & Engineering Associates (SEA). To initiate the development and funding process INDP issued a Request For Proposals (RFP) through NETL. CMST-CP personnel canvassed the DOE complex, including of course RFETS, to determine technical specifications. A Technical Evaluation Committee was formed to evaluate the proposals received, consisting of members from INDP and CMST-CP along with advisors from RFETS, Los Alamos National Laboratory (LANL), and Lovelace Respiratory Research Institute (LRRRI). SEA is currently funded to develop the real-time beryllium monitor based on their winning R&D proposal. SEA drafted and presented an Engineering Design shortly after funding was awarded; review and revision comments provided by RFETS end-user (D&D and Environmental Safety and Health), INDP, and CMST-CP personnel. Delivery and on-site evaluation of the prototype instrument is slated for early 2002.

Experience and teamwork

SEA's solution is based on its extensive experience with LIBS instrumentation. An important part of SEA's instrument design is proper consideration of aerosol behavior and properties, including size distribution. SEA will team with Lovelace Respiratory Research Institute (formerly the Inhalation Toxicology Research Institute) to provide the world class aerosol science capabilities needed to ensure that the end result is a robust instrument ready to meet the required performance certifications.

Demonstration and delivery

A critical development step is an on-site demonstration including federal and state regulators at a RFETS D&D facility. Because of the critical importance of regulatory acceptance to the ultimate deployment of

innovative technologies, every effort is being undertaken to involve regulatory bodies early in the development process, to help them acquire confidence in the instrument.

As of May 2002, two prototype airborne and surface beryllium monitors have been fabricated, tested with samples from the Lovelace Respiratory Research Institute and Rocky Flats following NIOSH guidelines, and are being demonstrated and deployed at Rocky Flats and Paducah. Additional monitors will be fabricated according to market demand.



UNDERSTANDING NATURAL PROCESSES AFFECTING CONTAMINANT FATE AND TRANSPORT

Filling this gap in basic scientific understanding is a high priority **VIP** for DOE-EM.

Reliable predictions needed to support closure and long-term stewardship

SCFA's highest priority Work Package has been "Vadose and Saturated Zone Characterization, Monitoring, Modeling, and Analysis." Related need areas identified by SCFA include improved understandings of permeability patterns, contaminant inventories, and distribution and movement in the vadose zone. Also needed are tools to better predict groundwater flow and transport.

Needs for improved subsurface characterization techniques were also cited in *Research Needs in Subsurface Science* (National Research Council, March 2000), which noted that "there is inadequate understanding of the details of the characteristics that must be understood in order to make reliable predictions of fate and transport. In addition, there are no adequate technologies for determining subsurface characteristics over large volumes with either direct or indirect techniques." It was also pointed out that "little progress has been made on developing predictive models that incorporate the entire range of processes that may affect contaminant transport." Every major DOE site has identified needs for defining the location and spatial distribution of contaminants, for estimating quantitatively the extent of contamination, and for developing or identifying methods to monitor the movement of subsurface contaminants.

Previous studies

Previous DOE-EM CMM projects in this area have included studies of flow and transport in fractured rock, groundwater modeling, and data fusion techniques for combining and interpreting information from diverse geophysical techniques. EMSP has also sponsored numerous studies in this area including assessments of factors that contribute to the transport of specific contaminants in the subsurface and the development of a variety of geophysical techniques for improved subsurface characterization. EMSP studies of transport mechanisms and soil fixation methods are related to high-priority needs cited at Hanford, Oak Ridge, and other DOE sites.

Geophysical characterization tools

DOE-EM should continue to develop geophysical characterization tools to better delineate subsurface characteristics. Many such techniques are being developed by the EMSP, including very early time-domain electromagnetic (VETEM), seismic, electromagnetic, and radar techniques, and combinations of these to provide high resolution subsurface mapping. Advances in these geophysical tools will lead into further development and demonstration phases to address DOE site needs for delineation of burial grounds and identification of buried wastes.

Contaminant fate and transport

With respect to other characteristics affecting flow and transport properties, DOE-EM Core Technology groups can aid in identifying site-specific needs for the following.

- ! Improving capabilities for characterizing the physical, chemical, and biological properties of the subsurface, particularly for deep and complex geologic settings
- ! Characterizing physical, chemical, and biological heterogeneity and providing improved models to enable more reliable predictions of migration
- ! Identifying and developing methods to integrate data collected at different spatial and temporal scales to improve estimates of contaminant and subsurface properties
- ! Incorporating complexities such as colloid formation, biological activity, and transport paths in fractured rock into transport models
- ! Conducting new experimental and modeling studies to account for the interacting chemical, physical, and biological processes that determine contaminant fate and transport

DOE-EM OST programs have supported projects involving geophysical characterization tools since their beginning; some of the earlier work was similar to basic science research efforts now being conducted by EMSP. It is anticipated, therefore, that future contributions in this area will involve working with EMSP and other programs to identify areas in which more basic research is needed and with the sites and other DOE-EM organizations to identify the EMSP projects that appear to be most suitable for extended demonstrations or deployment.



IMPROVED METHODS AND STRATEGIES FOR MANAGING AND INTERPRETING DATA

Evolution in characterization and monitoring technology will require parallel advances in data acquisition, storage, and interpretation as well as in regulatory strategies.

New technologies yield new types of data

Previous DOE-EM CMM R&D projects have produced significant advances in the efficient and effective use of real-time data in characterization (e.g., ESC and Hydrogeological Data Fusion) and remediation (e.g., Adaptive Sampling and Analysis Programs, PLUME - Groundwater Modeling Software, and RSS Software for Soil Excavation Control for Delineating Contamination in Soils). These projects provided ways of handling data generated on site and available within at most a few hours of sampling from a variety of types of measurements, and combining such data in producing reliable, accurate, and defensible characterization or remediation decisions.

There are three conceptual components to such systems.

- ! Data collection systems (hardware and software)
- ! Decision algorithms and concepts which enable better understanding and use of such data (data fusion and related decision support tools)
- ! Establishing and documenting processes to ensure regulatory and stakeholder acceptability of data obtained and decisions made

Data collection systems

Past advances in data collection systems include transmitting data from mobile radiation sensors along with global positioning system (GPS) location data by radio link to a central on-site facility. This process enabled real-time mapping of radiation levels at Fernald in support of soil excavation and remediation decisions.

The RSS Software mentioned above provides the real-time mapping and decision support for using this data.

Decision models and regulatory acceptance

Past advances in decision algorithms and concepts include the use of Bayesian geostatistical analysis to combine “soft” prior information (historical records, computer modeling results, institutional memory, etc.) about the likelihood of contamination at various locations on a site with “hard” sampling data to provide updated estimates of contamination likelihood or contaminant concentration contours. Adaptive Sampling and Analysis Programs (ASAPs) is a peer-reviewed procedure for such analyses. Peer review has also aided in the regulatory and stakeholder acceptance of the use of innovative data and decision methods, as with ASAPs and ESC; the latter, for example, is the topic of ASTM Standard D6235-98a.

Future development: hardware

Future challenges in this area will be to make similar advances with regard to long-term monitoring. Commercial entities are already working on developing and marketing monitoring networks which will be able to gather real-time data from in situ sensors, and this is a topic of considerable interest in the research communities (national laboratory and academia) as well. DOE-EM should promote and participate in appropriate forums for exchanging information about the state of the technology, on one hand, and DOE, regulator, and stakeholder requirements, on the other. Particular requirements for DOE long-term monitoring applications will include technologies to implement data quality issues such as sensor self-calibration and self-testing, data transmission and recording integrity comparable to current chain-of-custody protocols, etc., and development of automated data screening algorithms.

Future development: decision strategies

Parallel development of design and decision paradigms is needed. Such development must involve regulatory agencies, interested regulated parties, and ultimately other stakeholder groups. One path forward is to continue presenting proposed innovative methodologies for peer review and acceptance in professional publications as well as such forums as ASTM. Another is continued DOE-EM participation in inter-agency task groups such as the Interstate Technology Regulatory Council (ITRC), an association primarily of state regulators interested in easing the path toward adoption of innovative environmental technologies, and the Long-Term Groundwater Monitoring Task Committee of the American Society of Civil Engineers' Environmental & Water Resources Institute, consisting of professionals from DOE, DoD, U.S. EPA, U.S. Geological Survey, academia, and the private sector, and tasked with preparing a monograph *Long-Term Monitoring Design for Contaminated Groundwater Sites*. Such participation not only brings DOE expertise to the evolution of regulatory thinking on these issues but also ensures that DOE concerns will be represented in that evolution. In addition, DOE-EM should collaborate with other government agencies in sponsoring workshops on optimal monitoring and modeling designs, technologies, and software with invited participants from all sectors.

SUMMARY OF SOLUTION PATHS AND STRATEGIES

From the **VIPs** presented here we can abstract several general strategies and paths which DOE-EM can use for future R&D. These are outlined below, with reference to the **VIPs** which followed or are following each one.

- ! **Tryouts by invitation.** Organize comparative testing of invited commercially available technologies; identify those most likely to meet DOE requirements; fund further development by the vendor as needed to meet those requirements. **VIPs** following this path include the Mercury and Particulate Matter Continuous Emissions Monitors for Waste Treatment Effluent Monitoring. Development of the Mercury CEM is a joint effort with the U.S. EPA Environmental Technology Verification Program.
- ! **Procurement through a DOE lab.** Prepare functional and design requirements appropriate for the intended site deployments; work with a DOE laboratory to identify a technology provider who can meet those requirements, possibly with some funded development work. This path overlaps somewhat with the previous one; **VIPs** following it include Continuous Emissions Monitors for treatment process effluents.
- ! **RFPs to industry.** Develop functional requirements corresponding to site needs; publish these in Requests For Proposals (RFPs); review responses from industry and other respondents; contract technology development and provide oversight and review as needed. **VIPs** following this path include the Surface and Air Beryllium Monitor and the SEAtrace™ Barrier Validation System.
- ! **Leapfrog from past successes.** Identify successful technology solutions for related problems; fund adaptation, modification, and/or integration as needed for the current DOE requirement. **VIPs** following this path include modifying Neutron Etch Recorders for detecting and measuring radioactive contamination under tank floors and modifying the Pipe Explorer™ for characterizing sludges and difficult to access portions of tanks and other spaces.
- ! **Publicize unsolved problems.** Present DOE requirements for previously unaddressed problems to research communities including EMSP and DOE labs. **VIPs** following this path include next-generation robust, in situ, autonomous, self-calibrating and self-maintaining sensors for long-term monitoring; data collection methods and protocols for such sensors; and in situ tank waste characterization technologies capable of providing data satisfying regulatory certification requirements.
- ! **Fine-tune and expand available tools.** Fund integration and/or incremental evolution of successful technologies. **VIPs** following this path include soil excavation control technologies for precise, timely on-site delineation of contaminated regions during remediation; Expedited Site Characterization; Electrical Resistance Tomography; and Electrical Impedance Tomography.
- ! **Collaborate with researchers and stakeholders.** Organize and conduct workshops and participate in multi-agency and similar task groups on emerging technologies, DOE requirements, and emerging regulation. **VIPs** following this path include long-range planning for sensor technology development; development and evolution of regulatory paradigms and reference method performance specifications; evolution of methods, standards, and regulations for data reporting, recording, and interpretation; and parallel development of technology and regulatory standards for PM emissions for processes using High Efficiency Particulate Air (HEPA) filters.