CHARACTERIZATION, MONITORING, AND SENSOR TECHNOLOGY INTEGRATED PROGRAM (CMST-IP): AN OVERVIEW OF EMERGING TECHNOLOGIES IN SITE/WASTE CHARACTERIZATION AND WASTE TREATMENT MONITORING

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ABSTRACT

This paper summarizes FY-93 CMST-IP accomplishments and describes FY-94 new initiatives, with focus on those of relevance to meeting waste management needs. These activities include waste stream/process monitoring and controls, contaminant localization and determination in soils and groundwater, non-destructive evaluation/non-destructive assay (NDE/NDA) techniques, analytical methods/instrumentation for determination of radionuclides, and tank waste characterization, safety and operations.

This paper is intended to promote and publicize those technologies that are ready for demonstration, testing and evaluation as well as to report the planned deliverables and objectives of continuing or new projects.

INTRODUCTION

The U.S. Department of Energy Office of Environmental Restoration and Waste Management (EM) consists of five major programs: Waste Management; Environmental Restoration; Technology Development; Facility Transition and Management; and Transportation Management. Within Technology Development, the Characterization, Monitoring, and Sensor Technology Integrated Program (CMST-IP) promotes and coordinates applied R&D to meet the needs of its customers, i.e., the Office of Waste Management, the Office of Environmental Restoration, and the Office of Facility Transition and Management The scope of CMST needs encompass:

- initial location and characterization of wastes and waste environments prior to treatment;
- monitoring of waste retrieval, remediation and treatment processes;
- characterization of the performance of final waste forms; and
- site closure and compliance monitoring.

The mission of the CMST-IP is to provide the needed characterization and monitoring solutions required by the five Environmental Research and Technology Development Focus Areas:

- remediation and management of high-level waste tanks;
- characterization, treatment, and storage of mixed waste;
- cleanup of contaminant plumes;
- containment of existing landfills; and
- decommissioning and final disposition of the physical structures of DOE's weapons complex.

All Focus Areas have their respective characterization and monitoring needs. By working closely with stakeholders of these five Areas through systems engineering approach, the CMST-IP will identify technology gaps, integrate technology development to provide cost-effective solutions for meeting needs, and leverage resources to achieve the synergism of development efforts. These resources include those within the DOE complex as well as outside DOE, such as other federal agencies, private companies, and universities. For example, the CMST-IP is actively involved in promoting R&D from private sector through Cooperative Research and Development Agreements (CRADAs), Research Opportunity Announcements (ROA), Program Research and Development Announcements (PRDAs), Small Business Innovation Research (SBIR) and Technology Reinvestment Project (TRP). Collaboration with other federal agencies is accomplished through interagency agreements (IAGs). To coordinate and integrate technology development, the CMST-IP provides a focused approach that, in turn, accomplishes the delivery of needed characterization and monitoring technologies, timely and cost-effectively.

This paper presents a description of technology development activities relevant to the needs of the Focus Areas, i.e., high-level waste tanks and mixed waste. Other activities under development that primarily address the needs of the other three Focus Areas are not described. A detailed listing of all CMST-IP activities is available through the DOE program office by contacting the authors of this paper.

DESCRIPTION OF TECHNOLOGIES AND ACCOMPLISHMENTS

Highlights of FY-93 accomplishments and performance goals of selected projects are listed below. A brief description of each technology with contact information is also given.

Direct Measurement of Sr-90 and U-238 in Soils on Real-Time Basis

The long-lived ^{90}Sr (29yr half-life) is perhaps the fission product of greatest concern in nuclear waste clean up, but the analysis is difficult, time-consuming, and expensive. This task will develop, calibrate, and field demonstrate a real-time ^{90}Sr analyzer for direct measurements (based on the ^{90}Y daughter) in surface soils, on conveyor belts, or other locations. The technology will employ a sensor composed of multiple (<1mm thick) layers of organic fiber scintillators that can selectively detect high energy (2.29 MeV maximum energy) beta particles from the ^{90}Y daughter in the presence of other long-lived fission and activation products and gamma decay radionuclides. A similar detector, with minor modifications, was constructed in FY-93 to measure ^{238}U (based on the ^{234m}Pa daughter) in soils. The light-weight hand-portable sensor will employ coincidence and anticoincidence counting techniques to provide the required selectivity and the discrimination against other anthropogenic and natural radionuclides. The final demonstration, testing and evaluation of this analyzer should be completed in FY-94 for both ^{238}U and ^{90}Sr.

Accomplishment: Demonstrated real time analyzer for determination of ^{238}U in surface soils over a range of ≤35 pCi/g to >3000 pCi/g at the Fernald site in Ohio. Work is in progress to develop a portable analyzer for determination of ^{90}Sr in surface soils and washed soils on a conveyor belt. Field demonstration for strontium analyzer is scheduled in FY-94 with an anticipated detection level below 10 pCi/g and a relative error below 35%. (Principal Investigator: A. J. Schilk, PNL, 509-376-9510)

On-Line Measurements by Photoacoustic and Transient Infrared Spectroscopies

Polyethylene encapsulation of waste radioactive salts to immobilize the waste is a highly promising waste-processing method being developed at Brookhaven, Rocky Flats, and Hanford. This task will develop an on-line, real-time composition monitor for analysis of the molten salt-polymer stream as it exits the processor. Since the monitor will provide an analysis in real-time, the analysis can guide the waste processing operation so that the proper product composition is maintained. The analysis can also be used to document and certify the waste form composition. The monitor will use a technique invented by the principal investigators called Transient Infrared Spectroscopy (TIRS), which can acquire the mid-infrared spectrum of a moving solid or viscous-liquid process stream.

Accomplishment: Developed and demonstrated TIRS as a process monitor for polymer encapsulation of low-level waste (rad waste salt) at Brookhaven National Laboratory. Real time determination of nitrates in thermally hot, extruded polymer/waste mixture was achieved with an accuracy of ±3% up to a high end of 70% waste loading. (Principal Investigator: John F. McClelland, Ames, 515-294-7948)

Infrared Analysis of Tank Wastes

This task will develop the methods for the quantitative analysis of molecular and multi-atom ionic species such as nitrates and ferrocyanides found in the sludges and solids in storage tanks at the Hanford site via Fourier-transform infrared (FTIR) photoacoustic spectroscopy (PAS). Such species are of special interest because of their chemical reactivity. FTIR-PAS can identify and quantify these species using very small samples (approximately 1 mg) and with little sample preparation.

Accomplishment: Developed FTIR-PAS for analyzing hazardous organics and ferrocyanides in solids and sludges from underground storage tanks. Demonstrated a linear dynamic range of 15 to 40 % for ferrocyanides with an accuracy of ±1.5% using surrogate wastes. The FTIR-PAS technique is scheduled to be transferred to the Hanford site in FY-94. (Principal Investigator: John F. McClelland, Ames, 515-294-7948)

Improvements in Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

ICP-MS is a very sensitive method for elemental and isotopic analysis. It is expected to have major applications for monitoring both stable and radioactive elements in waste remediation. However, the precision of ICP-MS is not particularly good (RSD of ~ 5% for elemental concentrations, ~ 1% for isotope ratios). The goal of this project is to improve precision and accuracy by at least one order of magnitude by constructing a new type of ICP-MS device. The ion beam from the ICP will be split into two parts. Each part will be directed into a separate mass analyzer set to monitor a different isotope. With this "double beam" approach isotopes will be detected simultaneously rather than sequentially as with present devices. The anticipated benefits include: 1) improved accuracy for determining ultratrace elements; and 2) fast isotopic analysis at high precision and sensitivity with minimal sample preparation.

Accomplishment: The development of dual-beam ICP-MS technology for improved performance of measuring isotopes of uranium and thorium in soils is continuing. The technology is expected to be ready for demonstration in a laboratory-like environment in 1994. The anticipated detection level is ~1 pptr with a relative standard deviation of 5% for routine analysis, 1% with internal standard, and ±0.01% for isotope ratios. (Principal Investigator: R. S. Houk, Ames, 515-294-9462)

Development of a Continuous Emission Monitor for Incineration

The objective of this project is to develop and field-test a mobile Fourier transform infrared spectrometer (FTIR) as an EPA-certified method for continuously monitoring hazardous waste incinerators. The project consists of assembling and testing the performance of an FTIR system in laboratory experiments with subsequent performance verification on actual stack gas samples. The instrument will be field tested at an operating hazardous waste incinerator facility. An FTIR spectral library will be developed for the compounds of interest.

Accomplishment: Demonstrated FTIR continuous emission monitoring system for monitoring organic products of incomplete combustion at the K-25 Toxic Substance Control Act (TSCA) incinerator, which is located at the Oak Ridge site in Tennessee. (Principal Investigator: Jack Demirgian, ANL, 708-252-6807)

A related task involves the use of a novel mass spectrometric instrument for real-time monitoring of vapors and particulates sampled directly from the TSCA incinerator. This task is undertaken by a private firm under a PRDA-funded activity. (Principal Investigator: M.J. Coggiola, SRI International, 415-859-3045)

Sensing of Head Space Gases: Continuous In-situ Monitoring of Gaseous Components in Underground Storage Tanks Using Piezoelectric Thin Film Resonator Sensors (TFRs)

This task will develop miniaturized, field deployable gas sensors for use in the in-situ monitoring of head space gases in underground storage tanks (USTs) and at other remediation sites. The head spaces of USTs may contain explosive and toxic gases such as H_2, NO_x, hydrocarbons, and NH_3. Safe maintenance and remediation requires a delineation of the evolution and diffusion of such gases within the USTs. Just as importantly, the levels of these gases must be monitored continuously for long periods of time at many different UST sites. This task will develop low cost piezoelectric mass sensors, sensor arrays, and electronic readout instrumentation for the determination of the concentrations of several gases in the hostile environment of USTs. Using integrated circuit technology and specially developed sensor surface coatings, small sensor systems capable of long term, low maintenance operation will be fabricated as manufacturable prototypes and field tested to determine operational specifications.

Accomplishment: Developed a sensitive piezoelectric-based hydrogen gas sensor for use in the in-situ monitoring of head space gases in USTs or in drums of mixed waste. The prototype sensor produced a linear response over a concentration range of 500 ppm to 8% (v/v). Completed the fabrication of a prototype of a battery powered field deployable instrument. Work is in progress to develop arrays of sensors containing 8 to 64 individual piezoelectric mass sensors for detection of other hazardous gases such as NO_x, hydrocarbons, and NH_3 in USTs. (Principal Investigator: Glenn J. Bastiaans, Ames, 515-294-3298)

Development of Laser Induced Fluorescence (LIF) Imaging Capabilities

This task includes the development of hardware, software, and analysis methods for ground-based and airborne LIF systems for the detection of depleted uranium, VOCs, fuels, and vegetation stress. Hardware components include a gated line-scan camera, a pulsed laser system, and a computer acquisition system. Processing and analysis of field-collected data at ORNL, SRS, and DRI in Reno, NV, will be completed in FY94. A prototype configuration for a person-portable LIF system for uranium detection during D&D activities will be completed in FY94.

Accomplishment: Demonstrated laser-induced fluorescence imagery at K-27 Gas Diffusion Facility at Oak Ridge, TN. Identified residues of uranium on motor and diffusion compressor seals. (Principal Investigator: John DiBenedetto, EG&G/EM, 805-681-2240)

Associated Particle Imaging (API)

The API system is an active, non-intrusive, single-sided, neutron-based interrogation system that will permit analysis and spatial imaging of elemental composition (assay) of target materials. The API can assay contents of sealed crates, barrels, and other moderate-size waste containers. The purpose of this project is to demonstrate the API technology and transfer it to industry in fiscal year 1994. Scintillators and Ge detectors will be utilized in the laboratory to image contents of a standard waste barrel having compartments containing pieces of metal, cabling and other materials typically found in DOE waste drums. The laboratory portion of the API program will comprise physics measurements to characterize system effectiveness and to develop parameters for a field-transportable API system. If demonstration in the laboratory shows sufficient promise, the instrumentation will undergo final development, be loaded into a van and demonstrated on a real barrel of waste at a site yet to be determined.

The performance goals of API in detecting, locating, identifying, and quantifying radioactive and nonradioactive toxic materials in waste drums are resolution: 0.5"x0.5"x2" voxels; elemental identification: ≤ 50 g; penetration: 2-10 cm of steel; counting time: ≤ 10 mins; and output form: three-dimensional images. (Principal Investigator: Paul Hurley, EG&G-STL, 805-681-2472)

Coherent Laser Radar

The development of coherent laser radar, an Interagency Agreement project between NASA and DOE, is targeted for 3D surface mapping of high radiation environments in high level waste storage tanks or hot-cells during decontamination and decommissioning. The performance goals are 15 m range, field of view of 60 degrees, and 1-4 mm range resolution. Bench-scale testing is to be completed in May, 1994. (Point-of-Contact: Caroline Purdy, DOE EM, 301-903-7672)

Other projects which are of major significance to waste management activities include development of multi-spectral neutron logging tool for application to surveying contaminants in soils at tank farms, field-hardened fiber optic Raman probe for *in situ* determination of waste tank contents, and arrays of radiation probes for long-term post-closure monitoring and for tank leak detection.

NEW INITIATIVES

Several new projects starting in October 1993 address issues of waste tank safety and operations, and characterization of tank waste contents. These projects are:

Acoustic Characterization of Wastes in Stabilized Underground Storage Tanks (USTs)

This project will develop two acoustic monitoring instruments to support retrieval of USTs containing high level waste in the DOE complex. The first sensor will have the capability of monitoring the density of the waste that is surrounding it. The second sensor will have the capability to inform operators how large the "mixed" area of waste is within the tank in the vicinity of the mixer pump. The combination of these two sensors will furnish operators with "degree of mobilization" information. In simpler terms, it will provide information that will indicate if the sludge and supernatant components within the tank are completely mixed. These two monitoring devices are focused toward use in double shelled tanks. An additional study will be conducted that will ascertain the feasibility of using an acoustic density monitor in-line while recirculating wastes during sluicing operations in single shelled tanks. This type of monitor would provide operators with information that will allow them to switch from recirculation mode to transfer mode. (Principal Investigator: David Martin, Ames, 515-294-3344)

In Tank Interface Detection Using Time Domain Reflectrometry

This task will evaluate time-domain reflectrometry (TDR) for use in high-level waste tanks. TDR measures the propagation and reflection of electric signals through a medium. when the signal reaches an interface between materials with different properties, some reflection occurs. When properly calibrated, this method allows one to locate multiple interfaces, e.g., air/surface liquid, organic liquid/water, dry solid/wet solid. Primary criteria for success is to identify interstitial fluid levels to ± 0.25". Simulants of high-level waste will be used for test and evaluation in a laboratory environment. (Principal Investigator: H.R. Tilley, WSRC, 803-725-1876)

Laser Ablation Mass Spectrometry Scanning of Waste Tank Core Sample

This task will develop molecular speciation analysis techniques as well as data reduction and analysis techniques for analysis of waste tank core samples. It is a vital element of the overall advancement of the MARS program, with co-funding from the Office of Waste Management, which will develop, demonstrate and deploy equipment for using laser ablation mass spectrometry techniques to provide analysis of chemical species present in waste tank core samples. Successful completion of the MARS hot cell project will provide a capability for routine scanning along the length of cores to determine chemical concentrations and the compositional inhomogeneity as a function of distance along the core axis. (Principal Investigator: S. Colson, PNL, 509-375-6882)

TRU and Moisture Measurement in HLW Tanks by Neutron Activation

This task provides a copper foil sensor for measuring TRU waste and moisture content, addressing two driving safety needs for Underground Storage Tanks. This task is a companion to a cone penetrometer deployment system capable of penetrating through most forms of waste to the bottom of the waste tank. This addresses the need to measure fissile material, generally concentrated at the tank bottom. Core sampling methods do not recover the bottom 3 inches of waste material, but the cone penetrometer copper foil combination will access this area. A calibration mock-up facility will be assembled and analyzer calibration technique will be established. (Principal Investigator: R. L. Brodzinski, PNL, 509-376-3529)

Electromagnetic Moisture Measurement in Single Shell Tank Waste

This task will evaluate electromagnetic measurements in high-level waste tanks for determining moisture percentages and liquid levels. This task will establish a range of depths that electromagnetic waves can penetrate when placed in single shell tank waste by measuring electrical conductivity of core samples in hot cells. A resistivity comparison between core samples and existing stimulants will determine if the simulant formulas need modification for resistivity equivalence. If the penetration depth is within specified values, a laboratory-scale measurement system will be developed and evaluated for moisture measurement accuracy over acceptable moisture and interrogation distance ranges, using the appropriate simulated waste under waste tank conditions. (Principal Investigator: Ronald Hockey, PNL, 509-375-2813)

Imaging Through Obscuration for Sluicing

This task provides visual surveillance capability in tank while performing sluicing operations. Sluicing will cause mists, fog, or airborne particulates to obscure the imaging capabilities of standard cameras. This task will evaluate available methods, use existing equipment and work with commercial vendors willing to loan equipment for demonstration. (Principal Investigator: T. Peters, PNL, 509-375-2101)

Cone Penetrometer for In Site Waste Tanks Characterization

This task provides a cone penetrometer deployment system capable of penetrating through most forms of waste to the bottom of the waste tank. The cone penetrometer is capable of deploying a variety of sensors and of determining several physical properties of the waste. A companion task provides a copper foil sensor for measuring TRU waste and moisture content, addressing two safety needs. Other related task include the design of a Raman spectroscopy sensor to be deployed with the penetrometer, addressing additional safety needs as well as providing chemical characterization information to support retrieval and treatment processes. (Principal Investigator: L. Bunes, WHC, 509-376-9942)

In addition to technologies listed above, continuing efforts in developing advanced chemical sensors will lead to their deployment for in-tank sensing in the outyears. Examples include sol-gel chemistry and fiber optic arrays for determination of RCRA metals.

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