ENVIRONMENTAL AND WASTE MANAGEMENT: ADVANCES THROUGH THE ENVIRONMENTAL MANAGEMENT SCIENCE PROGRAM

Instrumental Analysis and Process Monitoring

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Wednesday, March 31, 2004

Organizers: T. Zachry

Presiding: P. Wang

Time	Paper
1:30 p.m.	Introductory Remarks.
1:35 p.m.	**Quantitation of organics in supercritical fluid aging experiments using FTIR spectroscopy.** C.J. Thompson, R.G. Riley, J.E. Amonette and P.L. Gassman
1:55 p.m.	**A new methodology for characterization of environmentally important radionuclide species *via* surface-enhanced Raman scattering (SERS).** S. Dai, L.-L. Bao, S. Mahurin and B. Gu
2:15 p.m.	**Plasma cavity ringdown spectrometer for elemental and isotopic measurements: Past, present and future.** C. Wang, C.B. Winstead, Y. Duan, S.T. Scherrer, S.P. Koirala, P.-R. Jang, G.P. Miller and F.J. Mazzotti
2:35 p.m.	**Advancements in the monitoring of highly concentrated slurry systems with optical low coherence reflectometry.** S.L. Randall, A. Brodsky and L. Burgess
2:55 p.m.	**Characterization of solid liquid suspensions utilizing non-invasive ultrasonic measurements.** P.D. Panetta, B. Tucker, S. Ahmed and R. A. Pappas
3:15 p.m.	Intermission.

3:35 p.m. **Inline ultrasonic rheometry of a non-Newtonian waste stimulant.** D.M. Pfund and R. Pappas

3:55 p.m. **Millimeter-wave measurements at 137 GHz of DWPF black frit glass flow and salt layer pooling in a pilot scale melter.** P.P. Woskov, S.K. Sundaram, W.E. Daniel, D. Miller and J. Harden

~~4:15 p.m.~~ **Effects of precipitation on the low-frequency electrical properties of zero valent iron: Implications for monitoring PRBs.** J. Choi, Y. Wu and L. Slater

4:35 p.m. **Monitoring air pollution in and around the premises of industrial parks using two types of electronic nose and gas chromatography-ion trap mass spectrometry.** J.Y. Liu, Sr. and Y.C. Ling, Sr.

4:55 p.m. Concluding Remarks.

ABSTRACTS

Quantitation of organics in supercritical fluid aging experiments using FTIR spectroscopy. Christopher J. Thompson, Robert G. Riley, James E. Amonette and Paul L. Gassman; Pacific Northwest National Laboratory, P.O. Box 999, MSIN K6-96, Richland, WA 99352, Fax: 509-372-1704, Chris.Thompson@pnl.gov.

Aging is a natural process in which hydrophobic organic contaminants slowly accumulate in the mineral pores and organic matter of soils and sediments. Contaminants in aged soils exhibit decreased bioavailability and slow release to the environment. Therefore, aging may have a significant influence on the applicability and effectiveness of remediation strategies (*e.g*., bioremediation and natural attenuation) and the accuracy of numerical transport models. Previous research in our laboratory has demonstrated that circulating supercritical carbon dioxide can be used to rapidly prepare artificially aged materials for studying slow-release behavior. In this investigation, FTIR spectroscopy was evaluated as a means of monitoring the progress of the aging process in real time. Solvent interferences, measurement sensitivity for selected halocarbons and the influence of temperature and pressure on the FTIR spectra were assessed. Application of this methodology to monitoring the incorporation of carbon tetrachloride into natural soils will be discussed.

A new methodology for characterization of environmentally important radionuclide species *via* surface-enhanced Raman scattering (SERS). Sheng Dai[1], Li-Li Bao[1], Shannon Mahurin[1] and Baohua Gu[2]; [1]Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, Fax: 865-576-5235, dais@ornl.gov; [2]Environmental Sciences Division, Oak Ridge National Laboratory.

Selective and sensitive detection and characterization of radionuclide contaminants in subsurface environments is essential to safely and to cost-effectively locate, treat, isolate or destroy contaminants encountered in DOE's environmental cleanup activity. Currently, techniques for monitoring and characterizing radionuclides rely primarily on liquid scintillation counting, ICP-MS and some limited use of the spectrofluorimetry based on fluorescence of radionuclide species under laser or UV excitation. These techniques require chemical handling, *e.g.*, the use of complexing media, scintillation cocktails and phosphoric acids, in order to enhance signals. Furthermore, only fluorescent radionuclides ($U^{22}O^{+}$, Cm(III) and Am(III)) can be detected by the last technique. Many environmentally-important radionuclides such as plutonium, neptunium and technetium species have no strong fluorescence signals and, therefore, can not be characterized *via* fluorescence spectroscopy. The research presented serves to replace existing radionuclide-detection techniques through the development of a novel surface-enhanced Raman scattering (SERS) spectroscopy to selectively and sensitively monitor and characterize the chemical speciation of radionuclides at trace levels. The SERS technique permits both of these measurements to be made simultaneously and results in significant improvement over current methods in reducing time of analysis, cost and sample manipulation.

Plasma cavity ringdown spectrometer for elemental and isotopic measurements: Past, present and future. Chuji Wang[1], Christopher B. Winstead[2], Yixiang Duan[3], Susan T. Scherrer[1], Sudip P. Koirala[1], Ping-Rey Jang[1], George P. Miller[4] and Fabio J. Mazzotti[5]; [1]Diagnostic Instrumentation and Analysis Laboratory, Mississippi State University, 205 Research Blvd., Starkville, MS 39759, Fax: 662-325-8465, wang@dial.msstate.edu; [2]Department of Physics and Astronomy, University of Southern Mississippi; [3]C-ACS, MS K-484, Los Alamos National Laboratory; [4]Department of Physics & Engineering Physics, University of Tulsa; [5]Department of Physics and Astronomy, Mississippi State University.

Recent studies using Plasma Cavity Ringdown Spectroscopy (plasma-CRDS) show much promise of this newly developed technique for ultra-sensitive elemental/isotopic measurements. Plasma-CRDS, since its introduction in 1997, has experienced three major stages: (i) the early stage demonstration of the technical feasibility, (ii) the recent advancement on its technical improvements and extensive applications for elemental/isotopic measurements as well as plasma diagnostics and (iii) the most recent progress on the improvement of the instrument configurations based on a diode laser-compact microwave plasma-CRDS. Research and development in many aspects of this technique is vigorously under processing in our laboratories. This paper reports a brief review on the plasma-CRDS technique, its applications and the most recent advancement. Discussions on future developments toward a new generation of plasma-CRDS-based spectrometers for ultra-sensitive elemental/isotopic measurements are also presented.

Advancements in the monitoring of highly concentrated slurry systems with optical low coherence reflectometry. Summer Lockerbie Randall, Anatol Brodsky and Lloyd Burgess; Center for Process Analytical Chemistry/Department of Chemistry, University of Washington, Box 351700, Seattle, WA 98195-1700, Fax: 206-543-6506, sr33@u.washington.edu.

Optical Low Coherence Reflectometry (OLCR) is a non-destructive optical technique that can be used to measure 180° coherent backscatter of light incident on a heterogeneous medium. Changes in particle size and concentration may be extracted from the OLCR decay profiles of highly concentrated slurries and emulsions, such as high-level waste. We have shown OLCR to be a valuable tool for monitoring changes in particle size over several orders of magnitude at high concentration.

We have made significant progress in the analysis of signals obtained from multi-scattering events. We have observed the appearance of Mie resonances, a non-monotonic oscillation of backscattered intensity dependent on optical parameters, over the interval where radii are comparable to the wavelength. Fundamental science development performed on model systems is essential for the analysis of polydispersity and the complex effects of clustering, sedimentation, gelation and other dynamic changes which may occur in an environmental waste system.

Characterization of solid liquid suspensions utilizing non-invasive ultrasonic measurements. Paul D. Panetta, B. Tucker, S. Ahmed and R. A. Pappas; Pacific Northwest National Laboratory, 902 Battelle Boulevard, Mail Stop K5-26, Richland, WA 99352, Fax: 509-375-6497, paul.panetta@pnl.gov.

Rapid, on-line characterization of the particle size and concentration of moderate to highly concentrated slurries is required for efficient waste remediation at the DOE complexes. This paper discusses the advancements achieved under the Environmental Management Science Program to accurately characterize high-level waste at the high concentrations expected at the DOE complexes. In addition, the results are applicable to efficient process measurement and control in many chemical and pharmaceutical manufacturing processes. Existing methods for determining the particle size and concentration of non-dilute slurries based on ultrasonic attenuation can become inaccurate due to the complex interactions of ultrasonic waves with the constituents of the slurries and the necessity for very careful transducer alignment. Two measurements that help to overcome these difficulties are the ultrasonic backscattering and diffuse field. The backscattering measurement is attractive because viscous, thermal and inertial effects have small contributions to the backscattering. In addition, the backscattering theories are simpler than attenuation theories and lend themselves to more stable inversion processes. Furthermore, the measurements of backscattering measurement do not require long travel distances and can be made with a single transducer thus eliminating alignment problems. We will present ultrasonic measurements and theoretical comparisons on solid liquid suspensions designed to elucidate the particle size and concentration at high concentration relevant to the high-level waste at the DOE complexes.

Inline ultrasonic rheometry of a non-Newtonian waste stimulant. David M. Pfund and R. Pappas; Fluids and Computational Engineering, Battelle Pacific Northwest National Laboratory, 904 Battelle Boulevard, MS K7-15, Richland, WA 99352, Fax: 509-375-2806, david.pfund@pnl.gov.

This is a discussion of non-invasive determination of the viscosity of a non-Newtonian fluid in laminar pipe flow over the range of shear rates present in the pipe. The procedure requires knowledge of the flow profile in and the pressure drop along the long straight run of pipe. The profile is determined by using a pulsed ultrasonic Doppler velocimeter. This approach is ideal for making non-invasive, real-time measurements for monitoring and control.

Rheograms of a shear thinning, thixotropic gel which is often used as a Hanford waste simulant are presented. The operating parameters and limitations of the ultrasound-based instrument will be discussed.

The component parts of the instrument have been packaged into a unit for field use. The presentation also discusses the features and engineering optimizations done to enhance field usability of the instrument.

Millimeter-wave measurements at 137 GHz of DWPF black frit glass flow and salt layer pooling in a pilot scale melter. Paul P. Woskov[1], S. K. Sundaram[2], William E. Daniel[3], Don Miller[3] and John Harden[4]; [1]Plasma Science and Fusion Center, Massachusetts Institute of Technology, NW16-110, 77 Massachusetts Avenue, Cambridge, MA 02139, Fax: 617-253-8648, ppw@psfc.mit.edu; [2]Thermal Processing Group, Environmental Technology Division, Pacific Northwest National Laboratory; [3]Savannah River Technology Center, Westinghouse Savannah River Company; [4]Clemson Environmental Technology Laboratory.

Nuclear waste vitrification in joule-heated melters would be greatly facilitated by the availability of on-line monitoring instrumentation for critical process parameters such as viscosity and salt accumulation. A field test of the applicability of millimeter-wave (MMW) technology to providing such tools was carried out on a pilot scale melter (EV-16) at the Clemson Environmental Technology Laboratory. Flow measurements of Defense Waste Processing Facility (DWPF) black frit glass over a temperature (T) range of 800 – 1150 °C and to depths of over 7 inches (17.8 cm) were made with an immersed ceramic waveguide. Pressure induced melt flow inside the waveguide was observed over an average velocity range of 0.1 – 10 mm/s consistent with a 1/T viscosity scaling. In another test, sodium sulfate salt ($NaSO_4$) was added to the melt to demonstrate salt layer detection. A 30% decrease in MMW melt emissivity was clearly observed as pools of salt formed and flowed under the waveguide.

Effects of precipitation on the low-frequency electrical properties of zero valent iron: Implications for monitoring PRBs. Jaeyoung Choi, Yuxin Wu and Lee Slater; Dept. Earth/Environmental Science, Rutgers University, 195 University Ave., Room 407, Newark, NY 07102, Fax: 973-597-1965, fiam3620@hotmail.com.

The ability of induced polarization (IP) to monitor reduction in reactive iron performance is being investigated in the laboratory. Low frequency (0.1-1000 Hz) electrical properties are sensitive to metal-aqueous solution interface chemistry. Measurements have focused on sensitivity of IP to changes in Fe^0 surface chemistry with aging due to mineral precipitation and aqueous electrochemical controls. High sensitivity of parameters defining polarization magnitude at/near the metal surface to total Fe^0 surface area is observed. Polarization magnitude and dominant relaxation time correlate with electrolyte activity for 0.001-1.0 M for $NaNO_3$, NaCl and $CaCl_2$. Both parameters depend also on valence. Observations are consistent with double-layer (EDL) theory for the thickness of the EDL, although the electrochemical polarization mechanism observed with IP is uncertain. Polarization magnitude shows no relationship to pH, indicating that the fixed charge does not contribute to IP. The effects of Fe-precipitation by OH, SO_4, PO_4 and CO_3 on electrical parameters was investigated for Fe^0-sand samples (10% Fe^0) over a period of induced precipitation. Aqueous chemistry was monitored and Fe^0 surface precipitation verified by x-ray diffraction/scanning electron microscopy. Changes in electrical parameters provide insight into the sensitivity of the low-frequency electrical method for monitoring PRBs.

Monitoring air pollution in and around the premises of industrial parks using two types of electronic nose and gas chromatography-ion trap mass spectrometry. Jen Yu Liu, Sr. and Yong Chien Ling, Sr.; Department of Chemistry, National Tsing Hua University, Taiwan, 101, Section 2 Kuang Fu Road, Hsinchu, Taiwan 300, Republic of China, Hsinchu 300, Taiwan, Fax: 886-03-5711082, g913418@oz.nthu.edu.tw.

Two types of electronic nose and GC-MS were used to monitor air pollution in the premises of seven industrial parks. Real-time analysis of air at the sites was performed using portable electronic noses. Air samples were analyzed from the up and down stream direction along the wind flow to investigate the effect or distribution of the pollutants on the surrounding environment. The advantage of multisensors in spatially resolved sensing for direct multicomponent analysis was explored to minimize tedious sample preparation procedure. Electronic nose could give characteristic odor fingerprints, which were correlated with the pollutants analyzed using GC-MS providing detailed diagnostic information such as the presence of hydrocarbons, halocarbons, phenols, nitrogenous benzenes, sulfur compounds, lipid-derived compounds,

polysiloxanes, etc. Subsequent principal component analysis helped in identifying the source of pollutants. The applicability of the electronic nose was demonstrated confirming it to be a simple and rapid screening method for identifying the pollutant source.