8:30 AM-12:00 PM Javits Convention Center -- 1A15/1A16

Environmental Management Science Program on Nuclear Waste Management

Characterization, Monitoring, and Analysis Techniques

Presiding: M. McIlwain

Organizer: Tiffany Zachry

8:30 AM		Introductory Remarks
8:40 AM	77	Fluorophores as chemosensors for Sr^{2+} and Cs^{+} based on calix[4]arenes and coumarin reporter groups **Gudrun Goretzki**, Gilbert M. Brown, Peter V. Bonnesen
9:00 AM	78	A new method for in situ characterization of important actinides via surface-enhanced Raman spectroscopy (SERS) **Sheng Dai**, Li-Li Bao, Shannon M. Mahurin
9:20 AM	79	Microchip analysis of toxic metal ions in support of DOE's EMSP **Greg E. Collins**, Qin Lu, Gang Deng
9:40 AM	80	Development of advanced electrochemical emission spectroscopy for monitoring corrosion in simulated DOE liquid waste **D. D. Macdonald**, Brian Marx, Balaji Soundararajan, Morgan Smith, Sejin Ahn, Jun Liu
10:00 AM		Intermission
10:25 AM	81	Glass melt emissivity, viscosity, and foaming monitoring with millimeter-waves **Paul P. Woskov**, S. K. Sundaram, William E. Daniel, Kamal Hadidi, Leslie Bromberg, Don Miller, L. A. Rogers
10:45 AM	82	Acoustic monitor for solid-liquid slurries measurements at low weight fractions **Lawrence L. Tavlarides**, Oleksandr Shcherbakov, Eric Dievendorf, Ashok Sangani
11:05 AM	83	Measurement of the particle size of a slurry using ultrasonic diffraction grating spectroscopy **Margaret S. Greenwood**, Anatol Brodsky, Lloyd Burgess, Leonard J. Bond
11:25 AM	84	Novel chemical detection strategies for TCE and PCE **Andrew C. R. Pipino**
11:45 AM		Concluding Remarks

ABSTRACTS

NUCL 77 [656224]: Fluorophores as chemosensors for Sr^{2+} and Cs^{+} based on calix[4]arenes and coumarin reporter groups

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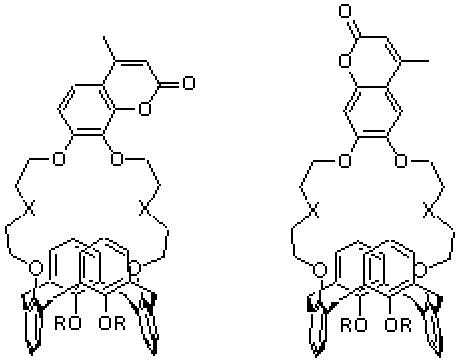
Abstract

Fluorescent sensors are being developed for Cs^{+} and Sr^{2+} which combine a molecular recognition element with an optical transduction element. Such sensors will be needed for real-time application in the characterization of nuclear waste and waste process streams. The fluorescent method is very important due to its high sensitivity and direct visual perception even in highly dilute solutions and its potential for remote application utilizing fiber optics. Crown ether bridged calix[4]arenes have been widely used as a three-dimensional platform for selective metal ion recognition. Coumarins show interesting photochemical and photophysical properties and are widely used in laser dye applications. These fluorescence probes increase their dipolar moment when excited. We will report the synthesis of calix[4]arene-crown-6 derivatives possessing 1,3-alternate conformation and incorporating a coumarin-based fluorescence reporter group. Selectivity for Sr^{2+} over Cs^{+} is obtained by using azacrowns and the sensitivity will be determined by varying the donor atom set as well as the substitution pattern of the coumarin.



R = benzyl, propyl R = benzyl, propyl

X=N,O

NUCL 78 [655760]: A new method for in situ characterization of important actinides via surface-enhanced Raman spectroscopy (SERS)

Sheng Dai[1], Li-Li Bao[2], and Shannon M. Mahurin[1]. (1) Chemical Sciences Division, Oak Ridge National Laboratory, PO BOX 2008, Oak Ridge, TN 37831-6201, Fax: 865-576-5235, dais@ornl.gov, (2) Chemical Science Division, Oak Ridge National Laboratory

Abstract

In-situ characterization of actinides and technetium compounds in high level wastes is essential to achieve shorter turn-around times for analytical results or to facilitate tank closure after retrieval. 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, phosphoric acids, in order to enhance signals. Furthermore, only fluorescent radionuclides [uranyl, Cm(III), 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. We have developed a novel characterization technique based on 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.

NUCL 79 [656346]: Microchip analysis of toxic metal ions in support of DOE's EMSP

Greg E. Collins, Chemistry Division, Code 6112, Naval Research Laboratory, 4555 Overlook Ave., S.W, Washington, DC 20375-5342, Fax: 202-404-8119, greg.collins@nrl.navy.mil, Qin Lu, GeoCenters, Inc, and Gang Deng, Research and Development Laboratory, United States Pharmacopeia

Abstract

The DoE currently has the daunting task of deactivating 7,000 contaminated buildings and decommissioning 900 contaminated buildings that remain from the United States' involvement in nuclear weapons development over the last 50 years. The Environmental Management team has highlighted the need for revolutionizing technologies capable of improving characterization, monitoring and certification of contaminated equipment and facilities with emphasis on real time characterization in the field. We will discuss our efforts to develop a portable, compact microchip capillary electrophoresis unit for rapid characterization and certification of ppb levels of surface and airborne toxic metal contaminants found or originating from scrap metal and building materials in real time within the field.

NUCL 80 [661873]: Development of advanced electrochemical emission spectroscopy for monitoring corrosion in simulated DOE liquid waste

D. D. Macdonald[1], Brian Marx[1], Balaji Soundararajan[1], Morgan Smith[1], Sejin Ahn[1], and Jun Liu[2]. (1) Center for Electrochemical Science and Technology, Pennsylvania State University, University Park, PA 16802, Fax: 814-863-4718, ddm2@psu.edu, (2) Materials LifeCycle Solutions, R&D, ATMI, Inc

Abstract

Various forms of general and localized corrosion represent principal threats to the integrity of DOE liquid waste storage tanks. These tanks, which are of a single wall or double wall design, depending upon their age, are fabricated from welded carbon steel and contain a complex waste-form comprising NaOH and $NaNO_3$, among other chemicals. Because waste leakage can have a profound environmental impact, considerable interest exists in predicting the accumulation of corrosion damage, so as to more effectively schedule maintenance and repair. In the present work, we are examining the corrosion of carbon steels in alkaline environments with the ultimate aim of: (1) Characterizing the general corrosion of iron and carbon steel in environments that are prototypical of DOE liquid waste systems; (2) Exploring the mechanism (s) of passivity breakdown and hence the initiation of localized corrosion; (3) Characterizing the mechanism (s) of caustic cracking in high strength steels that simulate weld heat-affected zones in DOE liquid waste storage tanks; (4) Development of deterministic methods for predicting the accumulation of general and localized corrosion damage in the storage tanks; and (5) Enhancing Electrochemical Emission Spectroscopy (EES) as a corrosion monitoring technique. The work has yielded a number of important findings, including an unequivocal demonstration of the role of chloride ion in passivity breakdown on nickel in terms of cation vacancy generation within the passive film, the first detection and characterization of *individual* micro fracture events in stress corrosion cracking, and the determination of kinetic parameters for the generation and annihilation of point defects in the passive film on iron. These latter data are now being used to deterministically predict the accumulation of general and localized corrosion damage on carbon in prototypical DOE liquid waste storage tanks. These findings will be discussed in the presentation, as time permits.

NUCL 81 [655661]: Glass melt emissivity, viscosity, and foaming monitoring with millimeter-waves

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Abstract

Nuclear waste glass processing efficiencies, improved melter control to anomalies such as foaming, and environmental compliance would be facilitated by the availability of on-line monitoring technologies. It has been shown that the millimeter-wave (MMW) range of the electromagnetic spectrum (0.3-10 mm) is ideally suited to hot melter environments by having wavelengths long enough to penetrate optically obscure views yet short enough to provide spatial resolution with reliable refractory quasi-optical components. A thermal return reflection (TRR) method has been developed that allows a millimeter-wave pyrometer to determine emissivity by returning a portion of the thermal emission as a probe. Melt glass viscosities in the range 20 -2000 Poise and specific gravities have been measured by rates of flow and displacements inside hollow MMW ceramic waveguides immersed into the melts. Glass foaming has been observed by detecting the melt surface swelling followed by the increase in surface emissivity after gasses break the surface.

NUCL 82 [654817]: Acoustic monitor for solid-liquid slurries measurements at low weight fractions

Lawrence L. Tavlarides, Oleksandr Shcherbakov, Eric Dievendorf, and Ashok Sangani, Department of Chemical Engineering, Syracuse University, Syracuse, NY 13244, Fax: 315-443-1243, lltavlar@ecs.syr.edu

Abstract

We have developed an acoustic monitor for accurate, real-time measurement of solids concentration in solid-liquid (S-L) and solid-gas-liquid (S-G-L) slurries at low solids weight percent (0.5 to 10 wt. %). The Syracuse Acoustic Monitor (SAM) has potential for slurry transport monitoring, processing stream monitoring, and process control capabilities for nuclear wastes treatment throughout the DOE complex. The SAM is based on theory that predicts attenuation of small-amplitude acoustic waves propagating through S-L and S-L-G suspensions. We developed a prototype in-line system with robust data acquisition capabilities to continually acquire attenuation data (response time of 0.5 sec) for a 0.6 - 12 MHz frequency range with an array of transducers. Test results on an integrated flow loop indicate high accuracy between 0.5 and 8.0 weight percent solids for ceramic microspheres (80 µm average diameter) and kaolin-bentonite slurries. Results of removal of the interference caused by gas bubbles, thus providing the solids weight percent, will also be discussed.

NUCL 83 [655014]: Measurement of the particle size of a slurry using ultrasonic diffraction grating spectroscopy

Margaret S. Greenwood[1], Anatol Brodsky[2], Lloyd Burgess[2], and Leonard J. Bond[1]. (1) Nondestructive Measurement and Characterization Sciences, Pacific Northwest National Laboratory, P. O. Box 999, Richland, WA 99352, Fax: 509-375-6497, margaret.greenwood@pnl.gov, (2) Center for Process Analytical Chemistry, University of Washington

Abstract

The objective of this work is to measure micron-sized particles using ultrasonics, which is advantageous for optically opaque systems. The ultrasonic diffraction grating is formed by machining parallel triangular-shaped grooves, spaced 200 microns apart, on the flat surface of a stainless steel half-cylinder. The grating is placed in contact with the slurry. Send and receive transducers are placed on the outside circular part of the half-cylinder at equal angles with the normal to the flat surface. Ultrasound from the send transducer travels through the stainless steel and strikes the back of the diffraction grating, where it is reflected to the receive transducer. The grating produces anomalies in the signal of the receive transducer, compared with data obtained using a flat surface on the half-cylinder. The nature of the signal anomaly will be discussed. The data for the measurement of particle size and theoretical models will be presented.

NUCL 84 [654469]: Novel chemical detection strategies for TCE and PCE

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Abstract

Results describing two new applications of cavity ring-down spectroscopy (CRDS) will be discussed: 1) detection of TCE and PCE by refractive-index change using surface-plasmon-resonance (SPR)-enhanced CRDS, and 2) C-H overtone detection of TCE by evanescent wave CRDS (EW-CRDS) with a determination of absolute adsorbate surface coverage. The SPR-enhanced CRDS measurements show a minimum detectable concentration of 70 nanomol/L and 20 nanomo l/L for TCE and PCE, respectively, based on a one minute response time at 555 nm. The EW-CRDS measurements use the first C-H overtone of TCE occurring around 1640 nm. Spectra for both surface and gas-phase species are obtained in the evanescent wave. Employing the absolute absorption cross section for the C-H overtone of TCE obtained from gas-phase CRDS measurements, the adsorbate spectrum and corresponding absolute surface number density are determined. The requisite measure of molecular orientation is provided by the polarization dependence of the surface spectrum.