*I*nstrumentation Development, Measurement and Performance Evaluation of Environmental Technologies

**Quarterly Technical Progress Report
for the period
April 1, 1999 - June 30, 1999**

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Executive Summary

The Diagnostic Instrumentation and Analysis Laboratory (DIAL) at Mississippi State University (MSU) will undertake three tasks for DOE EM during the period April 1, 1999 through March 31, 2000.

Task 1. Instrumentation Development

Instrumentation will be developed for unique DOE site needs. Some of the needs identified by the DOE sites require development of new instrumentation, for example, development of continuous emissions monitors for metals, or for dioxins and furans. DIAL, with its rare ability to both develop, adapt, and simulate field service of new instrumentation, is ideally suited for this mission.

Volatile organic compound monitoring using diode lasers. During the period from April 1 – June 30, 1999, significant progress was made toward the construction of a diode laser spectrometry system for measuring the concentration of selected volatile organic compounds in air. This system is under development to determine its measurement capabilities for potential application as a continuous emission monitor for organic species in stack gases and other related applications. Frequency modulation and standard absorption spectra have been obtained for well-characterized gases such as CO, CO_2, and CH_4, to

ensure that the system is yielding predictable, quantifiable, and reproducible measurements. Our first measurements of a volatile organic compound, namely benzene, have also been carried out. The theoretically predicted and measured absorbances associated with various concentrations of these species were in good agreement, implying that our initial estimates of eventual system performance should be on target.

Cavity ringdown monitors for transuranic elements. During the period from April 1 – June 30, 1999, efforts have continued in the development of cavity ringdown spectroscopy for trace elemental analysis. A new narrow linewidth pulsed dye laser is operational and the cavity ringdown system has been transitioned to this new laser. Both inductively coupled plasma and graphite furnace systems have been employed with the new laser. The narrow linewidth laser is a necessity to evaluate the ability of the ringdown system for resolving individual isotopes of a particular element. However, due to a number of regulatory requirements for using radioactive materials, no measurements have been carried out using uranium. DIAL's safety manager has been actively working through the licensing process to allow for the use of uranium in our experiments. In the interim, we continue to develop trace elemental analysis using cavity ringdown. The knowledge gained from these experiments will be directly applicable to measurements for uranium and other transuranic elements.

Guided wave nondestructive evaluation technique development and demonstration. The proposed research addresses the development of techniques for the measurement and evaluation of nuclear waste storage and handling structures and processes using guided ultrasonic wave techniques. These techniques, developed by DIAL for process monitoring (measurement of temperature, viscosity), have been developed and demonstrated. Efforts in the technology transfer and commercialization of the two process control sensors using ultrasonic techniques, a buffer rod shear-wave sensor and a torsion-wave sensor were carried out. New efforts in the area of structural integrity evaluation of tanks and tank liners were also be initiated. The long range ultrasonic

guided waves, and their generation using noncontact methods were the focus of the study.

Task 2. Measurement Support

Measurement services will be provided for DOE sites. In some cases, a specific site will not be able to justify the cost of a new instrument but will need it to achieve a programmatic objective. DIAL can take its instrumentation to the DOE site to provide the measurements needed.

Task 3. Performance Evaluation

The performance of environmental technologies will be evaluated for DOE. DOE EM needs a tool which will rapidly and without bias allow it to compare the performance of technologies against the field's needs, so that it can focus its development dollars on the highest impact targets. DOE EM also needs a tool to rapidly screen new technologies to assist in the most effective allocation of its development funding. Further, the technology developers (and DOE EM) need a tool to expedite the acceptance of developed technologies into the DOE EM user facilities. DIAL is ideally suited to address both of these needs. Through its network of contacts within the DOE sites, DIAL can rapidly elicit user needs. Through its knowledge of the technologies needed, and its network of contacts in industry, DIAL can rapidly identify promising candidates to satisfy those needs. DIAL's experienced multidisciplinary staff can then provide users with the information they need to make deployment decisions, by using DIAL's wide-ranging measurement capabilities in either its own testing facilities, or in those of its network of collaborators if more appropriate for a given application.

Validation and application of the environmental simulation program. Work is reported on the methods for reconciliation within the water analyzer module of the ESP software. Following these calculations a path for automating charge balances based on recursion to the percent water contained in the waste is proposed. The results have previously been distributed to customers at Hanford.

Wall removal monitor. In support of the DOE's decontamination and decommissioning (D&D) of concrete structures, DIAL has developed a technology for monitoring scabbling operations. To D&D a concrete structure, the thin (~.5 inch) layer of contaminated concrete is removed by a process called scabbling. Current technology requires a surveying crew to measure points on the structure at 1-foot intervals. After the survey is completed the scabbling contractor performs the removal operation, and then the surveying crew comes back to make measurements. This process is time consuming and complicated, and if the contractor does not remove the required amount of material, additional cost and time is required to correct and re-measure the results. The wall removal monitor runs in real time providing information about the amount of material removed while the scabbling operation is occurring. In tests, the system is placed ~30 feet from the wall (well out of the way of operating machinery) and measures 145 square feet at a time. Data collection takes only seconds, and set-up requires only 30 minutes. The wall removal monitor developed by DIAL is described in the technical memo, *Wall Removal Monitor for Concrete Scabbling Applications* (FTP 698).

Pressure in drums. Due to the aging of stockpiles of stored waste, especially those in 55-gallon drums, containers are becoming pressurized and are rupturing. Several events have been recorded in the DOE's Operating Experience Weekly Summary by the Office of Nuclear Safety (OEWS 95-02) where drums have ruptured and spilled hazardous contents or destroyed property (such as overhead light fixtures). A method of detecting drums that are under pressure has been developed at DIAL. The method relates the pressure in the drum to the frequency at which the lid vibrates. We are currently

refining our models, establishing detection limits, and searching for commercial partners.

Plasma treatment of VOC's and other off-gas components by pulsed micro-hollow cathode plasma array. Permission to engage a graduate student was not granted. Therefore, although preliminary design work was completed and purchase orders written for the power supply and vacuum components, additional progress has been delayed due to a lack of manpower.

Characterization of dioxin production. The test stand modifications were completed and the system was shakedown tested. Testing with fly ash injection and with fly ash doped with pentachlorophenol was started. Initial results of this work were presented at the Incineration and Thermal Treatment Conference in Orlando, Florida.

Evaluation of continuous emission monitors. Work continued on the study of the calibration technique for solid samples. LIBS spectra of various known composition solid samples were recorded and analyzed to construct LIBS calibration curves for solid measurement. Work on the feasibility study of applying artificial neural networks (ANN) to analyze LIBS data of solid samples also began. LIBS spectra of glass samples collected at different conditions are used to train neural networks. The trained neural networks will later be used to analyze the LIBS glass data.

TASK 1   *Instrumentation Development*

Many of the DOE sites require development of new instrumentation, for example, development of continuous emissions monitors for metals, or for dioxins and furans. DIAL is developing or adapting instrumentation to meet field needs. In each case, these instruments are being developed and tested under simulated service conditions to increase the probability of success.

DIAL is developing new instruments, or adapting existing instrumentation, to address DOE needs. This year, development of emissions monitors for metals and for dioxins and furans continues. Development of instrumentation to determine trace levels of actinides in process solutions or groundwater also continues. Development of more compact process monitors using diode lasers has been initiateed. The feasibility of using remote sensing techniques to characterize solid waste, and of a guided wave technique to determine whether a leak exists in a waste tank, is also being determined.

Subtask 1.1   Air Plasma Off-gas Emission Monitor

George P. Miller

Introduction

Technology Description

Increasing regulatory demands requiring significant reductions in the emission of hazardous air pollutants have led to the need for techniques capable of providing real time monitoring, at the stack, of toxic metals in combustion gas streams. These waste streams range from coal-fired boilers, and municipal waste combustors to plasma vitrification systems used for the remediation of low level radioactive waste. This lack of a fieldable continuous emission metal monitor (CEM) and process monitor (PM) has been recognized as a significant gap in the available technology. The system described below has been designed to fill this gap.

Over the last twenty years the use of argon ICP-AES for the measurement of trace elements in solution has matured into a standard analytical technique. However, unlike the laboratory ICP, it is essential for a CEM that the system be hardened sufficiently to handle the problems of a real-world environment. These problems include the ability to readily tolerate the introduction of a variety of molecular gas matrices, significant variations in moisture and particle loading as well as the thermal, vibrational and clogging problems found outside the laboratory. The system under development at DIAL has taken the advantages inherent in inductively–coupled plasma technology and incorporated them into APO-GEM, a CEM capable of tolerating the real-world environment while accurately measuring the real time concentration of metals in exhaust stacks. Although APO-GEM provides significant reduction in operating costs, the main advantages of the air plasma lie in its increased tolerance of molecular gases, particle load-

ing and reduced susceptibility to moisture content (due to more efficient heat transfer from the air plasma to the sample). On the other hand, it requires higher rf powers and the maximum available ionization energy is reduced from that available in an argon plasma.

The introduction of exhaust gases into the air plasma results in a considerably more complex spectra than the line spectra seen in an argon plasma. The emission spectra includes numerous molecular bands (e.g., OH, CN, NO, N_2^+) in the wavelength regions of interest (200 - 350 nm). This increase in interferences places stringent requirements on both the resolution of the detection system and the software used to analyze the data. We are developing two separate approaches to address these problems, a unique chemometric software package to handle the analysis and an on-going collaboration with Ames National Laboratory to reduce the size of the detection system while increasing the resolution.

The remaining hardware required to complete the system consists of an isokinetic sampling interface between the APO-GEM and the exhaust duct. The extractive sampling techniques used introduce the sample stream into a controlled environment where matrix effects are minimized and the plasma properties are stabilized. Calibration is handled by a unique system which mixes calibration standards with the combustion stream via the isokinetic sampling apparatus. This effectively compensates for any remaining matrix effects, options that are impossible for in-stack methods.

Instrumentation

The APO-GEM system incorporates a novel 3.5-kW solid-state 27.12-MHz rf generator with the load coil modified for air-plasma operation. This is coupled to a detection system with the off-gas sample being extracted from the duct and introduced into the air plasma via an isokinetic sampling system. Figure 1 is a schematic diagram of the APO-GEM continuous emission monitor.
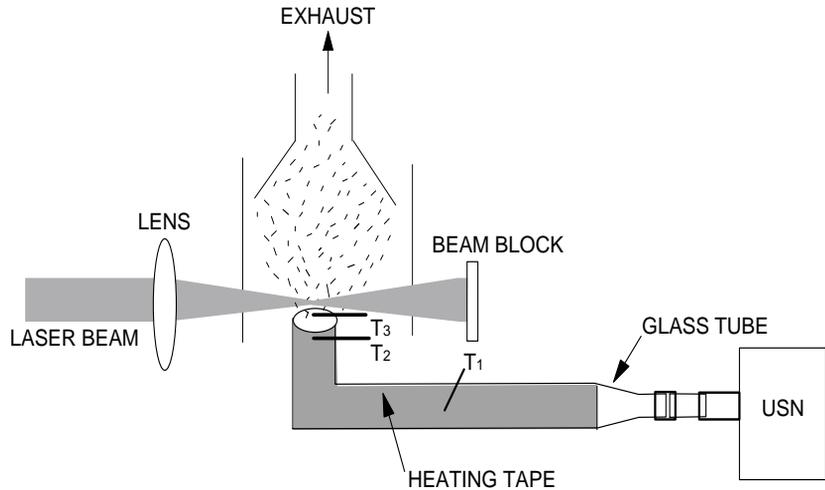
FIGURE 1. APO-GEM schematic diagram.

The APO-GEM plasma is started using argon and progressively switched over to air. Calibration is performed using an ultrasonic nebulizer. The detection system uses a 1-m monochromator, and CCD detector. This remains the largest single component of the system. It has adequate resolution but operates sequentially and is relatively large. It, nevertheless, provides the ideal platform for identifying and characterizing the spectral emissions and possible interferences arising from unidentified components making up exhaust gas emissions. (To provide simultaneous metal concentration measurements, this monochromator could be replaced by a polychromator.) In addition, we are evaluating a novel solid-state spectrometer developed for this project by Dr. David Baldwin at Ames National Laboratory. This instrument is compact, thermally and vibrationally stable. It uses a combination of an acousto-optic tunable filter and an echelle grating to provide the resolution of a 1.5-m monochromator into a 10-kg package. The successful combination of the solid-state APO-GEM and this spectrometer represents a large step forward in instrument development and will reduce the overall size and weight of the com-

plete package substantially (from the original ~1000 kg, to the present 250 kg, then to ~150 kg) while improving the resolution, and thereby the detection limits.

Isokinetic sampling system. To correctly measure the concentration of metals present within an exhaust gas stream it is necessary to introduce a sample from the exhaust gas stream into the ICP under isokinetic conditions. Therefore, a sampling system has been designed to extract such a sample from a gas stream and introduce it into the air plasma for analysis. The system operates by filling a loop with sample gas and then pushing this sample with air into the plasma. The robustness of the air plasma permits an optimum sample flow rate into the ICP of 1.14 sl/min, approximately three times more than tolerated by an argon plasma.

Calibration. An important concern with any CEM is the question of calibration. In this instance, instrument calibration follows a modified standard ICP calibration procedure.[1] An ultrasonic nebulizer is used to provide metal-containing aerosols at a known concentration ($\mu g/m^3$). This concentration is determined from

$$C_A = \frac{C_s u \varepsilon}{F} \qquad \text{(EQ 1)}$$

where C_A is the aerosol concentration (x 10^3 $\mu g/m^3$), C_s is the standard solution concentration ($\mu g/g_{solv}$), u is the solution uptake to the ultrasonic nebulizer, F is air flow rate to the plasma, and ε is nebulizer efficiency. The efficiency of the nebulizer was determined both in the laboratory and again on-site prior to the test. For the initial instrument calibration, the metal aerosol was mixed with ambient air. Instrument response was checked against standard calibration curves prepared previously. In the field, the presence of fly ash as well as variations in loading and exhaust gas composition allow the possibility of substantial matrix effects significantly impacting the results of any real-world analysis. This variation in composition between laboratory air and the exhaust gas composition renders any direct comparison of the labora-

tory air calibrations to the instrument off-gas response highly suspect. To circumvent this problem, we have developed a novel technique whereby the calibration standards are mixed with the exhaust off-gas at the entrance to the sampling loop while maintaining isokinetic conditions. This ensures that the standard and off-gas sample are matrix-matched. This allows recalibration and QA checks to be performed on-line under actual operating conditions.

To further improve the sensitivity of the instrument, a novel chemometric software package has been developed which, by modeling background spectrum (at the spectra regions of interest), effectively reduces the background noise and thus improves the instrument sensitivity. To apply this method accurately, data from the spectral regions of interest was collected during the shakedown period prior to the test. In addition, as the instrument presently employs a sequential detection system, wavelength calibration is essential. A chemometric-based software package was developed to check and, if necessary, correct wavelength calibration. This software checks the wavelength position with respect to the pixel position on the CCD every time the wavelength setting is changed as well as periodically checking for instrument drift.

Detection limits. The toxic metals species of concern to EPA and DOE include As, Be, Cd, Cr, Hg, Sb, and Pb. The present detection limits for a number of metals are given in Table 1. Further improvements in sensitivity are required to meet the expected emission limits.

TABLE 1. Detection limits for the APO-GEM for various metals.

Metal Instrument	Detection Limits (μg/dscm)
As	47
Be	0.07
Cd	2.5
Co	0.6

TABLE 1. Detection limits for the
APO-GEM for various metals.

Metal Instrument	Detection Limits (μg/dscm)
Cr	0.25
Hg	20
Mg	0.05
Ni	0.4
Pb	0.9
Sb	55
Sr	0.003

Metal concentrations and relative accuracy. The DOE/EPA demonstration at Raleigh was the first opportunity to check the accuracy and quality of the data provided by the APO-GEM. The relative errors with respect to EPA Method 29 are given in Table 2. Three of the five metals are within 30% for the high concentration level (75 μg/dscm). None are within that range at the low concentration level (15 μg/dscm). These results are excellent considering the uncertainty present in the RM data at these low levels.

TABLE 2. Relative accuracy of DIAL Air-ICP data.

	Be	Cd	Cr	Hg	Pb
RM 1 to 10	40%	26%	40%	13%	21%
RM 11 to 20	43%	46%	59%	67%	42%

Work Accomplished

The findings and recommendations in the Technical Peer Review Report from the AMSE Technical Review of the "Development of a Multi-element Metal Continuous Emissions Monitor" were evaluated. The review took place at the Characterization, Monitoring, and Sensor Technology (CMST) Crosscutting Program, March 8 - 12,

1999 in Gaithersburg/Columbia, MD. These recommendations were found to mirror the research program already underway at DIAL. Those recommendations not already in place were incorporated into the research plan.

Preparations were begun for testing the reduced pressure air-ICP being developed in collaboration with Ames Laboratory and Dr. David Baldwin. The test is scheduled for August/September 1999 at DIAL. The preparations included redesigning and modifying the secondary combustion test stand to include a vertical section to permit comparison measurements between the CEM to be tested and the relevant EPA reference methods.

Work Planned

The work in the next quarter will focus on preparations for the upcoming test on the reduced pressure air-ICP system.

Reference

1.   A. Montser and G.W. Golightly. 1992. *Inductively coupled plasmas in analytical atomic spectrometry.* New York: VCH.

Subtask 1.2   Detection of Chlorinated Organics by Cavity Ring-down Spectroscopy

Ram Vasudev

Progress on this subtask will be reported in the next quarterly report.

Subtask 1.3 Volatile Organic Compound Monitoring Using Diode Lasers

C. P. Winstead

Introduction

The United States Department of Energy currently operates three mixed waste thermal treatment facilities (TSCA at Oak Ridge, WERF at INEL, and CIF at Savannah River). A clearly identified need for these facilities is continuous emission monitoring for a number of volatile organic compounds (VATS). For example, Table II of the Savannah River Site Technology Need Statement #SR-1004 lists 16 organic species as potential candidates for continuous emission monitoring at the CIF. The primary motivations for application of CEM technology at the CIF are reducing or eliminating the need for periodic trial burn testing and reducing the scope of required feed testing. Increased public confidence in incinerator operations is also an important by-product of CEM implementation. A savings of approximately $108 M is estimated to result from successful installation of CEM technology at the CIF alone. In addition, numerous other DOE sites and facilities are interested in trace VOC measurements (e.g., widespread interest in measurements for TCE).

Diode lasers are extremely small and relatively inexpensive compared to other laser and spectroscopic systems. Because of similarities in vibrational frequencies for carbon-hydrogen bonds, absorption of diode laser light will be observable for a variety of VATS over a wavelength range of approximately 1.6 – 1.8 micrometers, a region accessible to quantum well distributed feedback diode lasers. Such lasers exhibit long lifetimes and robust performance and are well-developed for telecommunications applications. Thus, quantification of diode laser detection limits for VOUCHs is desirable for applications in continuous emission monitoring or other environmental measurement applications. The concentration of VOCs in air can be

determined by measuring the amount of laser light absorbed as the beam crosses a known pathlength of air.

Our initial measurements have focused on long-pathlength diode laser absorption spectroscopy. Should lower detection limits be required, these initial results will pave the way for future increased sensitivity methods such as diode laser cavity ringdown spectroscopy. An eventual organic CEM product is envisioned where multiple lasers are multiplexed into a single fiber for introduction into a sample cell. By modulating each laser at a different frequency or at different times, multiple species measurements can be carried out using a single fiber optic cable and one detector. Demodulation of the signals can yield multiple species measurements with one fiber much the same way multiple telephone calls are carried on one fiber.

The experimental configuration used for these initial investigations is depicted in Figure 2. Precision current and temperature controllers are used to drive the output from the diode laser. The wavelength of the laser is roughly controlled by laser temperature while fine wavelength control is exerted using the laser current. The output beam from the diode is directed into a multipass cell which, depending upon the number of passes that the beam makes through the cell, can be set for an optical pathlength of up to 50.4 meters. A mechanical vacuum pump is used to evacuate the cell and various gases are subsequently added when absorption measurements are to be made. The pressure in the cell is measured using a capacitance type pressure gauge. The laser light exiting the cell is detected on a photodiode detector connected to a lock-in amplifier. The ratio of light transmitted by the cell both with and without a sample gas present is used to calculate the total concentration of sample present. A beamsplitter placed between the laser and the cell can be used to divert a fraction of the laser beam, providing a reference signal unperturbed by absorption in the cell. A frequency generator can be employed to modulate the diode laser current and provide a reference

signal for the lock-in amplifier. The actions of the laser controller and the data acquisition are all managed by a personal computer.
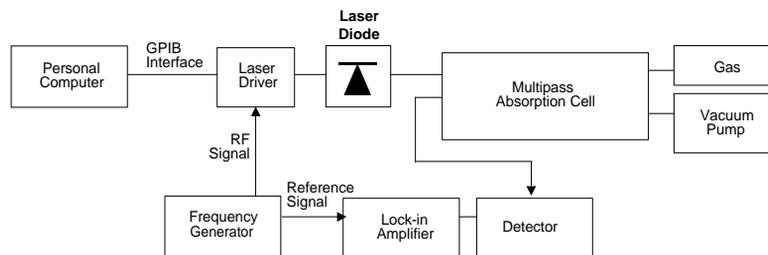
FIGURE 2. Experimental configuration for diode laser absorption spectrometry.

Work Accomplished

The system depicted in Figure 2 was tested for quantitative performance using a variety of well-studied gases. This allowed for performance verification of the system and also provided a method for laboratory personnel to learn the operation of the system under conditions that yield a readily predictable response. Two lasers were used in the following efforts, one operating near 1578 nm and the other near 1653 nm. Figure 3 depicts the reference (I_O) and direct absorption (I) signals obtained during ramping of the 1578-nm laser current. Since the wavelength of the laser is determined in part by the laser current, sweeping the current is equivalent to scanning the wavelength of the laser. The absorption evident in the center of the figure is associated with a particular rotational transition in a combination band of CO_2. This measurement was made using 30 torr of CO_2 in a multipass cell configured for a 5.6-meter pathlength. The current of the laser was centered at approximately 50 mA and was modulated with a 500-hz triangle waveform with a peak-to-peak voltage of 800 mV. The temperature of the laser was set to approximately 36.4^{o}C. The absorbance [$\ln(I/I_O)$] measured for this particular transition was 0.438 as compared to a theoretical value of 0.411, demonstrating the

excellent quantitative accuracy of the system. In fact, most of the small discrepancy between the measured and theoretical values is more likely due to difficulties in obtaining an accurate pressure measurement rather than measurement error in the diode laser system. Comparable performance was obtained on a number of CO_2, CO, and CH_4 spectral lines. The theoretical values were obtained using the HITRAN 96 spectral simulation package produced by the United States Air Force.
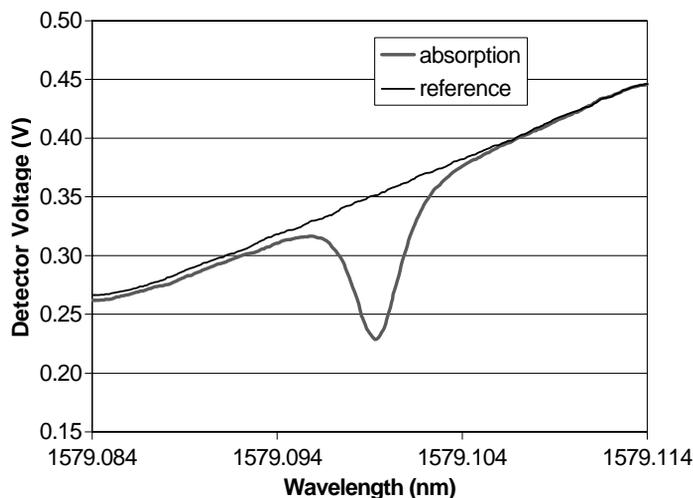
FIGURE 3. Examples of reference and direct absorption signals for a single rovibrational transition in CO_2.

Frequency modulation (FM) is often used for improving the signal-to-noise ratio in diode laser spectroscopy experiments.[2] We successfully implemented this technique in our diode laser system as well. Frequency modulation spectroscopy yields "derivative" spectra, i.e., spectra that are proportional to the derivative of the original absorption spectrum. If the laser is modulated at a frequency f and subsequently detected at the same frequency, the signal obtained is proportional to the first derivative of the absorption signal. If the sig-

nal is detected at a $2f$ frequency, the signal is proportional to the second derivative. This method allows the detection frequency range to be shifted above the laser noise frequency, thus improving the signal-to-noise ratio. Although FM techniques make a significant impact on the S/N ratio, the line widths of the VOC spectra described below were too large to make use of the advantages of FM spectroscopy. This technique is currently available for future applications, however.

Absorption measurements for benzene were carried out as a first example of VOC detection. The experimental system was modified somewhat from the configuration used for the standard gas measurements described above. A mechanical chopper was installed in the laser beam path to allow for physical rather than electronic modulation of the laser beam. A new sample introduction system based upon a benzene freeze-thaw cycle also was constructed. Figure 4 depicts the absorbance from benzene at various pressures in the cell at different laser temperatures. The wavelength of the laser increases as the laser temperature is increased, with the laser wavelength being approximately 1656.6 nm at 40°C. This particular laser was constructed primarily for CH_4 detection, and thus is not capable of reaching the actual peak absorbance of benzene at 1674.5 nm. The increasing absorbance with laser temperature depicted in Figure 4 yields a partial view of one side of the benzene absorbance peak. As depicted in Figure 5, a number of additional benzene absorbance measurements were made with the laser set at 35°C. This temperature was used to avoid long operation of the laser at its maximum temperature of 40°C, even though it caused a slight reduction in sensitivity. At this setting, a comparison with the photoacoustic spectroscopy data of Reddy, et al,[3] indicates that the sensitivity of the system should be approximately six to seven times less than if a laser operating at the peak benzene absorbance wavelength was used. It is encouraging to note that the data in Figure 5 for pressures between 0.1 and 1.0 torr and for 1.0 to 15 torr were taken several days apart and were separated by a complete overhaul of the system. This indi-

cates the excellent level of reproducibility of the data in that the calibration slopes match almost perfectly. The slope of this data indicates an absorption cross section for benzene at this wavelength of 1.24 x 10^{-21} cm^2, which, as expected, is approximately 6.3 times less than the peak cross-section reported by Reddy, et al.[3] Thus, our initial absorbance measurements for benzene are in complete agreement with our initial predictions.
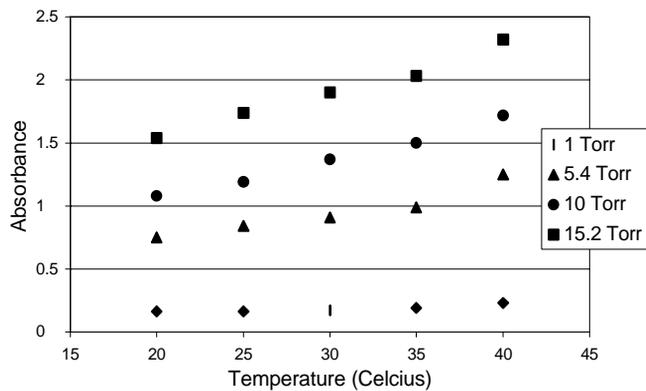
FIGURE 4. Measured absorbances for pure benzene at various gas pressures and diode temperatures.
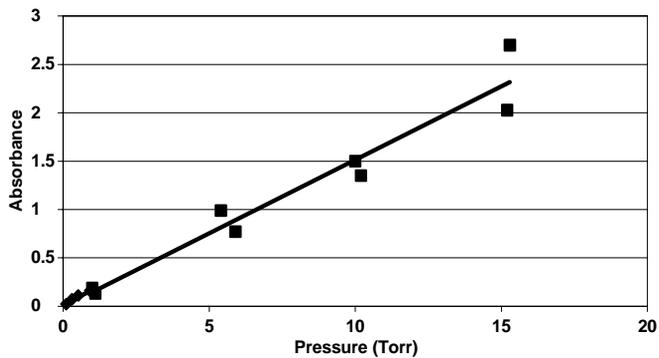
FIGURE 5. Measured absorbances for pure benzene at varying pressures with the laser temperature set at 35 C.

Work Planned

For the next quarter, we plan to investigate the response of the system for small concentrations of benzene in nitrogen and air at atmospheric pressure. The effects of additional gas components and the increase in pressure must be evaluated to determine the sensitivity of the diode laser approach for continuous emission monitoring at atmospheric pressure. Because the benzene absorption is quite broad, we expect minimal impact on absorption sensitivity. This must be demonstrated, however, before detection limits can be determined. If time permits, we will also begin to investigate the response of the system for an additional VOC such as chlorobenzene.

References

For example,

2.   J.A. Silver. February 1992. Frequency-modulation spectroscopy for trace species detection: theory and comparison among experimental methods. *Applied Optics.* 31:6:707-717.

   D.S. Bomse, A.C. Stanton and J.A. Silver. February 1992. Frequency modulation and wavelength spectroscopies: comparison of experimental methods using a lead-salt diode laser. *Applied Optics*. 31:6:718-731.

3.   K.V. Reddy, D.F. Heller, M.J. Berry. March 1982. Highly vibrationally excited benzene: overtone spectroscopy and intramolecular dynamics of C_6H_6, C_6D_6, and partially deuterated or substituted benzenes. *Journal of Chemical Physics*. 76:6:2814-2837.

Nomenclature

VOC	volatile organic compound
CEM	continuous emission monitor
FM	frequency modulation

Subtask 1.4 Laser-induced Fluorescence Spectrometry of Radionuclides

David Monts

Introduction

Purpose

The purpose of the Laser-induced Fluorescence (LIF) project is to provide the U.S. Department of Energy (DOE) with a robust, cost-effective technique capable of rapidly and accurately determining the concentrations and isotopic abundances of long-lived radionuclides (such as uranium and plutonium) without the need for lengthy sample preparation. Knowledge of isotopic abundances is necessary since different isotopes can have widely differing activities. The niche for this technique is determination of concentrations and isotopic abundances for cases where current techniques are severely limited by low throughput, such as: (1) cases where the radioactivity is so low that radioactive decay disintegration counting techniques cannot analyze samples during acceptable counting periods; and (2) cases where lengthy sample preparation is required for mass spectrometric determination. For these situations, LIF can save tax dollars by reducing or eliminating holding batch samples for time-consuming analyses. In addition, since this technique is applicable to a wide variety of other species, it may also be deployed as a monitor of other species of concern, such as Tc.

Methodology

Laser-induced fluorescence (LIF) spectrometry is a well-established, robust technique for detecting species of interest at low concentrations. In the LIF technique (Fig. 6), an electronic state of the species of interest is excited with a tunable laser and the resulting flu-

orescence intensity is monitored as a function of laser wavelength. Since the mass of isotopes are different from one another, the corresponding atomic energy levels are slightly different (Fig. 7). Consequently, when a sufficiently high-resolution tunable laser is scanned across an atomic electronic transition, the resulting LIF spectrum contains a peak associated with each isotope present; the intensities of the isotopic peaks are directly related to the concentration of the isotope. Hence, the isotopic abundances can readily be obtained from the LIF spectrum. In order that the individual isotopic transitions can be resolved, it is necessary that the species of interest be in the gas-phase. For the TRU elements of interest, an atomization source is required in order to volatilize and atomize the sample. A calibration curve is obtained by recording the LIF signal intensity as a function of concentration. Using the calibration curve, unknown concentrations can be determined.
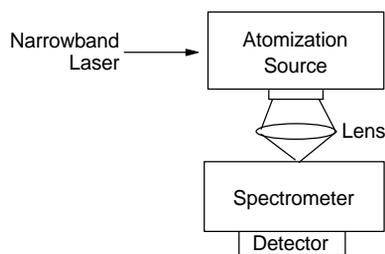
FIGURE 6. Schematic of the laser-induced fluorescence spectrometry technique.
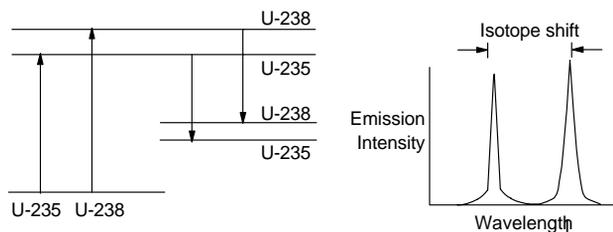
FIGURE 7. Schematic of isotopic energy shifts and the associated LIF spectrum.

Work Accomplished

Mississippi State University has applied to have its license extended to permit controlled usage of elements with atomic numbers in the range of 84 (Po) through 98 (Cf). It is anticipated that this license will be granted and that the University will have the required capabilities to implement the license in July. Until the license is granted and we receive permission from the local Radiation Safety Committee to perform experiments with uranium, we are restricted to the use of surrogates.

As an aid toward the goal of developing rapid identification and quantification of isotopic abundances, DIAL received a europium-doped surrogate during March from INEEL. Using standard europium solutions, we have familiarized ourselves with the LIF spectrometry of europium. In order to optimize conditions for standard europium solutions introduced into a laboratory flame, we tried different fuel/oxidant flames (air/acetylene and nitrous oxide/acetylene); the addition of easily ionized compounds (potassium compounds) in order to suppress ionization of Eu; and have performed LIF measurements with Cu and Cs to verify that our detection system was optimized. LIF calibration curves for standard Eu solutions (such as that shown in Fig. 8) have been obtained both for acetylene/air and acetylene/nitrous oxide laboratory flames.
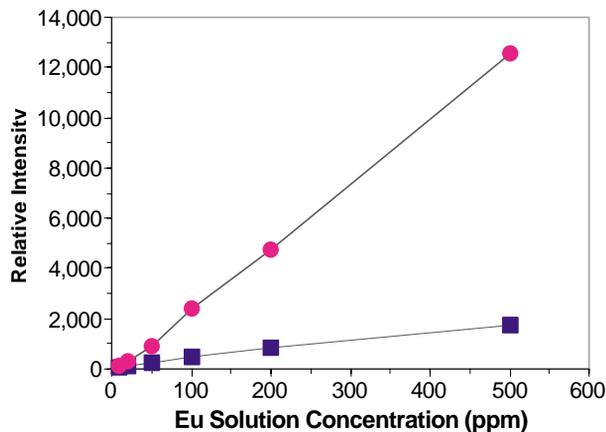
FIGURE 8. LIF calibration curves for LIF (■) and for atomic emission spectroscopy (•) for standard solutions of europium introduced via an ultrasonic nebulizer into an acetylene/nitrous oxide laboratory flame.

As Figure 8 illustrates, we have experimentally verified that, as reported in the literature,[4] Eu is one of a handful of elements for which the LIF detection limits in laboratory flames are higher than the atomic emission detection limits. This is due to the fact that for Eu the only electronic transitions that have sufficient intrinsic strength and sufficient population to yield a strong laser-induced fluorescence signal are the three resonance transitions (459.4 nm, 462.7 nm and 466.2 nm) that strongly emit atomic fluorescence in laboratory flames even in the absence of laser excitation. Thus for Eu, LIF detection consists of detecting the enhancement of the natural fluorescence (shown in Fig. 9) via gated detection.
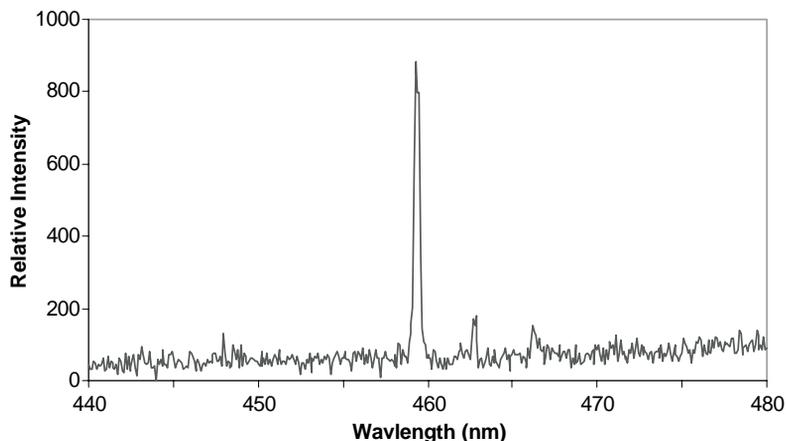
FIGURE 9. Laser-induced fluorescence enhanced emission spectrum of 20 ppm europium standard solution in an acetylene/nitrous oxide laboratory flame excited at 459.4 nm.

Initial experiments were performed on the europium-doped INEEL surrogate solution. One difficulty in performing experiments on the surrogate is its high viscosity, which causes the ultrasonic nebulizer to operate improperly. Diluting the surrogate enables the ultrasonic nebulizer to operate properly, but also dilutes the europium, which is only present in trace amounts in the surrogate. The manner in which the material can be introduced into the atomization source is different for an ICP plasma than for a laboratory flame. Therefore, further experiments with the INEEL surrogate are postponed until the delivery of the ICP generator system that has been ordered for this project, since the ICP system is required for efficient atomization of uranium.

Work Planned

In order to make progress on the use of LIF for isotopic determination of TRU elements, there are three prerequisite needs that must be meet. The first is that the University must have a regulatory license

to work with actinides. The University has negotiated with the state regulatory agency and is currently purchasing the required monitoring equipment. It is currently anticipated that the University will have the ability to begin working with actinides by late summer. Thereafter, we will be able to work with uranium rather than with surrogates.

The second need is the need for a sufficiently hot atomization source. An ICP atomization source has been ordered and delivery was expected during May 1999; delivery has been promised in the near future. An ICP system capable of operating with air as the carrier gas has been ordered, since many of the applications for which the LIF technique is applicable involve air.

The third need is for a sufficiently narrow-linewidth, tunable laser system that can be reproducibly scanned. DIAL's cavity ringdown spectroscopy group will permit us to use their new moderately high-resolution dye laser system to perform some preliminary experiments on surrogates in an ICP plasma. If, as expected, these LIF experiments prove that such a moderately high-resolution tunable laser system has sufficient resolution for the TRU elements, then funds for purchase of a comparable dye laser system will be requested for FY 2000; if the experiments indicate that even higher resolution is required, then additional funding will be sought in order to purchase an ultra-high resolution tunable laser system.

Reference

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Nomenclature

DIAL   Diagnostic Instrumentation and Analysis Laboratory
ICP   inductively coupled plasma

INEEL	Idaho National Engineering and Environmental Laboratory
LIF	laser-induced fluorescence
nm	nanometer
ppm	parts per million
TRU	transuranic

Subtask 1.5 Cavity Ringdown Monitors for Transuranic Elements

C. P. Winstead

Introduction

The Idaho National Engineering and Environmental Laboratory has expressed a need for monitoring residual transuranic (TRU) elements in treated high-level waste. Specifically, a need exists for on-line monitoring of the low activity fraction of this treated waste after dissolution and partitioning. Such a system could replace expensive off-line sampling and analysis and eliminate the need for holding tanks in the Idaho HLW process. However, detecting TRU elements at ultra-sensitive levels has proven to be problematic for traditional radiological counting methods due to the long half-lives of these predominantly alpha-emitter elements.

Cavity ringdown is a relatively new variant of absorption spectroscopy that has demonstrated extreme sensitivity in a variety of studies. In pulsed cavity ringdown spectroscopy, a pulse from a tunable laser is introduced through the end mirror of a stable optical cavity. This optical cavity is formed from two highly reflective mirrors, and serves to trap the fraction of the laser pulse that enters the cavity. The laser pulse interacts with an absorbing medium in the cavity for up to thousands of cavity round trips. The reflectivity of the mirrors

and the absorption of the sample in the cavity determine the decay time for the pulse. As the absorption in the cavity increases, the decay time for the light in the cavity decreases. By inserting into the cavity an appropriate atomization source, such as an inductively coupled plasma or graphite furnace, very low concentrations of the various chemical forms of TRU elements can be atomized and detected using cavity ringdown.

The primary objective of this project is to evaluate cavity ringdown spectroscopy as a technique for detecting and monitoring transuranic elements. No ringdown measurements of uranium or transuranic elements have been carried out to date. If these measurements prove to have the necessary sensitivity for monitoring needs, a monitor based on a ringdown method could be developed for DOE. This work is directly applicable for many DOE sites, including INEEL and Hanford as mentioned above, and if successful will likely find use in all DOE focus areas.

Work Accomplished

Due to regulatory requirements, no cavity ringdown measurements for transuranic elements were carried out during this time period. The proper licensing procedure for the use of radioactive elements is actively being pursued. Once the appropriate licenses and approvals are obtained, our initial efforts will focus on an evaluation of detection limits for uranium using cavity ringdown spectrometry. To this end, we have completely transitioned our cavity ringdown experiments to a new narrow linewidth dye laser. The measurements that we will make will be the first isotopically-resolved elemental cavity ringdown spectra. For such measurements, a narrow linewidth laser is a necessity. We have continued to optimize the operating parameters for our inductively coupled plasma system to enable its use as an efficient atomization source. This work has focused on heavy metal elements, but the results will greatly aid our efforts for uranium. In addition, we have developed a new data acquisition sys-

tem capable of carrying out cavity ringdown experiments using a graphite furnace atomization source. The atomization time for a graphite furnace is less than one second, and thus necessitates a completely different type of data acquisition than the continuous signal environment of the plasma system. This new system, constructed from a 100-Mhz sample rate, 12-bit resolution analog-to-digital converter, is capable of capturing a full ringdown waveform on every laser shot during the graphite furnace atomization. We have demonstrated the use of this system for a number of metallic elements. Thus, we are presently ready to investigate the performance of cavity ringdown spectrometry for uranium monitoring in both inductively coupled plasma and graphite furnace systems. Also during this time period, an invited book chapter on the use of cavity ringdown spectrometry for analytical chemistry applications was submitted.

Work Planned

A new ventilation system is being designed to provide a separate exhaust pathway for uranium used in our experiments. This system is part of the permitting process for allowing our use of radioactive materials. Upon receiving the appropriate permits following the completion of the ventilation system, we will carry out a number of experiments to determine the performance of cavity ringdown for uranium monitoring. These efforts will provide the information necessary to decide whether cavity ringdown has application as an on-line monitor for transuranic elements and uranium. Detection limits and the ability to discriminate isotopes will be evaluated.

Subtask 1.6   Feasibility of Characterizing Solid Wastes by Remotely Sensed Multi-spectral Imaging

David Monts

Introduction

Purpose

Characterization capabilities for site-specific wastes are needed for the DOE nuclear waste clean-up program. Many wastes are heterogeneous and have a mixture of both RCRA hazardous constituents and radioactive species in various forms and matrices. Characterization requirements vary from waste stream to waste stream. For example, some wastes have high radiation fields and therefore require characterization to be completed at some distance from the actual waste containers. Some wastes may require non-intrusive characterization. Currently however, comprehensive non-destructive testing (NDT), assaying (NDA) and examination (NDE) techniques do not exist for effective waste characterization. In the field of remote sensing, airborne imaging spectrometers have been used to mineral identification. For example, the vibrational overtone features for Al-OH (2.16 to 2.22 μm) has been used to identify minerals containing kaolinite [$Al_2(Si_2O_5)(OH)_4$]. The value of the technique lies in its ability to acquire a high resolution reflectance spectrum for each pixel in the image. Vibrational absorptions from compounds of heavier elements occur in the mid-infrared region. Not only will a portable remotely sensed imaging spectrometer system will provide non-intrusive, non-destructive characterization of solid wastes, it also will overcome some of the obstacles of the existing technologies (sample collecting, preparation, costly and timing consuming analysis). It is well established that the infrared spectrum can be used as a "fingerprint" to identify and characterize molecules. The species of concern (RCRA and radioactive elements) will be present primarily as compounds. Irradiation with an infrared light source will permit collection of reflectance spectral images.

Methodology

Compounds can be characterized by the spectrum of light that they absorb. In particular, the infrared spectral region contains a number of (vibrational) transitions that can be utilized to thoroughly characterize compounds. Absorption spectra can be obtained either by recording the light transmitted through a sample or by recording the light reflected off a sample. Transmission of light for generating absorption spectra is not an economically feasible option for the waste streams of interest to DOE. Therefore, as shown in Figure 10, the method under study consists of recording infrared light reflected off a sample. Instead of using a spectrometer to record the spectrum of the reflected light, a multi-spectral imaging system (MSIS) will be used in the final configuration. For the feasibility study experiments performed here, an infrared spectrometer and infrared detector will be utilized. Both scanning infrared spectrometer and a Fourier-transform infrared (FTIR) spectrometer will be used in these efforts.
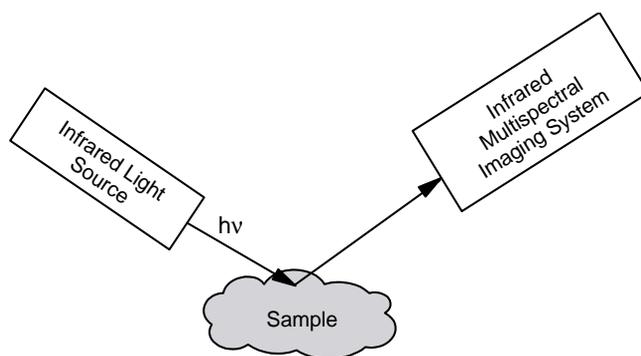
FIGURE 10. Schematic of infrared diffuse reflectance multi-spectral imaging technique (final configuration).

Work Accomplished

During this reporting period, we concentrated our efforts on evaluating available equipment for use on this study.

Work Planned

During the next quarter, we plan to purchase the equipment that is not currently available and initiate experiments utilizing known pure compounds.

Nomenclature

DOE	U. S. Department of Energy
FTIR	Fourier-transform infrared
MSIS	multi-spectral imaging system
NDA	nondestructive assaying
NDE	nondestructive examination
NDT	nondestructive testing
RCRA	Resource Conservation and Recovery Act

Subtask 1.7   Guided Wave Nondestructive Evaluation Technique Development and Demonstration

Krishnan Balasubramanium

Introduction

Corrosion and cracks in metal components constituting the pressure boundary poses a significant safety concern at nuclear storage and handling facilities of the Department of Energy-Environment Management (DOE-EM) facilities.

Project Significance[5]

The Tri Party Agreement (TPA) schedule requires retrieval of wastes in the Single Shell Tanks (SST) to begin by 2004 for future vitrification and permanent storage in a waste repository. There is already an on-going effort in the structural integrity assessment of the Double Shell Tanks (DST). A rapid nondestructive evaluation of tank wall and liner integrity needs to be performed prior to the selection of a retrieval method to assure successful retrieval of the waste from the tank. For example, in the case of a hot cell liner, if it can be determined that the cell liner is intact, an aqueous decontamination method can be used. Otherwise, a dry method must be deployed at a significantly greater cost. In the case of SSTs, sluicing is considered to be one of the primary methods to retrieve waste. It is possible that sluicing may not be a viable method for retrieval of tanks which have extensive corrosion damage. Other more expensive techniques may have to be employed for damaged SSTs. A rapid integrity assessment program for the tanks is needed in order to (a) estimate life time of the tanks and liners and prioritize the tanks with shortest remainder life for retrieval, and (b) evaluate new techniques for retrieval of damaged tanks which may have leaked.

Background

Cracks (both through wall and non-through wall cracks) and corrosion damage on tank walls and hot cell liners is a high priority concern. These flaws must be evaluated to determine the potential for tank rupture and estimate rates of leaks that may occur in the future and assess appropriate actions. Visual inspection is not the answer since most of the damage may not be visible due to buildup on the walls. Also, it is difficult to quantify the extent of damage, especially in the thickness direction, using visual techniques.

The current method uses a point-by-point ultrasonic or eddy current NDE approach to this evaluation and employs advanced signal

processing methods to characterize damage. This is a rather cumbersome and time consuming method. Also, damage detection is currently considered feasible, but damage quantification has not been reliable. The approach proposed here using guided waves can be used to rapidly ascertain the existence of cracks or corrosion larger than the critical size. Often this critical size is greater than 75% of wall thickness and in most cases a through-wall damage identification is sufficient. Here, the ultrasonic waves are generated at one end of the structure and detected at the other end and a 180-degree sweep will cover the entire tank wall. These tanks are large and many of them are buried with access only to riser penetrations in tank domes, which are 12 inches in diameter. To overcome this access problem, we proposed to design this sensor, during the implementation phase, onto a robotic manipulator arm mounted on a telescoping mast such as the Light Duty Utility Arm System (LDUA) developed by Westinghouse Hanford Company for the visual inspection of such tanks.[6]

Damage of the metallic components is suspected due to the long period of operation and the corrosive media which is being stored and handled. The low confidence in the currently available Nondestructive Evaluation (NDE) techniques to accurately determine damage could lead to the spread of contamination and/or regulatory concerns when retrieving the tanks. The corrosion challenges the integrity of the affected structure and may compromise the leak tightness property of the structure. Novel, reliable, remote, and cost effective techniques are needed for the evaluation of the structural integrity of these structures before handling. Successful development and demonstration of this technology will provide a needed assessment tool for assuring safe operation of the nuclear waste handling facilities. Unlike previous work, the proposed work uses remote ultrasonic transaction and has the advantage of long-range, multi-mode generation/detection, and hence improved safety, sensitivity and reliability of inspection for flaws in nuclear waste storage and handling components.

Methodology

Ultrasonic guided waves can be generated in geometrically narrow structures, such as plates, shells, pipes, and rods due to the effect of the interference of reflected and refracted waves which reverberate between the boundaries of the structure. Based on the geometry of the structures, these wave modes are called plate waves, cylindrical waves, rod waves, etc. These waves are generated and measured using several mechanisms.[7,8] The exact generation mechanism will depend upon the geometry of the structure. Remote methods of generation can be accomplished using either laser based ultrasonics or using Electro-Magnetic Acoustic Transducers (EMATS). These waves travel long distances, depending on the frequency and mode characteristics of the wave, and follow the contour of the structure in which they are propagating. These wave modes can also be classified, for example, into symmetric, anti-symmetric, and axi-symmetric modes based on the type of cross-sectional displacement profile exhibited by the wave during propagation. The use of guided wave modes is potentially a very attractive solution to the problem of inspecting the embedded portions of metal components because they can be excited at one point on the structure, propagated over considerable distances, and received either at a remote point on the structure in a through-transmission mode or back at the point of generation, in a pulse-echo reflection mode. The received signal contains information about the integrity of the metal between the transmitting and receiving transducers.

Although these wave modes propagate longer distances, the presence of waste material limits this range. This is caused by the leakage of energy into the waste. This leaked ultrasonic energy is relatively small and poses no threat to waste material chemistry. The sensitivity of the sensing system will also deteriorate as the range of inspection is increased above a certain distance. Also, there is a mode conversion phenomena when the wave encounters a sharp bend. Hence, in order to evaluate the structure, the sensor parameters such

as mode selection, energy generated, transmitter-receiver separation, and data interpretation must be optimized.

Most of the work conducted thus far using the guided waves has investigated the inspection of plates, piping and tubing, which are not embedded. It has been demonstrated that nondestructive modes which propagate long distances are sensitive to wall thinning, cracks, and pits that may be present in the material being examined.[5] The long range propagation and detection of the plate wave modes have been optimized[6] and their interaction with defects have been reported.[9] Measurements of 100 meters or more have been demonstrated.[7] Since, each individual mode has a unique cross-sectional displacement and stress profile and because several modes can be selectively generated and received using the same set of transducers, it is feasible, even in a field deployable system, to utilize the sensitivities of multiple wave modes and simultaneously measure several damage parameters such as location, size, type, and shape of the damage.

DIAL has the laser ultrasonic capability for remote generation and reception of the ultrasonic guided waves. Wave propagation models are also available at MSU for the simulation and parameter selection in order to conduct efficient experiments. The instrumentation for conducting experiments with electromagnetic transduction (EMAT) also exists at DIAL.

Work Accomplished

Results and Discussion

Process monitoring sensor. This work is conducted under the DOE-OIT program in association with Argonne National Laboratory. The glass industry selected is Techniglass of Columbus, OH. A long buffer rod sensor wave developed similar to the short buffer rod

method (3 inches) to measure the melt temperature and viscosity. There were several problems encountered during the testing of the long buffer rod probes (18 inches) of the sensor at the temperatures above 1000$^\mathrm{o}$C. The signal strength changes abruptly, and the measurements are not reliable above 1000$^\mathrm{o}$C. This has been attributed to the material property changes of the Alumina AD-90 used in the experiment. Alternative materials such as coated graphite must be investigated.

Guided wave tank NDE technique. Preliminary models were developed using a finite element modeling technique for the investigation of the feasibility of generation of ultrasonic guided wave modes in plates. This was accomplished using ANSYS. Corrosion and cracks in the plate were modeled and a visualization protocol of the wave propagation results was established.

Conclusions

Based on the results from the guided wave modeling, there is a significant scope for the generation and propagation of guided plate waves in tank walls. Also, the reflected signals from the damage show sufficient sensitivity. The effect of concrete and soil which may be loading the metal tank wall must be investigated.

Project Status

All tasks are currently active.

Work Planned

Process monitoring sensor. It is planned to design and procure l8-inch long graphite rods with zirconium coatings and test the rods under simulated high temperature conditions at DIAL.

Guided wave tank NDE technique. It is planned to investigate the effects of loading of soil and other materials such as concrete and waste materials on the guided wave propagation in the tank walls through modeling.

References and Notes

5. Single shell and double shell waste tanks (Tanks Operations Program - Identification Nos: RL-WT05, RL-WT055-S, RL-WT022, PNL, tap://www.pnl.gov/stcg/science/tanks/rlwt5.stm, rlwt55.stm, and rlwt22.stm) and Stainless-steel hot cell liners (Decontamination and Decommissioning Program - Identification No; RL-DD011 - PNL- http://www.pnl.gov/stcg/decon/rldd11.stm).

6. B.A. Carteret. February 1995. *Light duty utility arm system for underground storage tank applications.* Westinghouse Hanford Company, Sixth Topical Meeting on Robotics and Remote Systems, ANS Robotics and Remote Systems Division.

7. D.N. Alleyne and P. Cawley. 1995. The long range detection of corrosion in pipes using Lamb waves. *Review of Progress in Quant.* New York: NDE, Plenum Press. 14:2075-2080.

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9. D.N. Alleyne and P. Cawley. 1992. *The interaction of Lamb waves with defects.* IEEE Trans. on Ultrasonics, Ferroelectrics, and Frequency Control. 39:3:381-397.

TASK 2 *Measurement Support*

Measurement services will be provided for DOE sites. In some cases, a specific site will not be able to justify the cost of a new instrument but will need it to achieve a programmatic objective. DIAL can take its instrumentation to the DOE site to provide the measurements needed.

Subtask 2.1 Diagnostic Field Applications Coordination and Testing Support

Robert L. Cook

Activities in this task have been rescheduled to a later date due to man power demands in other tasks.

Subtask 2.2   *On-line Imaging for Thermal Treatment Processes*

David L. Monts

Activities in this task have been rescheduled to a later date due to man power demands in other tasks.

Performance Evaluation

Subtask 3.1 Validation and Application of the Environmental Simulation Program

J. S. Lindner and R. K. Toghiani

Introduction

Project Significance

The Office of River Protection (ORP, formally the Tank Waste Remediation System) is responsible for pretreating the legacy wastes contained in the double and single-shell tanks at Hanford and delivering these streams to the privatization contractor, British Nuclear Fuels Limited. The stored wastes contain three discernible constituents, high ionic strength liquid, sludge, and saltcake. Most of the experimental and theoretical modeling efforts to date have been concerned with the sludge and liquid fractions; however, a large portion of the waste, estimated to be 60% by mass in some tanks, exists as saltcake. Recognizing this deficiency, the Tank Focus Area (TFA) issued Technical Response 671:PBSTW05. The work described here is the result of a successful proposal funded by TFA with cost-sharing from DIAL.

Thermodynamic modeling of complex, multi-component electrolyte solutions at high ionic strengths and with proper consideration of solids formation is a formidable task. Workers evaluating the waste at Hanford have selected, based on initial comparisons between experimental results and an assessment of available software, the Environmental Simulation Program (ESP, OLI Inc.). The code has subsequently been used for modeling laboratory sludge leaching experiments and tank contents.[10-12] To our knowledge, the work reported here is the first application of the model to saltcakes. The short time period in which ESP has been in use at Hanford suggests, however, that evaluation of the code for different applications is an evolving process. Thus, the work performed here is implicitly centered on model validation.

All of the work connected with this subtask has been aimed at providing end-users at Hanford with additional information regarding the performance of the ESP code. A main goal of the work is to increase confidence in the predictive capability of the model. A proven, validated process engineering tool could result in considerable cost savings. For example, proper modeling of the pretreated waste will indicate the propensity of the waste to foul transfer lines; thereby eliminating the high costs of effecting repairs and slipped delivery schedules. In addition, analytical characterization of the large volume of waste at the site, 55 million gallons along with the process streams that will be generated upon retrieval of the waste, is impractical. A tool is needed which can describe the waste and associated process streams with sufficient reliability such that costly characterization studies can be minimized.

Background

The previous work at Hanford has indicated some limitations in the application of ESP.[10-12] Solid-liquid equilibrium (SLE) model calculations have been found to agree with laboratory results for aqueous solutions containing most of the pertinent single salts (NaCl,

$Na_2C_2O_4$, $NaNO_3$, etc.). At elevated ionic strengths, however, the solubilities from the model are less than experimental observations. Consequently, the code predicts higher solids loadings, and this has potential ramifications on the privatization contract through the amounts and types of diluents used for pretreating the waste.

Other questions regarding the code concern the quality of the data used in the integral software databases. Analytical results on the tank wastes at Hanford have indicated the presence of a number of double salts such as Na-F-PO_4, Na-F-SO_4, and Na-SO_4-CO_3.[13] Literature data on these systems are rare. What results are available indicate that various types of solids structures, crystals and gels, can result depending on composition. Natrophosphate, $Na_7F(PO_4)_2 \cdot 19H_2O$, for example, has been observed to form gels.[14,15] Sodium phosphate $Na_3PO_4 \cdot XH_2O$ can form different crystal structures depending on the extent of hydration. Accurate modeling of the partitioning of the solids and liquid phase constituents will only be as good as the fundamental data used in the model.

Methodology

Some identified options for validating the ESP code include: (1) comparisons to experimental data on actual tank samples; (2) determination of the SLE behavior for those systems which are of direct importance to the end-users at Hanford; and, where literature results are fragmentary, (3) comparison of the results of the model to other thermodynamic models; and (4) examination of the thermodynamic data called by the code.

Little is known about the pretreatment requirements of saltcakes and experimental studies on this portion of the waste are lacking. An evaluation of the predictive capabilities of the ESP model is possible by comparing code predictions with the results of experimental studies. Other comparisons of the model to tank sample analysis include direct customer requests.

Critical evaluation of the fundamental thermodynamic constants called by the model permit an assessment of the quality of the data used by OLI Inc. and can identify possible error sources. In many instances, especially with regard to the double salts systems cited above, sufficient data does not exist in the literature and any compilation will only consider the available information as estimates. Determination of the solubilities and associated phase diagrams for selected systems provides a means for ensuring the quality of the experimental data and a path for model sensitivity calculation.

Different theoretical representations can be used to calculate the SLE behavior of aqueous systems. Comparison of the results from ESP with other thermodynamic models allows an independent check on the thermodynamic framework used and may also indicate deficiencies in the ESP model or associated database.

Work Accomplished

Options for Automating the ESP Reconciliation Process

Background. A need has been identified to accelerate the ESP program through automated operation of the water analyzer (WA) charge reconciliation process. The action corresponds to the application of ESP to the 154 tanks located at the Hanford site. Specifically, tracking all of the various chemistries is a direct requirement for assuring compliance with anticipated vitrification schedules.

Based on this charge a series of studies have been initiated that focus on ways to automate the reconciliation procedure while limiting the potential surpluses or shortages that may be predicted by the thermodynamic code. At the same time it must be recognized that the ESP model still has some potential shortcomings, particularly with the quality of some of the fundamental data called by the program and with the use of the software in high ionic strength (15 - 20) regimes.[10] Studies of the observations from the work for the first year

of the Saltcake Dissolution Program are continuing and are aimed at further evaluations of the thermodynamic model as compared to laboratory experiments and to obtaining the requisite fundamental data which will improve the accuracy of the model predictions. In addition, companion studies are being performed with other thermodynamic models to shed light into the predictions of ESP at high ionic strength.

The work summarized below is intended to be a guide for users at Hanford to permit selection of a method whereby reliable charge reconciliation s can be automated within the ESP software. Such an approach must be based on one or more a fundamental parameters from analytical chemistry experiments on the tank contents. All of the associated analytical data is eventually downloaded to the Best Basis Inventory (BBI).

In the work performed in these laboratories in connection with Hanford tank 241-SY-101 (SY-101) all of the simulation data was obtained from the BBI.[11-13] This includes tank temperatures, cation and anion concentrations, tank waste volumes, percent H_2O in whole tank samples or composites, and densities. Required inputs to the WA module include ion concentrations, temperature and bulk densities.

Within the WA are the means to: (1) create a chemistry model; (2) input concentrations for the ionic species associated with the model; (3) determine the solids scaling tendencies; (4) generate a molecular stream suitable for use within the ESP process module; and (5) collate the results. All of these functions, with the exception of the prediction of the solids scaling factors, have been examined.

Of importance in using water analyzer is the ability to select different ions upon which charge reconciliation can be performed. Specifically, the charge can be balanced by either subtracting or adding one or more ionic species to attain electroneutrality. The problem with respect to the Hanford tanks amounts to the extent of charge bal-

ance needed and the selection of the appropriate ion or ions with which to perform the neutrality calculation. In essence, the means to attain the charge balance may be different for the various tanks and one method, such as balancing with Na^+ may be adequate for one waste stream but not for another. Other methods of reconciliation such as balancing with the OH^- and NO_3^- ions may also have drawbacks. In the case of hydroxide increasing or decreasing the concentration (mg/L) will increase or decrease the pH of the system. Upon generation of the molecular stream and thereafter running the ESP process module (PM) additional solids may be formed or lost thereby leading to inaccurate solids loading predictions. Shortfalls in solid loading may have ramifications with regard to the delivery of the waste streams to the privatization contractor. Similar comments may apply to balancing with the generally dominant ions, Na^+ or NO_3^-. In the vast majority of the simulations performed to date the dominant molecular species predicted by the code is $NaNO_3$. The question amounts to what is the best species with which to perform the reconciliation and what are the potential errors. One might suggest a safety factor for the percent solids by volume criteria associated with the privatization contract; alternately spreading the difference in charge balance over all of the ions present in the simulation may have advantage.

General comments. Automation of the process must be performed based on some type of recursion to existing data. Therefore, selection of the appropriate parameter is critical with regard to the success of the automation process. It appears that the most suitable quantity may be the percent water of the waste stream. Discussions indicate that this parameter will generally exhibit smaller errors than, for example, the bulk density.[16] One might think that the supernate density would be a suitable comparison point, however, the results provided below indicate that this parameter is somewhat insensitive to changes in the reconciliation method selected.

The WA will calculate a pH and a density, but these values are slightly different than those obtained in ESP process. The percent H_2O for the stream could, in principle, be calculated based on the molecular stream generated within the software, however, the generated stream contains species that are acidic and that would not be expected to exist in the high pH conditions of the wastes. In addition, the solids predicted in the PM are normally not reflected in the molecular stream obtained in water analyzer.

If the percent water quantity is used the automation must include portions of WA and ESP process. Furthermore, the percent water is not a parameter directly calculated within ESP. It should be straightforward to obtain this value directly within the code.

Another change that needs to be considered in the PM relates to the inaccurately calculated solids volume and resulting solid phase densities. While this change will have no bearing on the automation of the reconciliation process, the desired solids volumes and densities, and therefore the percent solids loading by volume (a parameter upon which the privatization contract is based) must now be calculated off-line using a spreadsheet. It would make some sense to get the vendor to include the proper calculation by incorporating the densities of the various solids formed and converting the mass of solids to volumes such that the calculation would not have to be performed off-line. Workers could then concentrate more on any necessary operations regarding pretreatment and delivery.

Calculations and simulations. Questions regarding reconciliation within WAM have previously been noted by Dan Reynolds.[17] During a discussion in November, Reynolds stated that he did not trust the reconciled values generated and that his preferred way of ensuring electroneutrality was to perform spreadsheet calculations. Shortly after this meeting a spreadsheet file was developed and named ESPtemplet.xls.

Some words of caution are required with regard to off-line neutrality calculations. First, the molecular stream generated within the WA is specific to a particular chemistry model. The same species must be used in the spreadsheet if an effective comparison is desired. Second, many of the ions present in the waste are partitioned to different species. For example, Na^+ is distributed to caustic, $Na_7F(PO_4)_2 \cdot 19H_2O$ and to $Na_6(SO_4)_2CO_3$. WA may generate additional sodium containing species and then more algebra will be needed to properly account for the molecular stoichiometry.

Partitioning may also exist for the fluoride, phosphate, sulfate, and carbonate ions. In practice the software automatically accounts for fractionation of the ions to the various molecular stream species. Finally, distribution of the ions to the various species will depend on the concentrations of the ions present. Thus if the same spreadsheet, without modification, is used for wastes that significantly vary in ionic concentration, the resulting streams may be radically different than those obtained in water analyzer. Proving that the WA performs the reconciliation properly would alleviate any questions as to the operations specified by the ESP code.

The ESPtemplet spreadsheet file was augmented to apply to the waste for Hanford tank 241-S-106. Supernate from this tank was recently used in the model of saltwell pumping to tank 241-SY-102 as part of the on-going operations regarding SY-101. The water analyzer module was run with the same input concentrations and temperature for reconciliation based on sodium ion for four different input densities. WA was also run to examine the effects of reconciliation using NO_3^-, OH^-, and proration. In this latter method the charge make-up is established by distributing the charge needed to all of the cations or anions in a given stream. The spreadsheet was not altered to account for each of these other reconciliation options but has been primarily used to examine the effects of the input density on the final results. Following the generation of the molecular stream within WA the data was saved to file and then run through the ESP process module using

a simple Separate block. Output files from the PM calculations were edited and imported to spreadsheet where the necessary calculations for percent water and bulk density were made.

Effect of input water analyzer density on waste composition. The spreadsheet is given in Tables 3 and 4. It can be shown that the WA module performs the electroneutrality calculations based on balancing with water. The ions present in the model along with the associated concentrations are used with the atomic weights to calculate the moles of ions present. The moles of ions are summed and subtracted from the input density to calculate the mass of water present in the system. The calculations assume a 1-L volume. The moles of ions present and the mass of water, obtained by difference, are used to determine the ionic molality. This concentration is then multiplied by the ionic charge to yield the term m dot. Corresponding m dot values are summed for the cations and anions and then subtracted to determine the offset in charge balance. This difference is then applied to the sodium ionic molality to obtain the reconciled molality. No changes are made to any other input concentrations. The reconciled m dot values are summed and then compared and if the balance was performed properly the resulting difference is zero.

TABLE 3. Spreadsheet for reconciliation studies.

1500 Input density in g/l

912.55474 CALCULATED SUMS ANIONS + CATIONS (g/l)

0.58744526 CALCULATED DIFFERENCE (kg/L)

CATIONS	Atomic Weight	input conc mg/L	moles ion	ionic molality	reconciled charge m		m dot	m rec. dot
AL+3	26.98154	22188.00	0.8223	1.3999	1.3999	3	4.1996	4.1996
BI+3	2.09E+02	137.24	0.0007	0.0011	0.0011	3	0.0034	0.0034
CA+2	40.08	139.30	0.0035	0.0059	0.0059	2	0.0118	0.0118
CRIII+3	51.996	6902.90	0.1328	0.2260	0.2260	3	0.6780	0.6780
FEIII+3	55.847	1902.40	0.0341	0.0580	0.0580	3	0.1740	0.1740
K+1	3.91E+01	908.00	0.0232	0.0395	0.0395	1	0.0395	0.0395
Mn+2	5.49E+01	71.10	0.0013	0.0022	0.0022	2	0.0044	0.0044
NA+1	22.98977	256400.00	11.1528	18.9852	19.5795	1	18.9852	19.5795
NI+2	58.71	33.40	0.0006	0.0010	0.0010	2	0.0019	0.0019
PB+2	207.2	79.70	0.0004	0.0007	0.0007	2	0.0013	0.0013
SR+2	87.62	7.03	0.0001	0.0001	0.0001	2	0.0003	0.0003
UO2+2	270.0278	447.87	0.0017	0.0028	0.0028	2	0.0056	0.0056
Zr+4	91.22	8.20	0.0001	0.0002	0.0002	4	0.0006	0.0006
	Sum cations	289225.14				Sum mdot	24.1057	24.6999

	Charge Balance	I48-I22	0.594238848	ionic molaity	
	Reconciliation With Na+		0.349082795	moles=c4*molality	
		mg/L Na+	8025.333158	mg/L=moles*1000*AW Na+	
	CHECK	0	7984.8 from ESP		
	WATER	OH USED FACTOR	2.26E+01 1.389283	sums for MOH etc- OHION Molality	

ANIONS	Atomic Weight	input conc mg/L	moles ion	ionic molality	reconciled molality	charge	m dot	m rec. dot
OH-1	17.0073	7.00E+04	4.1159	7.0064	7.0064	1	7.0064	7.0064
CL-1	35.453	3949	0.1114	0.1896	0.1896	1	0.1896	0.1896
CO3-2	60.0092	39281	0.6546	1.1143	1.1143	2	2.2286	2.2286
F-1	18.998403	2650	0.1395	0.2374	0.2374	1	0.2374	0.2374
H3SIO4-1	9.51E+01	1.85E+03	0.0195	0.0331	0.0331	1	0.0331	0.0331
NO2-1	46.0055	3.62E+04	0.7868	1.3394	1.3394	1	1.3394	1.3394
NO3-1	62.0049	4.31E+05	6.9580	11.8445	11.8445	1	11.8445	11.8445
ACETATE	59.0445	997.6	0.0169	0.0288	0.0288	1	0.0288	0.0288

TABLE 4. Continuation of the spreadsheet developed for analysis of the WA reconciliation process.

Rho = 1500	Spreadsheet	ESP Output	% Difference
$ACET_2$	0.0200	0.0200	-0.1058
$AlOH_3$	1.9448	1.9445	0.0154
$Bi(OH)_3$	0.0016	0.0016	0.1996
$Ca(OH)_2$	0.0082	0.0082	-0.0058
$Cr(OH)_3$	0.3140	0.3139	0.0152
$FeIII(OH)_3$	0.0806	0.0806	-0.0483
H_2CO_3	1.4317	1.4315	0.0161
H_4SiO_4	0.0460	0.0460	0.0600
H_6F_6	0.0010	0.0010	-0.3029
HCL	0.2399	0.2399	0.0125
HNO_2	1.8608	1.8605	0.0185
HNO_3	16.4554	16.4530	0.0144
KOH	0.0549	0.0549	0.0412
$Mn(OH)_2$	0.0031	0.0031	0.0227
$Na_6(SO_4)_2CO_3$	0.1163	0.1163	0.0434
$NaFPO_4 \cdot 19H_2O$	0.3238	0.3238	0.0140
NaOH	24.2366	24.2330	0.0148
$Ni(OH)_2$	0.0013	0.0014	-0.3393
OXALAC	0.0407	0.0406	0.1283
$Pb(OH)_2$	0.0009	0.0009	-0.0344
$Sr(OH)_2$	0.0002	0.0002	-0.1331
UCl_6	0.0039	0.0039	0.0647
$Zr(OH)_4$	0.0002	0.0002	-0.1915

At this point the ionic stream must be converted to the molecular stream through a balance on the H_2O molecule. The amount of hydroxide needed to satisfy the stoichiometric demands for the various cations is taken simply from the reconciled m dot values that include the stoichiometry of the molecule. Here also the eventual partitioning of the sodium must be considered. This cell "OH USED" amounts to a concentration of OH$^-$ from the water that is implicitly

used in the initial correction of the density. This value is not known, a priori, since the extent of charge bias is initially unclear.

The cell "Factor" performs the final calculation of the water present and is based on the equation

$$Factor = (55.5087)/(55.5087 - OH \ used - free \ OH^-). \qquad \textbf{(EQ 2)}$$

The free OH ion concentration is given in the listing for the anions. The factor is used, along with simple expressions for partitioning, to normalize the reconciled ionic molalities to 1 kg of water.

The spreadsheet calculations do not consider any water bound up in hydration of the various species of the molecular stream. A quick inspection of the composition of the molecular stream reveals one, and possibly more molecules, for example the sodium-phosphate-fluoride double salt, that are associated with hydration. At present we neglect further correction of the factor. Therefore, any results comparison to the molecular streams generated within water analyzer will not be exact but will reveal a small difference that will be distributed across all species. This error does not effect the overall conclusions as to the accuracy of the WA or as to how water analyzer performs charge reconciliation and the subsequent generation of the molecular stream.

Table 4 provides the molecular stream composition and immolates and includes the fractionation of the various species in a cell type format. The bottom portion of the table compares the molecular streams calculated with the spreadsheet and that obtained directly from the water analyzer module. Percent differences are small and are generally within $\pm \, 0.1\%$.

Data in this section of Table 4 indicate that the method employed within the WAM module has been successfully reproduced by the spreadsheet calculations.

A main result from these calculations concerns the effect of the initial selection of the stream density. As noted above, the density is directly used within water analyzer to obtain the molecular stream molalities. It might be suggested that varying the density will result in different molecular stream concentrations and this is correct. This has been established by running both the WAM and the spreadsheet calculations with different input densities. The molecular streams are not included here; however, the results from ESP process calculations are collected in Table 5.

Increasing the density within the WAM module causes the dilution of the waste stream and the increase of the percent water by weight. As more water is added to the stream the pH is reduced. The liquid density changes little so this parameter is probably not the most appropriate quantity upon which a recursion to the actual data should be made. The total solid mass in the stream is decreased with an increase in the input density employed in the water analyzer program.

The percent water by weight changes considerably. This and the relatively low anticipated errors for this quantity suggest that the recursion may best be performed based on this parameter. The BBI listed the water loading for a whole tank sample of S-106 at 43.26, 42.86, and 45.04%, respectively for an average of 43.72%. Examination of the data predicted by ESP indicate that the 43.72% value was obtained for the molecular stream that was based on the input WAM density of 1700 g/L.

TABLE 5. **Results of density tuning WA calculations for S-106.**

Tuning of S-106	6RHO1.TXT	6RHO2.TXT	6RHO3.TXT	6RHO4.TXT
Water Analyzer Input Rho	1500	1600	1700	1800 g/L
LIQOUT				
Temperature C	24.89	24.89	24.89	24.89
H_2O	2.46E+05	2.62E+05	2.76E+05	2.88E+05
Total kg	4.60E+05	4.88E+05	5.11E+05	5.31E+05
Volume L	3.23E+05	3.44E+05	3.62E+05	3.78E+05
Density kg/L	1.42	1.42	1.41	1.41
PH	14.91	14.81	14.73	14.67
Ionic Strength	12.92	12.38	12.00	11.73
SOLID				
$AlOH_3$	1.83E+04	1.69E+04	1.56E+04	1.44E+04
$Ca_3(PO_4)_2$	1.59E+02	1.43E+02	1.30E+02	1.19E+02
$Cr(OH)_3$	5.77E+03	5.22E+03	4.76E+03	4.37E+03
$FeIII(OH)_3$	1.39E+03	1.26E+03	1.15E+03	1.06E+03
$Na_2C_2O_4$	9.53E+02	8.28E+02	7.28E+02	6.44E+02
Na_3FSO_4	3.22E+02			
$NaFPO_4 \cdot 19H_2O$	3.98E+04	3.54E+04	3.14E+04	2.80E+04
$NaNO_3$	1.53E+05	1.06E+05	6.67E+04	3.37E+04
$Ni(OH)_2$	2.19E+01	1.98E+01	1.80E+01	1.66E+01
$SrCO_3$	5.25E+00	4.70E+00	4.25E+00	3.87E+00
Total kg	2.19E+05	1.66E+05	1.20E+05	8.23E+04
Volume L	9.78E+04	7.38E+04	5.38E+04	3.68E+04
Density kg/L	2.24	2.24	2.24	2.24
TOTAL STREAM				
Total Mass kg	6.79E+05	6.53E+05	6.32E+05	6.13E+05
Total Vol L	4.21E+05	4.18E+05	4.16E+05	4.15E+05
%H_2O by wt.	36.14	40.16	43.72	46.96
%H_2O BBI			43.72	
Bulk Density	1.62	1.56	1.52	1.48
Bulk Density BBI				1.45
pH	14.91	14.81	14.73	14.67
Water Analyzer Calcs.				

pH	14.66	14.39	14.17	14.00
Density kg/L	1.57	1.52	1.48	1.45

The bulk density of the stream was also considered for recursion purposes. The solids volumes were determined off-line and then the bulk density was calculated from the liquid and solid densities and volume fractions for both phases. The calculated densities decrease with an increase in the density supplied to the reconciliation routine within WAM. Comparison to the bulk density values in the BBI (1.45 kg/L) indicate that this value is not approached for the WAM calculations performed. The smallest stream density that was calculated was 1.48 kg/L and this corresponded to running WAM with an input density of 1800 g/L.

Other parameters might be suggested to enable the recursion. At this point, however, the errors for these parameters are unknown and are best addressed by the analytical experts at the site. The saltcake conference calls have made it somewhat clear that the percent water is superior to the bulk density and this is somewhat borne out in the calculations given in the tables. Other parameters that are listed in the BBI may also be of interest; however, we are unsure of what these may be.

Selection of a reconciliation method. As noted above there are a number of options available within WAM to obtain an electroneutral-input stream. The required charge balances based upon reconciliation using the sodium ion are contained in Table 3 along with the input ion concentration. The spreadsheet predicted that 8,025.3 mg/L of Na^+ are needed whereas ESP predicted 7,984.8 mg/L. The prediction by water analyzer amounts to the addition of 3.11% sodium ion.

This particular input stream has a net negative charge. Therefore, if a reconciliation is based upon OH^- or NO_3^- the original concentrations of these species would have to be reduced by ~ 8,000 mg/L. This factor is small to be sure and the examination of other Hanford

streams may be more suitable for determining the best method to be used for the reconciliation. However, the calculations performed using the S-106 stream provide some valuable information with regard to the choice of the ion or ions to be used.

Tables 6 and 7 provide the ESP PM results for the molecular streams generated in the WAM using the four methods listed. In examining the approaches that are most suitable for reconciliation it becomes necessary to consider the analytical error on the concentrations and any effects imposed by changing a specific ionic concentration. From the initial concentration data for S-106 the system had a net negative charge. Adding sodium ions, especially at a level of around 3%, would not be expected to alter the chemistry of the system significantly. Subtraction of OH^- anion, however, was observed (Table 6) to result in a pH that is 0.2 units lower than that for the sodium option. This stems from the relatively low concentration of hydroxide, (70,000 mg/L, Table 3) originally present in the system. Clearly 8,000 mg/L of the original 70,000 mg/L amounts a loss of greater than 10% in OH^- concentration. This has the tendency to reduce the pH considerably and changes the solids distribution as shown in Table 6. The use of hydroxide for reconciliation may result in the generation of additional or fewer solids present than what would be expected. For example, if the initial pH of the system was at 15.15 one would anticipate the presence of both sodium nitrite and sodium nitrate solids. Lowering the pH will result in solubilization of the sodium nitrite and the prediction for the percent solids in the stream will be less than expected unless other solids form or increase in loading. In any event, the hydroxide concentrations in the BBI are considerably less than those for sodium or nitrate ions; an equivalent change based on charge will exhibit a more drastic effect on the overall solution chemistry.

TABLE 6. Reconciliation using different options available in the water analyzer module.

BALANCE METHOD	NA ION	OH ION	PRORATION	NO$_3$ ION
LIQOUT			+2.47% all cations	
H$_2$O	2.46E+05	2.47E+05	2.46E+05	2.49E+05
Total kg/sec	4.60E+05	4.64E+05	4.60E+05	4.67E+05
Volume L/sec	3.23E+05	3.26E+05	3.23E+05	3.28E+05
Density kg/L	1.43	1.43	1.43	1.43
pH	14.91	14.74	14.88	14.91
Ionic Strength	12.92	12.84	12.90	12.92
SOLID				
Al(OH)$_3$	1.83E+04	2.18E+04	1.98E+04	1.86E+04
Ca$_3$(PO$_4$)$_2$	1.59E+02	1.60E+02	1.63E+02	1.61E+02
Cr(OH)$_3$	5.77E+03	5.94E+03	5.95E+03	5.86E+03
FeIII(OH)$_3$	1.39E+03	1.48E+03	1.45E+03	1.41E+03
Na$_2$C$_2$O$_4$	9.53E+02	9.44E+02	9.51E+02	9.68E+02
Na$_3$FSO$_4$	3.22E+02	1.12E+02	2.83E+02	3.27E+02
NaFPO$_4$·19H$_2$O	3.98E+04	4.00E+04	3.98E+04	4.04E+04
NaNO$_3$	1.53E+05	1.43E+05	1.50E+05	1.41E+05
Ni(OH)$_2$	2.19E+01	2.26E+01	2.26E+01	2.22E+01
SrCO$_3$	5.25E+00	5.29E+00	5.38E+00	5.32E+00
Total kg/sec	2.19E+05	2.13E+05	2.19E+05	2.09E+05
Volume L/sec	9.08E+04	8.82E+04	9.03E+04	8.63E+04
Density kg/L	2.41	2.41	2.43	2.42
% NO$_3$ by wt solid	69.86	67.14	68.49	67.46
% change NaNO$_3$ from base	N/A	-6.54	-1.96	-7.84

TABLE 7. Total stream compositions for the various reconciliation methods.

BALANCE METHOD TOTAL STREAM	NA ION	OH ION	Proration	NO_3 ION
Mass	6.79E+05	6.77E+05	6.79E+05	6.76E+05
Volume	4.14E+05	4.14E+05	4.13E+05	4.14E+05
% Solids by wt.	32.25	31.46	32.25	30.92
% H_2O by Weight	36.23	36.48	36.23	36.83
Volume Fraction Liq.	0.78	0.79	0.78	0.79
Den Liq.	1.43	1.43	1.43	1.43
Vol. Frac. Sol.	0.22	0.21	0.22	0.21
Den Solid	2.41	2.41	2.43	2.42
ESP Bulk Density kg/L	1.65	1.64	1.65	1.64

A number of the effects associated with the use of a specific ion to reconcile a stream are somewhat difficult to quantify. However, the use of hydroxide ion should probably be avoided for both of the reasons described above.

In all of the calculations reported here no effort was made to change or tune the resulting stream based on the pH. In some instances, such as with SY-101, it was possible to change the pH of the system since sufficient data had been obtained on that tank to permit an effect of the change. In most cases, however, all the data that would be available would come from the BBI. Thus, it is possibly best in light of the strong pH dependence that effect solids formation, to avoid any manipulations of this parameter.

Interesting results were also observed when the reconciliation was based on nitrate anion (Table 6). Here a charge difference of 8000 equivalents only amounts to a 1.86% loss in total NO_3^- concentration. Many of the PM stream parameters are the same as for the "baseline" reconciliation case with sodium ion. The pH values are identical and the percent waters by weight for the two reconciliation methods are similar. The main difference is in the solids loading for $NaNO_3$. The reduction in the nitrate concentration required for a neu-

tral charge balance resulted in a loss of ca. 8% in the total sodium nitrate solids as compared to balancing with sodium.

Another, perhaps more appropriate view of this effect is that the sodium nitrate loading changed by some 12,000 kg depending on whether the charge balance was made with sodium or nitrate. Assuming that an original solution existed that did not require the addition of any ion (was electroneutral) and that any additional sodium would be converted to $NaNO_3$ then the sodium nitrate loading would be 3% less than that found for the baseline stream. The sodium loading would be predicted to be 1.48 x 105 kg. This still amounts to a loss of around 5% in sodium nitrate if the balance is done on nitrate ion. The change in solids loading between the case where sodium and nitrate were used for reconciliation is also evident in the percent solids loading by weight. The number is reduced, albeit not tremendously, when nitrate is used instead of sodium.

Some of the differences under discussion may take on greater or less meaning at different ionic strength and pH values. Moreover, the source of the data used for the calculations, whether, the OLI provided public or private databases or the compilation used by many at the Hanford site, is expected to have a significant influence on the solids distribution. More tanks require analyses of the type reported here.

The only reconciliation method that has not been described thus far is proration. For the S-106 stream proration was accomplished by adding slightly over 2% to the concentrations of each cation. The overall tank results are very similar to the reconciliation with sodium ion and, as expected, the addition of a lower amount of Na ion results in a lower sodium nitrate loading. The main disadvantage to using proration may be for those cations that are typically found in sludge. For example, the addition of 2+% of nickel, chromium, and iron cations will increase the overall sludge loading by that amount. For the purposes of pretreating the waste this could have some bearing on the

amount of sludge washing that may be required. If caustic is used for leaching operations then the total amount of sodium that would be predicted based on the output of the code will be larger than actually required. This could lead to sodium excesses in the waste delivered.

The use of proration may clearly have some advantages with regard to a more accurate prediction of the sodium solids that may be formed. Further studies will be needed to ascertain if the increased amount of sodium that will be required for sludge washing, based on this approach, will be substantial compared to that amount currently anticipated. At some point the increase in the amount of sludge that will have to be washed will have a detrimental effect on planning.

Conclusions

Examination of the reconciliation process used in the water analyzer model of ESP revealed that the program correctly accounts for the charge balance and that the molecular stream is generated based upon a further balance of the water present in the system. The molecular stream molalities determined within water analyzer have a pronounced dependence on the density input for the calculations. These differences are clearly observed in the output to the ESP process module where the percent water by weight was observed to change from a low of 36.14% with an input density of 1500 g/L to a high of 46.96% with an input density of 1800 g/L. The actual value listed in the BBI was 43.72% and this value was obtained with an input density to the water analyzer module of 1700 g/L. Examination of the bulk density calculated from the process module with the BBI yielded poor agreement. Even at an input density of 1800 g/L the bulk density was 1.48 kg/L as compared to 1.45 kg/L from the BBI. The bulk density was observed to change significantly over the input range investigated but has been noted as being prone to significant analytical errors.

Work on the selection for a "universal" method for reconciliation was begun. Reconciliations were performed for the S-106 input stream at a density of 1500 g/L using balancing by sodium, hydroxyl, and nitrate ions, and by proration. Some of the disadvantages and advantages of each were described. Balancing the charge difference using the addition or subtraction of OH⁻ ion is not recommended. Here small changes in concentrations that would be typical for sodium or nitrate will have a large bearing on the resulting OH ion concentration, as these latter concentration levels are considerably less than those of sodium or nitrate. A consequence of this is that the pH will be altered and this will or can radically effect the solids distribution obtained within the process module.

For the S-106 stream, balancing with nitrate anion resulted in a loss of nitrate in the compositions and this resulted in a reduced sodium nitrate loading. As compared to reconciliation with sodium ion, the pH and percent water ultimately obtained were the same or similar, respectively. The lower sodium nitrate loading was 5% less than that expected based on an electroneutral system with the initial concentrations as S-106. The total loss in nitrate ion amounted to less than 2% so a disproportionate change was observed. Based on the privatization contract parameter of 5% solids by volume it may not be prudent to underestimate the solids loading using ESP.

The use of proration was found to give sodium solids loadings similar to what would be expected based on starting with an electroneutral stream. The main problem observed with proration is that additional solids of all types will most likely results and the added sludge components may falsely signal a need to use additional caustic in sludge washing operations. Further studies are needed by site engineers to ascertain the effect of additional sludge type molecules on the pretreatment and delivery requirements for the privatization contract.

Automation of the WAM Reconciliation Program

The results above indicate that a recursion type calculation can be performed in water analyzer assuming that all of the data are available to the developed software. As described, the differences of the output from water analyzer and from ESP process are significant and a way to perform the recursion within the water analyzer subroutines is not deemed feasible without code modifications. It will be necessary to couple the routines in water analyzer for charge balance and for molecular stream generation with a simple process model consisting of a Separate block. The density to the WAM can then be input, the molecular stream generated and the Separate block run. The calculation of the percent water can be performed and compared to the BBI value and then the WAM input density can be incremented until a convergence criteria is attained. At this point the input stream will have the same percent water as the tank data.

One important caution that will be required concerns the chemistry models that will have to be used. Ionic species are specific to water analyzer but are not permitted as components of the chemistry model in ESP Process. Two equivalent models will have to be used but this should not cause problems in executing a revised code.

Once the reconciliation is automated it will be easier to determine whether balancing using sodium ion or proration is the preferred choice. Knowledge of the ultimate sodium levels for the pretreated waste will permit better integration with the privatization contract requirements.

Project Status

Work is continuing on validation of the ESP software. Studies on the dissolution of additional saltcake samples from Hanford will be completed and laboratory evaluation of the solid-liquid equilibrium behavior for NaF and the double salt $Na-F-PO_4$ system as a function

of temperature and ionic strength are in progress. Comparisons of the theoretical calculations for the double salt systems, in conjunction with workers at ORNL) are being performed.

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Subtask 3.2   Wall Removal Monitor

Gary Boudreaux

Introduction

One technique for the decontamination and decommissioning (D&D) of concrete structures within the Department of Energy and the nuclear industry is to remove a layer of material from the surface using a technique known as scabbling. The agency responsible for D&D of the facility, the contracting agency, generally specifies to the scabbling contractor the depth of material to be removed, e.g., 0.5 inch off the surface of a floor or wall. Under current practice, measurements are made, before and after, at discrete points on the wall with laser-based survey instruments. Feedback is on the order of days, instead of hours or minutes. With near-real-time feedback the contractor can remove the correct amount of material the first time avoiding both repeating a costly visit and generating more waste than is warranted. Another obvious limitation to this technique is that there is no way to be sure that the contractor has met the specification between survey points, which can be a foot apart.

Another method to deal with the problem is to weigh the amount of concrete that is removed. The average depth of material removal can then be calculated by measuring the density of a small sample cut from the surface. The feedback from this technique is almost immediate, but it does not take into account variations in depth of removal or density that can occur in practice. Thus, a technique that can measure the amount of material removed over a given area and in near-real time would benefit both the agency and the contractor. A wall removal monitor has been developed at DIAL to serve this need. The monitor uses Fourier transform profilometry (FTP), which is an imaging technique that can measure the surface profile of an object.

The FTP technology, based on image processing techniques implemented at DIAL, can measure the profile of a surface. When a pattern of straight lines is projected onto a surface the pattern is distorted, or warped by irregularities. Areas of the object that are closer to the camera cause the lines to squeeze together and areas farther from the camera cause the lines to spread apart. This difference in line spacing provides information on the shape, or profile, of the surface. If changes are being made to the surface then images of the surface need to be acquired, both before and after the change, from the same position. When the two images are compared then changes in height can be determined. It is particularly well suited, but not limited to, relatively flat surfaces.

The system consists of a standard slide projector, a digital camera (a video recorder or film camera can also be used), and a computer. The projector and the digital camera are mounted on a tripod, which can be placed anywhere from 2 feet to 30 feet from the surface in question. However, this distance affects the size of the area being imaged; a larger area can be imaged by setting up farther away from the surface. A grid of lines is projected onto the surface and an image is captured with a digital camera. The image is processed on the computer in order to determine the profile information.

The Wall Removal Monitor can be operated in harsh environments, is easily calibrated in the field in a matter of seconds and can currently run in near-real time. Advances are being made to allow the process to run in real-time. The spatial resolution (the distance between points on the surface) depends on the area of the surface being imaged. If a one square foot area is imaged, the spatial resolution turns out to be approximately 0.01 inches. For comparison, the spatial resolution of the laser-based techniques is on the order of several inches or feet. The resolution in the depth direction depends on several factors: the spacing and contrast of the grid lines; the size of the area being imaged; and the background "noise" in the image. Tak-

ing these considerations into account, 0.1 inch is a reasonable esti-mate of the depth resolution for the concrete scabbling application.

Work Accomplished

We visited Waterways Experiment Station and performed a dem-onstration of measuring defects that are generated in concrete struc-tures. The results were very good and an extensive trip report was written. A proposal to WES was written, accepted, and funded. The technology transfer has been slow due to the legal aspects involved.

The phase unwrapping technique with a new faster algorithm developed at the University of Ohio was converted to a MatLAb for-mat. A new phase unwrapping algorithm was tested, a minimum binary tree approach.

We looked at vibrating structures and made a few movie files and a phase 0 SBIR was conducted with Miltec to look at moving objects.

Conclusions

A system has been demonstrated in a real world scenario that can accurately measure large areas with a high degree of precision on "noisy" surfaces. The system has been constructed with the durability of fieldwork in mind and uses easily attainable commercial parts. All necessary calibration field measurements are quick and easy to make, and processing is in near-real time. FTP fits the role of wall removal monitor well, as it can measure a surface profile relative to the origi-nal surface. From the depth information gathered using FTP it is pos-sible to calculate volume of material removed, point-wise depth removal, and minimum and maximum depths of removal. Although a surveying method is capable of such calculations, the data is so sparse that numbers for point-wise measurements are useless. Finally, the system can be used at the job-site while the contractor is working,

potentially saving the contractor and the contracting agency time and money by preventing costly re-visits, ensuring quality, and providing accurate measurement archival.

Work Planned

We will continue to seek a commercial partner to commercialize the technology for this and other applications. New applications are being explored, and technology transfer should be completed to WES. We will continue to expand the capabilities of the system to handle other applications, especially moving objects. The intent is to make a basic measurement system capable of doing in-house and field measurements for a variety of applications.

Subtask 3.3   Pipe Decontamination

Gary Boudreaux

Introduction

The Department of Energy has radioactive and hazardous con-tamination inside many of its process piping and duct systems. Con-taminants remain in these systems after liquid is drained from them, adsorbing onto metal and other surfaces or depositing as residual liq-uids or solids. Many of the piping systems are not directly accessible because parts of them are buried underground or under concrete floors. A tube cleaning system (TCS) has been developed at Missis-sippi State University (MSU) in collaboration with the Tennessee Valley Authority (TVA) and the Southwest Research Institute (SwRI). The TCS utilizes repetitive high-voltage electrical discharges in water or other fluids to produce acoustic shock waves which are effective in removing scale, silt, and other fluid-saturated deposits from tube inner surfaces. The TCS minimizes the generation of sec-

ondary waste while at the same time minimizing worker exposure to radiation.

The TCS uses repetitive high-voltage electrical discharges in fluids (principally water) to produce acoustic shock waves. Laboratory and field testing has shown these shock waves to be very effective in removing scale, silt, and other fluid saturated deposits from the interior walls of steam condenser and heat exchanger tubes. This method is a noncontact, nonchemical method for removing these deposits. The necessary equipment, developed under this program, includes a high-voltage power modulator (i.e., power supply) to generate the high-voltage, high-current electrical pulses, and an applicator tip that can withstand the intense stresses caused by the acoustical and electrical pulses.

The arc discharge applicator tip is mounted on a coaxial cable which can be in excess of one hundred feet long. As the cable enters the pipe, it passes through a water tight bushing to prevent the egress of contaminated water. As the applicator assembly is fed into the container, the remotely located power modulator transmits electrical pulses via a long coaxial cable to the applicator assembly which produces acoustic shock waves that are directed at the interior pipe wall. The pulsed acoustic shock wave successively removes accumulated scale and other deposits as the arc discharge source is moved down the tube by the TCS operator. Foreign matter scrubbed from the wall by the shock impulse and cavitation is ejected from the wall into the water. Microscopic particles remain in suspension, where they may be removed from the water via conventional means. Field testing of the existing tube cleaning system suggests that the applicator can be fed into the pipe at rates between 0.3 and 1 ft./sec., however, the feed rate may vary considerably with application.

Work Accomplished

The interlock safety features for the front and rear doors of the second tube cleaning system, being built at DIAL, have been designed and tested. The High Voltage Lab has completed tests of the IGBT electronic modules using the test driver circuit.

National Heat Exchange Company came to MSU for a visit and demonstration. They are still interested and are planning the joint on-site demonstration at a DOE facility (Portsmith Gaseous Diffusion Plant).

We have now followed up and sent information to several companies, GTS Duratek, Schlumberger, Commerce Services Corporation, Allegheny Power and Light, MTSI, and Gap-Tech which have potential applications for the TCS.

Conclusions

The TCS has been successfully demonstrated at Sequoyah Nuclear Power Plant (TVA) and the Wabash River Coal Fired (Plant Public Service of Indiana) to clean scale and other deposits from 1-in. diameter heat-exchanger tubing. This previously developed and demonstrated technology provides an excellent basis for further developing a system that will decontaminate radiologically contaminated surfaces. This method appears suitable for cleaning and decontaminating tubes, pipes, and other cylindrical storage containers capable of containing fluids.

There are several advantages of this technique over existing technologies. The primary advantage is that the exposure of workers to hazardous and radioactive materials is minimized. This is because the cable can be fed through a bushing into the pipe so that workers do not come into contact with the material within the pipe. Further, the generation of secondary waste is minimized, or avoided. The water in

the pipes transports the scale out of the pipes. This same water can be reused to clean other pipes after the foreign matter has been separated from it using conventional means (filtration, centrifuge, settling). Since deposits are knocked off the surface of the pipe through its interaction with the acoustic wave, the use of brushes or chemicals is avoided, further reducing the generation of secondary wastes.

Work Planned

The new, improved Pulsed Acoustic Pipe Cleaner is soon to be completed at DIAL. Other safety features of the Power Modulator cabinet will be designed and tested. The solid state switch will be installed in the original power modulator cabinet at the High Voltage Lab. Pipes with different types of fouling will be cleaned with this system in order to determine the effectiveness of the TCS for different applications and to establish operating parameters. We will continue to seek a commercial partner and will schedule an on-site demonstration at a DOE facility when the initial testing of the new Pipe Cleaner is completed.

Subtask 3.4   Plasma Induction Cold Crucible Melter

J. A. Etheridge

Activities in this task have been rescheduled to a later date due to man power demands in other tasks.

Subtask 3.5   Drum Pressure Monitor

Gary Boudreaux

Introduction

At many waste sites, transuranic (TRU), low-level, and mixed wastes are stored in 55-gallon drums. Many of these drums contain hazardous, organic wastes as well. Radiolysis or other physical or chemical processes may result in gaseous emissions inside these drums. When this occurs the pressure within the drum will increase, sometimes to unacceptable levels. In more drastic cases, these emissions may produce flammable or explosive atmospheres (e.g., hydrogen from radiolysis). Currently regulatory procedures require that each drum be individually opened and inspected for the presence of hazardous organic waste. This situation will be dangerous for workers if any of the conditions described above exist (high pressure or flammable atmosphere). A non-intrusive technique that would detect any increase in pressure over ambient would alert workers of potential danger and greatly increase safety. Conversely, it would allow the segregation of suspect drums, and more rapid treatment of safe drums.

A simple, non-intrusive technique has been developed that will allow workers to determine whether a drum is pressurized. The natural frequency of the drum lid is determined by tapping the lid, recording the audible signal with a microphone, and converting the time-domain signal to a frequency spectrum using a fast Fourier transform. It turns out that the natural frequency of the lid is a function of the pressure within the drum. These results have been confirmed using Finite Element Analysis (FEA). These results are being used to design a simple, hand-held instrument that requires no specialized training to operate and works in real time.

Work Accomplished

We continue to further our understanding of how uncontrollable factors affect the measurement of pressure using modal analysis. We have collected more data on the corrosion studies and time change of the response. Also, several drum vendors were located and documented.

Commercialization of the technology with Military Technologies (Miltec) continues. MSU/Miltec submitted the proposal (SBIR) to put the technology in service. That proposal was rejected, but we are still pursuing a joint proposal (Miltec and MSU).

Conclusions

It has been demonstrated that the frequency of vibration of the lid on a 55-gallon drum is proportional to the pressure inside the drum. This dependence of frequency on pressure is being used to develop an instrument that will detect pressurization within drums. It was shown, however, that different type drums may require different calibrations, i.e. those with and without stiffening rings.[18]

The ultimate goal of this work is to design an instrument that can test drums for pressure in the field. A prototype has already been built. This instrument would ideally be hand held, utilizing a microphone, which has certain advantages over an accelerometer. By using a microphone an inspector would save time since contact with the drum would be minimized. The inspector would simply tap the drum, the signal would be recorded with a microphone that was either internal to the device or attached to a lapel, the signal would be recorded, and the inspector would move on to the next drum. Another advantage is that the spectrum from the microphone signal is usually much simpler, since many of the higher modes do not radiate acoustically. Thus, the spectrum is easier to interpret with software.

More information can be obtained from the frequency response of the lid. Although the goal is to design a simple instrument capable of quickly and efficiently locating pressurized vessels, it has been determined that the fill level of the drum can be determined from characteristics of the drum response. In addition, the time it takes for the signal to dampen can be used to distinguish between different types of contents.

Work Planned

The corrosion tests and time change of the response tests will continue. We will continue building a statistical database looking for similarities and differences between drum lids by manufacture and lot. We will continue to seek a commercial partner, and plan to re-schedule the field test.

Reference

18.   H. Patel, R.D. Costley, M. Henderson, E.W. Jones, and A. Tomlinson. 1999. Drum pressure monitor. *Review of Progress in Quantitative Nondestructive Evaluation, Vol. 18,* D.O. Thompson and D.E. Chimenti, eds. New York: Plenum Press.

Subtask 3.6   Ceramic Regenerative Heat Storage Device for Dioxin Control and Heat Recovery

C. C. P. Pian

Activities in this task have been rescheduled to a later date due to man power demands in other tasks.

Subtask 3.7   *Plasma Treatment of VOCs and Other Off-gas Components by Pulsed Micro-hollow Cathode Plasma Array*

G. Miller

Introduction

Low pressure hollow cathode devices are used for a number of applications, most commonly as a narrow-line width source lamp. The possibility of operating these devices in air at atmospheric pressure opens up a wide range of opportunities including the destruction and removal of VOCs from exhaust off-gas streams.

Operation in air is achieved by reducing the cathode opening in size down to approximately 100 microns in diameter. This study reported that, at atmospheric pressure, the electric power for a single discharge was measured at 8 W with a gas temperature in excess of 1000 K.

The device is very simple and consists of two layers of metal separated by an insulator (mica) with a hole approximately 100 microns in diameter punched through the top metal and insulator layers. A potential difference is applied across the two conductors causing the plasma discharge to form. Due to the low power requirements for each micro-hollow cathode, it is simple to connect a number of these devices in parallel to form a plasma array over which the gas to be treated is flowed.

Advantages: simple and cheap to develop, high gas temperature, can be built to the size required.

Experimental Arrangement & Analysis

A system is envisioned where TCE is introduced into an air stream passed through the plasma. Emission spectroscopy will be used to obtain information on the plasma processes. At low gas temperatures VOCs can be converted to intermediate products that may require further treatment. For example, removing CCl_4 from air using an e-beam produces phosgene as one of its end-products. The end-products will be analyzed using diode laser atomic absorption, FTIR and GCMS. The gas will then be bubbled through water to remove HCl and other end-products and then either trapped with a cold trap or vented out of the building. Subject to the results of this analysis, a plasma chemistry model will be developed to allow the rapid optimization of the technique.

VOC Candidate

While many possible VOC candidates present themselves, one example of interest to DOE, is the remediation of trichlorethylene (C_2HCl_3 or TCE). TCE is a major solvent contaminant for which alternative remediation methods are sought. TCE makes an ideal candidate for plasma remediation since it reacts in the gas phase with atomic oxygen and hydroxyl radicals, components that are efficiently manufactured in low temperature plasmas. In remediating TCE, the ideal stoichiometry is

$$C_2HCl_3 + 4OH \longrightarrow CO_2 + 3HCl + H_2 \qquad \textbf{(EQ 3)}$$

$$C_2HCl_3 + 4O \longrightarrow 2CO_2 + HCl + Cl_2 \qquad \textbf{(EQ 4)}$$

This is ideal since HCl and Cl_2 are easily removed from the gas stream by a water spray (or bubbling), H_2 and CO_2 can be simply be vented to the atmosphere. This stoichiometry is, however, difficult to achieve with high efficiency at low gas temperatures (300 - 500 K) at which most non-thermal plasmas operate. The higher gas temperature present in the MHCP will help overcome this problem.

DOE Need

SR-1017 Pollution Prevention Technologies, SR-1021 Need to Reduce the Dioxin and Furan Emissions from the CIF. ID-2.1.41 HLW Process Off-gas Treatment. ID-3.1.31.

Objectives

To build and evaluate a micro-hollow cathode array for the treatment of VOCs, using TCE as an example.

Work Accomplished

Preliminary design work was completed and purchase orders written for the power supply and vacuum components. Permission to engage a graduate student was not granted therefore progress has been delayed due to a lack of manpower.

Work Planned

Subject to time restraints and hardware delivery, assembly and testing of the system will begin.

Reference

19.   R. Block, et al. October 1998. Temperature measurement in micro-hollow cathode discharge in atmospheric air. GEO98.

Subtask 3.8   *Small Scale dc Graphite Arc Melter for Process Evaluation and Sensor Development*

J. A. Etheridge

Activities in this task have been rescheduled to a later date due to man power demands in other tasks.

Subtask 3.9   *Characterization of Dioxin Production*

J. A. Etheridge

Introduction

Many tests have been performed, and the results published by a number of authors, in an effort to characterize the production of dioxins and furans in municipal waste incinerators. The results of these tests are often contradictory and confusing. Bench scale systems are often used for a test bed; however, the results may give some indication, but may not adequately scale up to represent the actual mechanisms at work in a full scale system. Full scale incinerators are also used for dioxin testing, and although they can give good results, they are not the well controlled environment which would be ideal for conducting mechanistic dioxin studies.

DIAL's combustion test stand can be a pilot scale simulator for a municipal waste incinerator. It is well characterized and extremely well controlled. With the addition of an isothermal test section, it is being used to perform a mechanistic study of dioxin production.

Work Accomplished

DIAL's combustion test stand has been reconfigured and initially characterized to conduct pilot scale mechanistic studies for dioxin formation. For this experimentation, the test bed was configured to produce gas stream temperatures in the range of 300 to 700°C in a specially designed, virtually isothermal eight-foot long test section positioned approximately 20 feet downstream from the combustor. In this configuration, the test bed has an eight-inch inside diameter for its entire length and provides a gas stream flow rate of approximately 600 pounds/hour.

Preliminary testing has commenced with determination of ash feed rates and extractive sampling times. Particle loading has been monitored using a transmissometer to verify the consistency of the ash feed rate. Both EPA Method 23A and high grain loading impactors have been employed for sample collection. Additionally, capabilities to tailor collection of CO, CO_2, O_2, NO, and hydrocarbons analyzer data have been demonstrated. The off-gas data, taken on several different days, shows a high degree of consistency in gas stream chemistry. Gas samples have been collected from different locations and analyzed by GC/MS to provide insight into the BTEX PICs present in downstream test stand sections as a function of the fuel to air ratio. Fly ash from Illinois # 6 coal, fluidized bed bottom and fly ash from combustion of lignite, and bottom ash from a medical waste incinerator have been characterized with regard to dioxin/furan congener concentrations. Additional characterization of particle size distributions and elemental composition have also been performed. Fly ash that is virtually free of dioxins has been injected into flame and post flame zones followed by downstream collection using a Method 23A sampling train to evaluate any influences caused by injection location. No differences were determined for the fuel to air ratios studied. Proof of scale testing was conducted to identify injection and sampling locations, in conjunction with off-gas chemistry and temperature profiles for studying dioxin formation from chlorophenols.

Fly ash with low dioxin concentrations was doped with pentachlorophenol and fed into an isothermal section of the test stand. Detectable levels of dioxins were present in Method 23A samples collected and dioxin levels were proportional to the level of dopant used.

The initial work on this task was presented at the IT3 Conference in Orlando Florida.[20]

Work Planned

The testing phase of this project will continue in the first quarter of 2000.

Reference

20.   J. Etheridge, R. ArunKumar, D. Miles, C. Waggoner, R. Wiser, T. Meaker and J. McCown. 1999. *Studies to reduce the uncertainties associated with the temperature and metal content dependence of dioxin/furan concentration in MSWI fly ash.* IT3 Conference, Orlando, FL.

Subtask 3.10 Evaluation of Continuous Emission Monitors ~ Laser Induced Breakdown Spectroscopy

C. F. Su, F. Y. Yueh and J. P. Singh

Introduction

LIBS is a laser-based, nonintrusive, and sensitive optical diagnostic technique for measuring the concentration of various atomic and molecular species in test media.[21,22] It uses a high power laser beam to produce a laser-induced plasma at the test point. The plasma atomizes and electronically excites the various atomic species present in the

test volume in a single step. The intensities of the atomic emission lines observed in the LIBS spectrum are used to infer the concentration of the atomic species. Over the past years, we have obtained sufficient experimental data to satisfactorily identify the elements present in the vitrified glass samples, to infer the elemental physical quantities, and to observe the effects on their spectral intensities under various experimental conditions. The glass samples used for the project were produced by an EnVitCo joule-heated glass melter at Clemson University and Westinghouse Savannah River Company's Transportable Vitrification System. Besides identification of the elements in the samples, the plasma temperatures, electron densities, and concentration ratios of elements to iron have been evaluated at different sample temperatures. The effects of both the various sample temperatures and the melting temperatures of the elements on the spectral intensities have been studied as well.[23]

Work Performed

During this work period, the relationship between the spectral intensities and the concentrations of the elements in different samples was investigated. In principle, at a certain sample temperature for a given emission line, the spectral intensity is linearly proportional to the elemental concentration present in the sample. However, the matrix effects, excitation condition, and other factors may affect the accuracy of measurements. Five different aluminum alloys with known concentrations of elements were used for the preliminary investigation. The setup used for the LIBS measurements is shown in Figure 11. LIBS data of the different samples were recorded under the
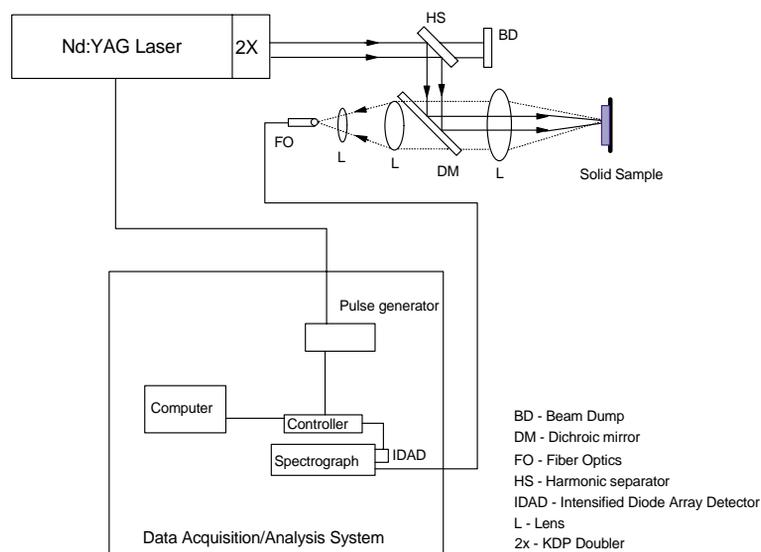
FIGURE 11. LIBS experimental setup.

same laser energy and detection gate. Figure 12 shows a LIBS spectrum of an aluminum alloy at the spectral region of 341 nm. The identified emission lines are marked in the plot. Data were also collected at various wavelength ranges. The emission lines with minimum spectral interference were chosen for the calibration study. The intensity of analyte lines for different samples were used to construct the calibration curve. Figure 13 show a calibration curve for Cu in Al alloy. The calibration curve for Cu 324.75 nm is linear up to 1.6 Wt%. At higher Cu concentration, self-absorption of this resonance line occurs and causes the slope changes. Due to the problem of self-absorption, this calibration curve can only be used for Cu concentration below 1.6 wt percent. A calibration curve from an alternate Cu line (nonresonance line) will need to be constructed for high Cu concentration measurement.
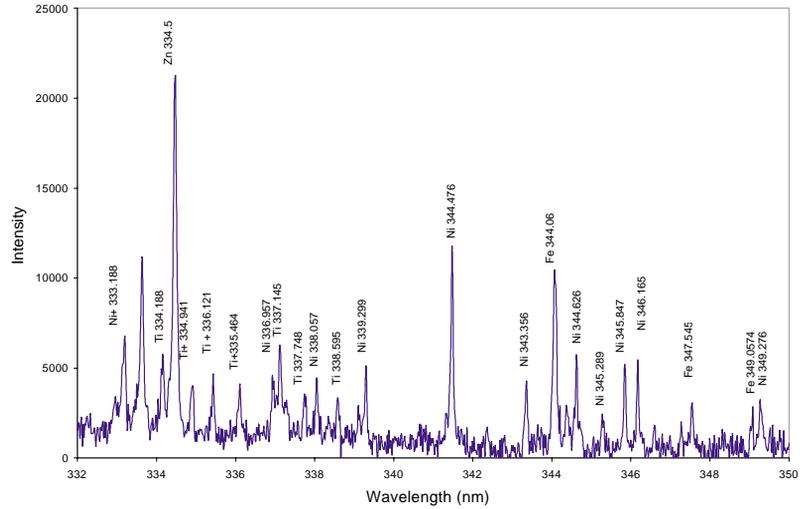
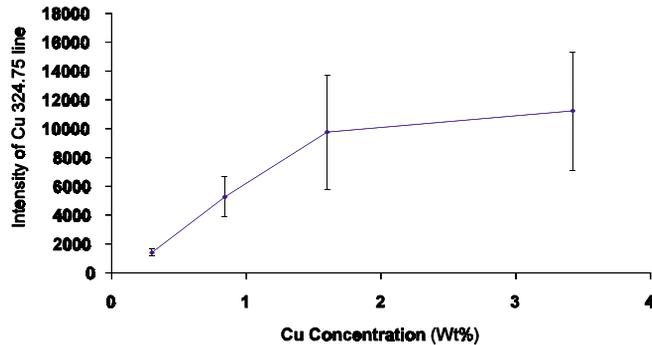**FIGURE 12. LIBS spectrum of aluminum alloy.**

FIGURE 13. Calibration curve for Cu in alloy.

Work also began on the feasibility study of applying ANN to analyze LIBS data of solid samples. The glass and melt glass data collected at different conditions were used to train neural network. The neural network learns to recognize these correct patterns using a mathematical model. After being trained to recognize input patterns,

the neural network can make good decisions even for new and unfamiliar patterns.

Work Planned

The feasibility study of applying ANN to analyze LIBS data of solid samples will continue. LIBS calibration data for Al samples will be collected at different experimental conditions. Studying of the effects of gas stream conditions to LIBS measurement will continue in a DIAL mini-test stand.

References

21.   D.A. Cremers and L.J. Radziemski. 1987. Laser plasmas for chemical analysis, in *Laser Spectroscopy and its Application,* L.J. Radziemski, R.W. Solarz, J.A. Paisner, eds. New York: Marcel Dekker. Ch. 5, p.351.

22.   L.J. Radziemski and D.A. Cremers. Spectrochemical analysis using plasma excitation, in *Laser Induced Plasmas and Applications,* L.J. Radziemski and D.A. Cremers, eds. New York: Marcel Dekker. Ch. 7, p. 295-326.

23.   C.F. Su, S. Feng, J.P. Singh, F.Y. Yueh, J.T. Rigsby, D.L. Monts, and R.L. Cook. In press. Glass composition measurement using laser-induced breakdown spectroscopy. *Glass Technology*.