
*Instrumentation Development,
Measurement and Performance
Evaluation of Environmental
Technologies*

**Quarterly Technical Progress Report
for the period
October 1, 1999 - December 31, 1999**

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Table of Contents

Executive Summary	1
Task 1. Instrumentation Development	1
Task 2. Measurement Support.	2
Task 3. Performance Evaluation	2
TASK 1. Instrumentation Development	5
Air Plasma Off-gas Emission Monitor	6
Detection of Toxic Compounds by Cavity Ring-Down Spectroscopy	15
Volatile Organic Compound Monitoring Using Diode Lasers	16
Laser Induced Fluorescence Spectrometry of Radionuclides	21
Cavity Ringdown Monitors for Transuranic Elements	25
Feasibility of Characterizing Solid Wastes by Remotely Sensed Multi Spectral Images.	28
Guided Wave Nondestructive Evaluation Technique Development and Demonstration	31
TASK 2. Measurement Support	37
Diagnostic Field Applications Coordination and Testing Support	37
On-line Imaging for Thermal Treatment Processes	40
TASK 3. Performance Evaluation	7
Dissolution of Hanford Salt.	48
Wall Removal Monitor	59
Pipe Decontamination	61
Drum Pressure Monitor.	64
Plasma Treatment of VOCs and Other Off-gas	

Components by Pulsed Micro Hollow Cathode	
Plasma Array	65
Laser-induced Breakdown Spectroscopy	68

List of Figures

FIGURE 1.	APO-GEM schematic diagram	8
FIGURE 2.	Experimental configuration for diode laser absorption spectrometry	18
FIGURE 3.	Absorbance measurements for pure chlorobenzene with diode laser temperature set at 35 C	20
FIGURE 4.	Absorbance measurements for chlorobenzene in 730 Torr of air with diode laser temperature set at 35 C	20
FIGURE 5.	Schematic of the laser induced fluorescence spectrometry technique	23
FIGURE 6.	Schematic of isotopic energy shifts and the associated LIF spectrum	23
FIGURE 7.	Schematic of infrared diffuse reflectance multi- spectral imaging technique	29
FIGURE 8.	Schematic of spectral imaging system and conventional emission spectrometry system used for proof of concept experiments performed using the DIAL combustion test stand	42
FIGURE 9.	Spectral image of sodium at 589 nm recorded on the DIAL combustion test stand and the resulting histogram of pixel intensities within the selected area of interest.	44
FIGURE 10.	Calibration curve of injected sodium concentration vs. average pixel intensity within the user selected area of interest, obtained from DIAL combustion test stand experiments. Error bars correspond to one standard deviation	44
FIGURE 11.	ESP and SOLGASMIX calculations for Natro- phosphate, 25°C	52
FIGURE 12.	SOLGASMIX calculations and selection of the experimental concentrations for the 25°C 1-m hydroxide compositions	53
FIGURE 13.	Experimental results for the data from Figure 12 compared to the theoretical predictions	55

FIGURE 14. Solids compositions from the data in Figure 13 56

FIGURE 15. Temperature dependence of the solubilities for the
Na-F-PO₄-OH system 57

FIGURE 16. Schematic of the optical fiber LIBS system 69

FIGURE 17. Results of the long-term durability test for a 1-mm
core diameter UV fiber 70

FIGURE 18. LIBS spectrum of a stainless steel tube obtained with
the fiber optic LIBS probe. 71

List of Tables

TABLE 1.	Detection limits for the APO-GEM for various metals. . 10
TABLE 2.	Relative accuracy of DIAL Air-ICP data 11
TABLE 3.	Analysis results for RM-29 sampling and the continuous sampling Air-ICP CEM at DIAL 12

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.

Air plasma off-gas emission monitor. We evaluated the Technical Peer Review Report findings and recommendations that arose from the AMSE Technical Review of the “Development of a Multi element Metal Continuous Emissions Monitor” that 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 largely mirror the research program already underway at DIAL. The additional recommendations not already in place were incorporated into the research plan. Instituted a

search to find a replacement for Dr. Zhu. The position was filled with the hiring of Dr. Tao. Preparations were begun for testing of the reduced pressure air-ICP, being developed in collaboration with Ames Laboratory (Dr. David Baldwin), scheduled for August/September 1999 at DIAL. A paper was submitted to the Journal of Air and Waste Management Association.

Volatile organic compound monitoring using diode lasers. Diode laser absorption spectroscopy was employed to carry out measurements of trace quantities of chlorobenzene under vacuum conditions and in atmospheric-pressure air. To our knowledge, these are the first such measurements. The results obtained correlated well with our previous atmospheric pressure measurements for benzene. As with our benzene studies, these efforts indicated that atmospheric pressure broadening does not negatively impact our ability to measure chlorobenzene in air. Due to the better overlap of our laser wavelength with the chlorobenzene absorption, our detection limits for chlorobenzene were improved over those obtained for benzene.

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.

Dissolution of Hanford Salt. Experimental results are presented for the Na-F-PO₄-OH system. This data is critical since two of the three molecular components, trisodium phosphate and natrophosphate have a tendency to form large crystals that may lead to pipe fouling and eventual plugging of transfer lines. The data are briefly compared with the theoretical predictions from two different thermodynamic models. Additional fitting of the data followed by the development of a reference database will improve the ESP predictions for this important system.

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.

Drum pressure monitor. 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 VOCs and other off-gas components by pulsed micro-hollow cathode plasma array. 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.

Laser-induced breakdown spectroscopy. An all-optical fiber LIBS probe was built for glass measurement in the thermal waste process facility. The optical fiber for transmitting the laser beam was tested to determine its capability to withstand high laser energy for a long period of time. To evaluate the performance of the optic fiber LIBS system, LIBS measurements of solid sample were made using this optical fiber LIBS probe.

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 initiated. 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.

Air Plasma Off-gas Emission Monitor

G. 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, N₂⁺) 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 ongoing 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.

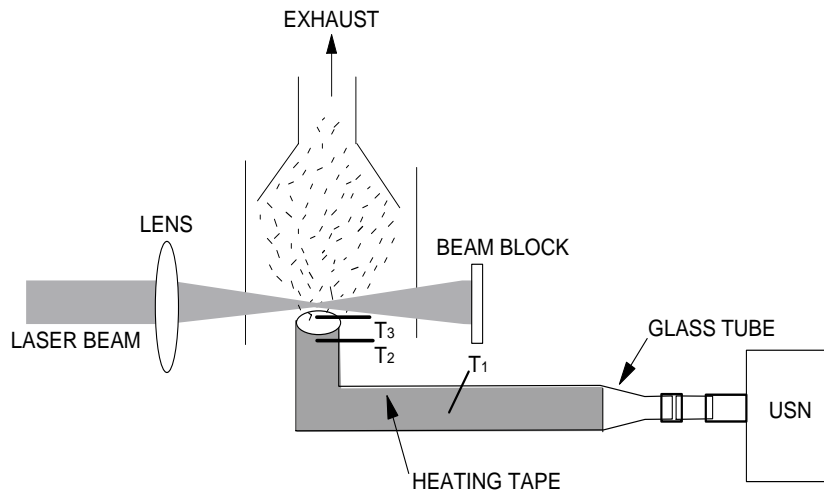


FIGURE 1. APO-GEM schematic diagram.

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 ($\mu\text{g}/\text{m}^3$). This concentration is determined from

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

where C_A is the aerosol concentration ($\times 10^3 \mu\text{g}/\text{m}^3$), C_s is the standard solution concentration ($\mu\text{g}/\text{g}_{\text{solv}}$), u is the solution uptake to the ultrasonic nebulizer, F is the air flow rate to the plasma, and ε is the 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 compar-

ison of the laboratory 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 ($\mu\text{g/dscm}$)
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

Analytical results for the RM-29 samples collected during the testing of the continuous-sampling at DIAL were received after completion of the last quarterly report and are included below. A certified, off-site analytical laboratory obtained these results, using standard analysis methods to determine the metal concentrations for the solu-

TABLE 3. Analysis results for RM-29 sampling and the continuous sampling Air-ICP CEM at DIAL.

RM-29 Results ($\mu\text{g}/\text{dscm}$)			
	Run 1	Run 2	
Beryllium	70	73	
Cadmium	75	87	
Chromium	60	63	
Lead	70	74	
Mercury	66	-	

Continuous Sampling Air-ICP Values ($\mu\text{g}/\text{dscm}$)			
	Run 1		Run 2
	RM-29 Sampling	Calibration Spiking	
Beryllium	73	52	-
Cadmium	-	-	-
Chromium	63	57	-
Lead	56	44	-
Mercury	-	-	-

Difference (%)			
	Run 1		Run 2
	RM-29 Sampling	Calibration Spiking	
Beryllium	(+)4.3	(-)25.7	-
Cadmium	-	-	-
Chromium	(+)5.0	(-)5.0	-
Lead	(-)20.0	(-)37.1	-
Mercury	-	-	-

tions collected during the DIAL test. The results for Be, Cd, Cr, Pb, and Hg are listed in Table 3, for the two RM-29 sample sets collected on September 16, 1999. The values for all five metals are fairly con-

sistent, with most of the determined values between 60 and 75 $\mu\text{g}/\text{dscm}$. For Run 1, the average value for the five metals is 68.2 $\mu\text{g}/\text{dscm}$, and the relative standard deviation (rsd) is 8.2%. For Run 2, the average value for the four metals (Hg was not determined) is 74.3 $\mu\text{g}/\text{dscm}$, and the rsd is 13.3%. The higher average and rsd for Run 2 are primarily due to the higher values obtained for Cd.

The aerosol concentrations determined by continuous sampling air-ICP for Be, Cr, and Pb are listed in Table 3. Cadmium and Hg were not detected using the air-ICP system during the testing at DIAL, so no values are tabulated for these metals. As discussed in last quarter's report, the detection limits for Cd and Hg during the testing at DIAL were poorer than laboratory determined air-ICP values, and higher than the RM-29 measured aerosol concentrations for these metals. For Be, Cr, and Pb, two values are listed in Table 3 for RM-29, Run 1. The "calibration spiking" column lists the values obtained for the time scan monitoring and calibration spiking experiments performed after the RM-29 sampling. The "RM-29 sampling" column of air-ICP values lists the metal aerosol concentrations for the time scan monitoring performed during the RM-29 sampling period, calculated using the calibration curves obtained from the spiking experiments. The air-ICP aerosol concentrations listed in Table 3 were calculated using measured values for the ultrasonic nebulizer efficiency and gas flow rate through the Teflon sampling chamber, obtained at the completion of testing at DIAL. The difference in the measured and estimated nebulizer efficiency (14.2% and 15%, respectively), accounts for the difference in the calculated and measured sampling chamber gas flow rates (22 and 20.75 L/min) reported in the body of test report. No air-ICP concentrations for Be, Cr, and Pb are listed in Table 3 for the second RM-29 sampling period. These three metals were detected using the continuous sampling air-ICP system during the second RM-29 run on September 16 at levels comparable to the values measured during Run 1, but no calibration spiking experiments were performed during or after this sampling period. In addition, a change in the optical alignment of the 0.2-m monochro-

mator-echelle spectrometer made at the beginning of RM-29 Run 2 making the calibration curves for Be, Cr, and Pb obtained for Run 1 invalid for Run 2.

For Be, Cr, and Pb, higher air-ICP signal intensities were measured during the RM-29 sampling period than those measured later, during the calibration spiking experiments that were done. Therefore, the RM-29 air-ICP determined aerosol concentrations listed in Table 3 are higher (73, 63, and 56 $\mu\text{g}/\text{dscm}$ for Be, Cr, and Pb) than the calibration spiking values (52, 57, and 44 $\mu\text{g}/\text{dscm}$, respectively). The reason for this difference is not known but is being investigated. The sampling probe used for the RM-29 sampling was removed from the stack after RM-29 Run 1, prior to the air-ICP calibration spiking experiments. This may have caused differences in the stack gas flow patterns in the vicinity of the air-ICP probe for the calibration spiking experiments compared to the RM-29 sampling time period. After the RM-29 probe was removed from the stack, the Roots blower speed was reduced slightly to re-establish the same gas flow rate into the axial channel of the ICP torch (0.3 in. of water differential pressure indicated on the oil filled manometer) that was used during the RM-29 sampling period. As discussed in test report, if calibration spiking experiments had been performed during and after the RM-29 sampling (rather than only after the sampling period), more insight into the likely reasons for the differences between the calibration spiking and RM-29 air-ICP results would have been obtained. The accuracy of the air-ICP determined aerosol concentrations compared to the RM-29 results is also listed in Table 3. For Be and Cr, the air-ICP concentrations determined during the RM-29 sampling period are about 5% higher than the RM-29 results; for Pb, the air-ICP determined concentration is less accurate, 20% lower than the RM-29 value. The reason for the poorer accuracy for Pb, compared to that for Be and Cr, is not known. The calibration spiking air-ICP aerosol concentrations for Be, Cr, and Pb, determined after the RM-29 sampling period, are about 5 - 40% lower than the RM-29 results.

Future Work

A small spectrometer has been ordered as a temporary replacement for the broken AOTF. The cost of multi frequency AOTF replacement has been included in next year's budget. The spectrometer will be used to continue development of the system until it arrives. In the meantime, work will focus on evaluating the Hg lamp-echelle spectrometer as an elemental mercury monitor.

Reference

1. D.P. Baldwin, D.S. Zamzow, D.E. Eckels, R. Wiser, S-Q. Tao and G.P. Miller. September 1999. Testing of a Continuous Sampling Air-ICP System as a Continuous Emission Monitor at the Diagnostic Instrumentation and Analysis Laboratory. Ames Laboratory-US DOE Report IS-5138.

Detection of Toxic Compounds by Cavity Ring-Down Spectroscopy

Ram Vasudev

Introduction

The goal of this project is to apply cavity ring-down spectroscopy (CRDS) to the detection of toxic compounds, the current emphasis being on chlorinated organic compounds of environmental concern. For a general description of the technique and experimental setup, the reader is referred to our earlier reports.

Recent Work

Work is continuing on acquiring spectra of chlorinated aromatics by CRDS and on improving the detection limits. We are finding that

the absorption wavelengths are quite sensitive to the location of chlorine substituents on the phenyl ring (i.e., the molecular structure). In addition, the band shapes (rotational contours) are also sensitive to molecular structure. These spectroscopic properties will be useful for distinguishing different toxic compounds (including structural isomers) in eventual field experiments. Work is also continuing on spectroscopic simulation programs for comparison of experimental results with calculations. These results will be the subject of a paper to be submitted for publication.

Future Plans

Work will continue on toxic compounds of interest to DOE and those in EPA's TRI list.

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 (VOCs). 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 \$108M 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 VOCs 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 VOCs 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 are focusing 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 con-

trollers 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 beam splitter 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.

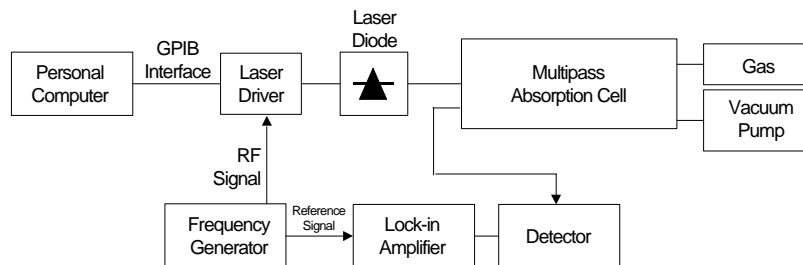


FIGURE 2. Experimental configuration for diode laser absorption spectrometry

Work Accomplished

The system depicted in Figure 2 was employed to make measurements of trace levels of chlorobenzene under vacuum and in air in a

similar manner to benzene measurements reported in our last quarterly report. The volume ratio sample introduction system described in last quarter's report was again used to provide small concentrations of chlorobenzene in near atmospheric pressure air.

Figures 3 and 4 depict the results of chlorobenzene absorption experiments carried out using 1656 nm light in vacuum and in 730 Torr of air, respectively. The 730 Torr pressure is just slightly below atmospheric pressure so that the sample will not leak from the vacuum cell. This slight reduction has no significant effect on the results, as is evidenced by comparison of Figures 3 and 4. The change from vacuum to higher pressure experiments does not decrease the sensitivity of the measurements for chlorobenzene, as is evidenced by the similarity in the slopes for the linear fit in each figure. While this may seem counter to usual experience, the basis for this result is that the chlorobenzene spectrum is already very broad even at low pressures due to overlapping rotational transitions. Hence, the broadening of individual rotational lines does not cause a reduction in sensitivity. Note that the scatter observed for previous benzene experiments is significantly reduced in Figures 3 and 4. While benzene rapidly adsorbs onto the cell surfaces, thus changing its partial pressure very rapidly, chlorobenzene is much more stable. Thus the reduction in scatter is actually due to an increased accuracy of the pressure measurement, and not the absorption measurement itself. Although the wavelength of the laser used for these studies was not optimized for chlorobenzene detection (the laser was constructed for monitoring CH₄), an atmospheric pressure detection limit of 54 ppm for chlorobenzene in air was achieved for the 47.6-meter pathlength sample cell configuration used here. By obtaining a laser constructed for the maximum absorption wavelength of chlorobenzene, and by focusing on electronic noise reduction, this detection limit could readily be lowered by up to an order of magnitude.

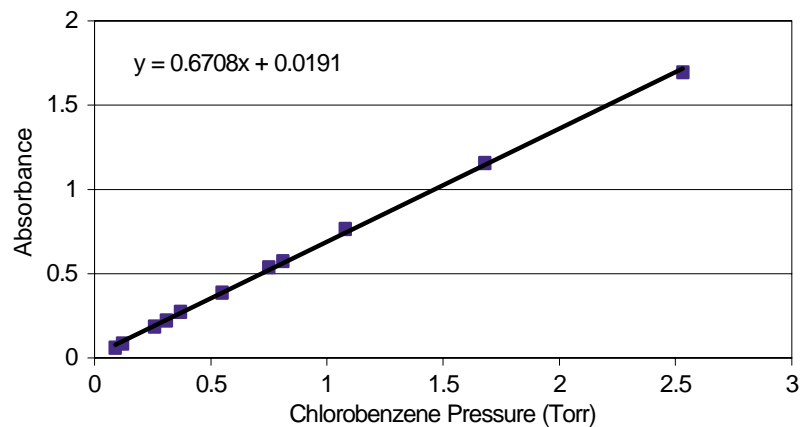


FIGURE 3. Absorbance measurements for pure chlorobenzene with diode laser temperature set at 35 C.

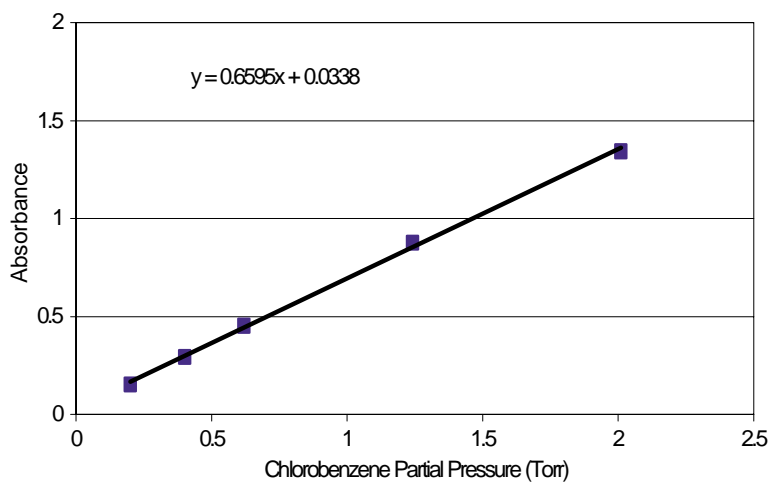


FIGURE 4. Absorbance measurements for chlorobenzene in 730 Torr of air with diode laser temperature set at 35 C.

Work Planned

In the next quarter, we will continue our efforts to develop methods for increasing the sensitivity of these diode laser measurements further. While the simple absorption experiments carried out thus far could easily be extended to a sensitivity level sufficient for making indoor air quality monitoring measurements, the detection limits must be lowered significantly for continuous emission monitoring from incinerator stacks. We will investigate methods available for achieving these lower detection limits, including methods such as diode laser cavity ringdown spectroscopy, and will design a system for construction in our next fiscal year.

Nomenclature

VOC: Volatile Organic Compound

CEM: Continuous Emission Monitor

FM: Frequency Modulation

Laser Induced Fluorescence Spectrometry of Radionuclides

David L. 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. 5), an electronic state of the species of interest is excited with a tunable laser and the resulting fluorescence 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. 6). 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.

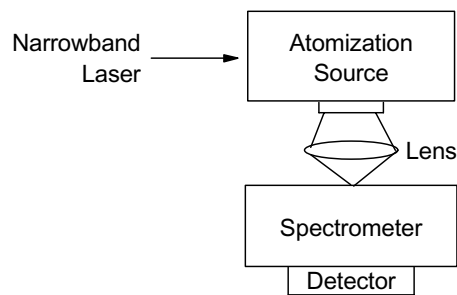


FIGURE 5. Schematic of the laser induced fluorescence spectrometry technique.

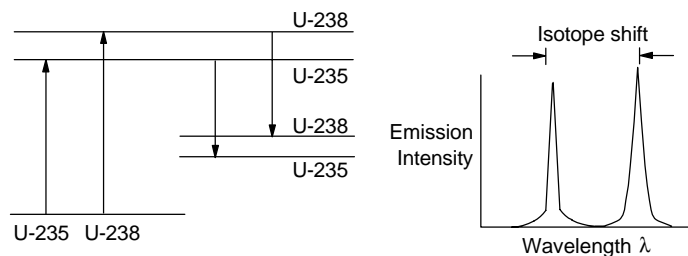


FIGURE 6. Schematic of isotopic energy shifts and the associated LIF spectrum.

Work Accomplished

In order to make progress on the use of LIF for isotopic determination of TRU elements, there are three prerequisite needs that must be met. The first is the capability to work with actinides, such as uranium. Mississippi State University's license has been extended to permit controlled usage of elements with atomic numbers in the range of 84 (Po) through 98 (Cf). The license extension was granted to the uni-

versity, and the university had the required capabilities to begin implementing the license in July. An application to the university's Radiological Safety Committee for permission for us to perform the laser induced fluorescence spectrometry experiments on dilute uranium solutions was approved during August, contingent upon us having in place a dedicated vent line and standard capabilities for routinely working with radiological samples. Construction of the dedicated vent line began and was almost completed; delay in delivery of HEPA filters for the vent line precluded completion during this quarter.

The second prerequisite need is the need for a sufficiently hot atomization source in order to efficiently atomize uranium. During January, an ICP atomization source was ordered with a promised delivery date in May. This ICP atomization source was not delivered during May; in fact it was not delivered during either the second or third quarter of 1999. Because of the prolonged delay in delivery of this essential piece of equipment, progress on this project was severely hampered during this quarter since the next group of experiments require this equipment. Therefore during this quarter we concentrated most of our efforts on our other projects for DOE.

Work Planned

When the ICP atomization source is received, we will begin a series of experiments to optimize operation of the ICP system initially using argon as the carrier gas and surrogates and then uranium as the analyte species.

The third prerequisite need for successful completion of this project 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 in an ICP plasma. If, as expected, these LIF experiments prove that such a mod-

erately 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.

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

Cavity Ringdown Monitors for Transuranic Elements

C. P. Winstead and G. P. Miller

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 restrictions, no cavity ringdown measurements for uranium or transuranic elements were carried out during this time period. However, the permitting process is very nearly complete and final approval for the use of uranium is expected in early 2000. A new ventilation system with HEPA filtration was installed to provide a separate exhaust pathway for uranium. We have continued to optimize the operating parameters for our inductively coupled plasma system to enable its use as an efficient atomization source. These efforts have primarily focused on mercury during this reporting period. However, the experience gained in developing cavity ring-down for other elements will be directly applicable to measurements for uranium and eventually other transuranic species.

Work Planned

Final regulatory approval for our use of uranium is expected in early 2000. As soon as possible after receiving approval, we will begin our optimization experiments for detecting uranium in an inductively coupled plasma. This will require converting our laser system from the present configuration used for mercury studies to the longer wavelengths needed for uranium. The pump wavelength from the Nd:YAG laser will be changed and the optics in the dye laser will be replaced. To attempt isotopic resolution we need to achieve the absolute minimum linewidth possible from the dye laser. Thus, significant effort likely will be needed to optimize the laser realignment. This is the only major modification required for the uranium work to commence. Pending regulatory approval and the completion of our mercury investigations, this modification will begin.

Feasibility of Characterizing Solid Wastes by Remotely Sensed Multi Spectral Images

David L. Monts

Introduction

Purpose

Characterization capabilities for site specific wastes are needed for the DOE nuclear waste cleanup 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 nonintrusive characterization. Currently however, comprehensive nondestructive 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 $[\text{Al}_2(\text{Si}_2\text{O}_5)(\text{OH})_4]$. 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 nonintrusive, nondestructive 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 com-

pounds. 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 7, 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 multispectral 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.

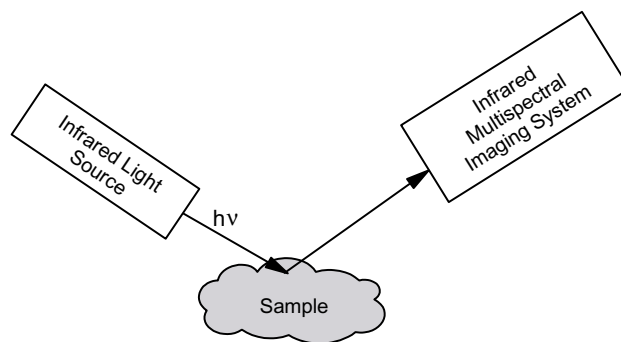


FIGURE 7. Schematic of infrared diffuse reflectance multispectral imaging technique (final configuration).

Work Accomplished

During this period, we found that the available infrared light sources did not have sufficient intensity for the proposed experiments and have utilized available funding to place an order for a high intensity infrared light source with an anticipated delivery of four to six weeks after receipt of order.

Work Planned

When the high intensity infrared light source is received, we will initiate a series of experiments using several known, pure compounds that can be expected to be present in the waste streams.

Nomenclature

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

Guided Wave Nondestructive Evaluation Technique Development and Demonstration

Krishnan Balasubramaniam

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

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 ongoing 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.

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. 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. The long range propagation and detection of the plate wave modes have been optimized and their interaction with defects have been reported. Measurements of 100 meters or more have been demonstrated. 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

Process Monitoring Sensor. An 18 inch long graphite rods with zirconium coating was design, procured and tested under simulated high temperature conditions at DIAL. Graphite coated with zirconia was tested as the material of choice for the design and fabrication of buffer rod. The coating process was not very reliable due to thermal expansion, contrary to the claims made by the coating process vendor. This lead to the oxidation of the graphite rods. Alumina does not have this problem, but when dealing with long rods, the attenuation in the rod changes with temperature and becomes an issue beyond 1000 C.

Guided Wave Tank NDE Technique. The modeling of the ultrasonic waves using ANSYS code was further developed. The FEM code was further studied to simulate the wave propagation in pipes and the issue of interaction of ultrasonic waves with cracks and interfaces. Also, corrosion damage modeling was investigated. This is a complex problem since there a myriad types of corrosion damage.

Conclusions

The buffer rod material problems remain the key to solving the problem of long distance access to the melt. The technique has been demonstrated using short buffer rods and hence there is confidence in the technology.

Based on the initial results from the guided wave modeling, there is a significant scope for the generation and propagation of guided plate waves in tank walls. Although modeling of corrosion is feasible, it may not be possible to cover all types of corrosion. The effect of

concrete and soil which may be loading the metal tank wall must be investigated.

Project Status

All tasks in the projects are currently active.

Work Planned

Process Monitoring Sensor. It is planned to investigate other types of coatings and buffer rod materials which can withstand high temperatures.

Guided Wave Tank NDE Technique. The modeling of defects in solids will continue. Incorporation of external loading in the form of soil and concrete will be completed by the next quarter.

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.

Diagnostic Field Applications Coordination and Testing Support

Robert L. Cook

Introduction

The Dfacts effort provides a mechanism for improved industrial participation by directly soliciting participation by industries developing diagnostic instruments. In this way, untapped resources from the commercial sector for new diagnostic instrumentation and/or off the shelf instruments can be recruited and utilized. Demonstrations and testing are done in conjunction with DIAL's field tests and via special arrangements making use of other DOE test beds. Hence, a wider array of diagnostic systems can be tested/evaluated. By making

use of DIAL's mobile field laboratories, rapid response can be provided at a low cost. With a relatively small added investment, a significant value added benefit can be obtained from the wide array of testing being carried out across the complex.

Work Accomplished

We have recently sent some 50 letters describing the Dfacts program to various program leaders and facility managers. Also, discussions were held with visitors from the MWFA and CMST on ways for the Dfacts program to contribute to their efforts.

A number of needs for the MWFA and CMST-CP have been identified which can be addressed by the Dfacts program and these are outlined below. Exact scheduling will be determined in consultation with appropriate DOE and facility representatives.

PM CEM testing at TSCAI began this past summer and is expected to be completed in March. DIAL personnel and capabilities via DIAL's Dfacts program can provide substantial contributions to the success of these and future tests. DIAL will work with TSCAI and MWFA/CMST representatives to determine a mutually beneficial role. For example, DIAL personnel could observe and critically assess the operation of the PM monitors and the baseline methods with respect to the installation and selection of monitors for the demonstration at WERF.

Work Planned

The PM CEM demonstration at WERF is planned for FY 00. DIAL personnel via DIAL's Dfacts program can aid in: the selection of the PM CEMs to be evaluated; in the actual performance of the demonstration at WERF; and in the data analysis and reporting. The demonstration is expected to determine the performance capabilities

of the PM CEM, focusing particularly on how its performance measures up to the EPA Performance specifications (and/or Guideline) for PM CEM.

Reliable standards must be developed and introduced into the off-gases at known concentrations. In particular, elemental mercury and mercuric chloride gas phase standards are needed. Similarly, polydisperse standards and multimetal standards are needed together with procedures to introduce these standards into the off-gas stream for the calibration of CEMs. DIAL can, via the Dfacts program, assist in preparation for proposed Hg CEM testing at TSCAI. DIAL personnel can work closely with TSCAI personnel on compliance issues concerning the correlation of CEM data with laboratory reference method test and calibrating the CEMs in accordance with the recently promulgated MACT Rule. Long term operational performance, reliability, and maintenance requirements and issues can also be addressed in the selection of Hg CEMs at TSCAI (and other DOE incinerators) for permanent deployment.

Visits to several DOE incinerators are planned for February. In addition, we will attend the Mixed Waste Focus Area End User Program Review to be held on February 8 and 9, 2000 in Salt Lake City. We will use this opportunity to introduce the Dfacts program to the participants of this meeting.

On-line Imaging for Thermal Treatment Processes

David L. Monts

Introduction

Purpose

Many of the DOE waste streams, particularly those currently stored in steel barrels, are poorly characterized or even uncharacterized. Given the variety of contents that can dramatically vary from barrel to barrel, it is necessary for thermal treatment systems (TTS) to quickly change operating parameters and/or implement divert and treat measures when specific species of environmental concern (such as mercury) are suddenly introduced into the TTS. It is desirable to monitor species of concern inside the primary TTS chamber in order to provide the maximum possible response time and because concentrations will be higher here and hence easier to detect.

Digital images contain a wealth of information that if extracted, could be of immense value for monitoring/controlling a process. Imaging spectroscopy combines conventional imaging, spectroscopy, and radiometry technologies to produce images for which a spectral signature is associated with each spatial resolution element (pixel). The emphasis of this project is on extending previous work to include extraction of information on concentrations, concentration distributions, and other parameters of use for process control of thermal treatment systems of interest to DOE. Using visualization and neural network techniques, the information can be presented in such a manner as to assist decision making. Extraction of information from the primary thermal treatment chamber will provide sufficient time for operational parameters to be changed to maintain optimum operational performance and/or to allow divert and treat actions to be taken for species of environmental concern. Previous work at DIAL has

shown utility of digital images for visual display of thermal distribution contours and for determination of average temperatures.

Methodology

Combining spectral and spatial analyses allows application of imaging technology to species characterization and detection inside primary chambers of thermal treatment sources for mixed hazardous waste processing. We are developing a spectral imaging system by combining a charge coupled device (CCD) camera with narrowband optical filters. For the proof of concept experiments, a series of narrowband interference filters are utilized to obtain images of the combustion chamber at wavelengths characteristic of selected metal species. Subsequent efforts will employ an acousto-optic tunable filter (AOTF) in order to significantly increase the number of different wavelengths (and hence species) that can be monitored by the imaging system. The digital images are analyzed using commercially available software that has been modified to meet the needs of this project. We are also developing the methodology to calibrate the spectral imaging system. Analysis of the spectral images will be combined with neural network techniques in order to provide facility operators with practical information on a time scale short enough to enable process control decisions to be made.

Work Accomplished

We have assembled a prototype spectral imaging system by using narrow band interference filters and available CCD cameras. The spectral imaging system was tested by monitoring the concentration and concentration distribution of selected metal species (such as Eu, Mn, Hg, Na, K) in a laboratory flame; calibration curves were obtained for selected metal species. Commercially available image processing software has been modified to extract information about concentrations of selected metal species from spectral images. The

methodology to calibrate the spectral imaging system has also been developed and tested.

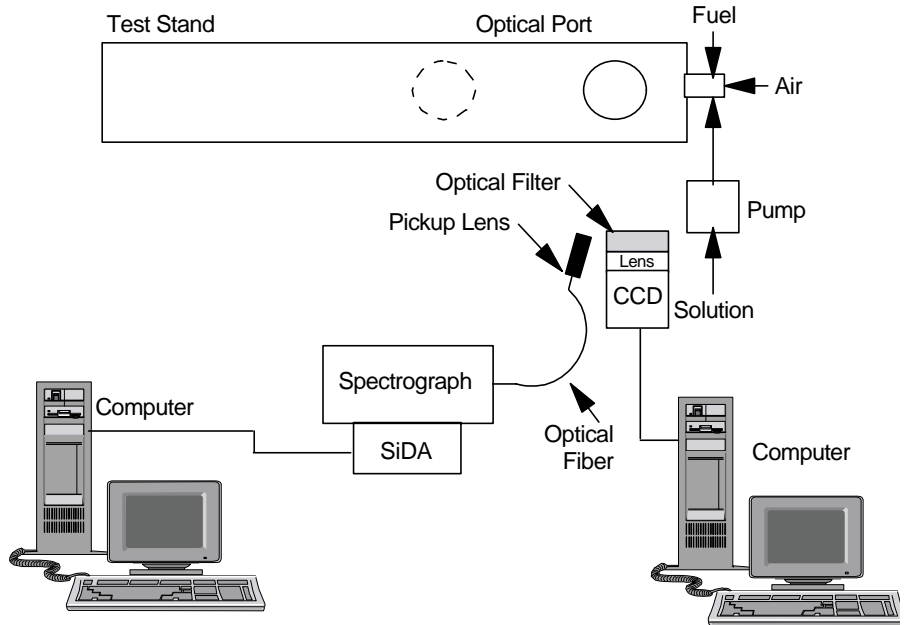


FIGURE 8. Schematic of spectral imaging system and conventional emission spectrometry system used for proof of concept experiments performed using the DIAL combustion test stand.

In order to prove that our imaging system and software can also be applied to large scale TTS, we conducted proof of concept experiments on the DIAL combustion test stand; the experimental set up is shown in Figure 8. Calibration curves for selected metal species were obtained from data collected during the test stand experiments. The results clearly demonstrated that spectral imaging can quantitatively detect metal species and their spatial distributions in a practical combustion chamber. The experimental results are consistent with conventional emission spectrometry results, which were simultaneously obtained during the test stand experiments for the purpose of evaluat-

ing the spectral imaging system. Both the spectral imaging system and a conventional emission spectrometry system were focused on the combustion chamber through an optical port (as shown in Fig. 8). Sodium and potassium were chosen as the surrogate metals for this test because of environmental safety and operational reasons. Using a peristaltic pump, known concentration solutions of sodium and potassium were injected into Fuel Oil #1 (kerosene based) before the fuel entered the combustion chamber. A typical image at 589 nm recorded through the optical port by the camera is shown in the upper left corner of Figure 9; this wavelength was chosen because it corresponds to the resonance transitions of sodium. A user selected rectangular region, area of interest (AOI), was chosen to extract information from all the images recorded during these test stand experiments. A histogram of the AOI is shown at the lower right corner of Figure 9. The correlation between the average pixel intensity in the AOI of the images and the concentration of the solutions injected to the combustion system enabled us to determine the concentrations of sodium and potassium inside the combustion chamber and also gave us spatial distributions of the selected metals. The resulting calibration curve of sodium concentration injected into the combustion chamber vs. pixel intensity of the spectral images is shown in Figure 10. The linear regression does not pass the origin because of the presence of sodium and potassium in the undoped fuel. The test showcased the biggest advantage of the spectral imaging technique, its spatial resolution. Not only can it detect the presence of selected species inside a practical combustion chamber, but also where the species are located. In addition, spectral images also provide direct visual information to human operators for process control decisions.

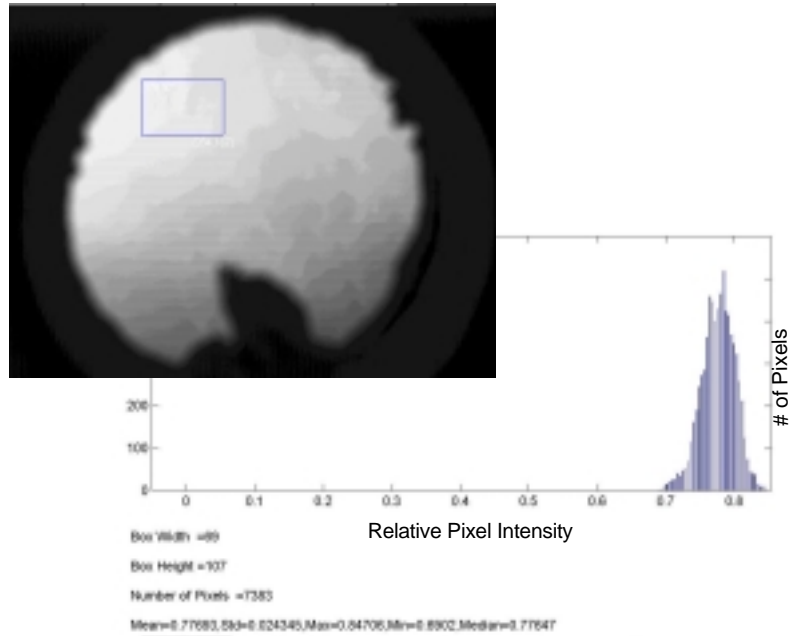


FIGURE 9. Spectral image of sodium at 589 nm recorded on the DIAL combustion test stand and the resulting histogram of pixel intensities within the selected area of interest (AOI).

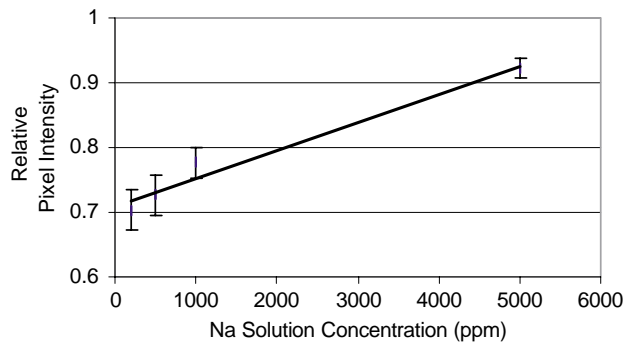


FIGURE 10. Calibration curve of injected sodium concentration vs. average pixel intensity within the user selected area of interest, obtained from DIAL combustion test stand experiments. Error bars correspond to one standard deviation.

Work Planned

After completion of the “proof of concept” experiments reported above, we have already begun working toward our next milestone, which is purchasing essential equipment and assembling the imaging spectrometry system for multi species detection. We have contacted the manufacturer of the ultraviolet acousto-optic tunable filter (UV AOTF) and have discussed design criteria in preparation for placing the order. The UV AOTF order will be placed during the next reporting period. We plan to test the imaging spectrometry system using the DIAL test stand and use the results of those tests to improve the performance of the hardware and software associated with this research effort. We have begun planning the next round of DIAL test stand experiments in order to obtain the maximum usage from each such experiment.

Acronyms

AOI	area of interest
AOTF	acousto-optic tunable filter
CCD	charge coupled device
DIAL	Diagnostic Instrumentation and Analysis Laboratory
Eu	europium
Hg	mercury
K	potassium
Mn	manganese
Na	sodium

Task 2. Measurement Support

nm nanometer

UV ultraviolet

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.

Dissolution of Hanford Salt

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 for 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 efforts described here are the results 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. Personnel 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.²⁻⁴ 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.²⁻⁴ 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, Na₂C₂O₄, NaNO₃, 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-PO₄, Na-F-SO₄ and Na-SO₄-CO₃. Literature data on these systems are rare. What results are available indicate that var-

ious types of solids structures, crystals and gels can result depending on composition. Natrophosphate, $\text{Na}_7\text{F}(\text{PO}_4)_2 \cdot 19\text{H}_2\text{O}$, for example, has been observed to form gels.^{5,6} Sodium phosphate, $\text{Na}_3\text{PO}_4 \cdot \text{XH}_2\text{O}$, 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:

- comparisons to experimental data on actual tank samples;
- 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;
- comparison of the results of the model to other thermodynamic models; and
- 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

Results and Discussion

Previous work in these laboratories has focussed on theoretical predictions of the solid liquid equilibrium (SLE) behavior of natriphosphate ($\text{Na}_7\text{F}(\text{PO}_4)_2 \cdot 19\text{H}_2\text{O}$). ESP and SOLGASMIX calculations were performed at 25°C in water, 1-M and 3-M hydroxide.⁴ A comparison of these predictions is presented in Figure 11 where the molality of the total phosphate in solution is plotted against the molality of fluoride in solution. Good agreement was observed between the calculations in 1-M hydroxide. In water the ESP predictions indicate higher solubility than that from SOLGASMIX and in 3-M hydroxide SOLGASMIX predicted larger solubility. Shelves are observed in both 1-M and 3-M hydroxide and indicate regions of constant solids formation. For example the first shelf at low fluoride ion concentrations indicates the presence of solid trisodium phosphate ($\text{Na}_3\text{PO}_4 \cdot 0.25\text{NaOH}$), at high fluoride concentrations the data predicts the presence of NaF. Between these two extremes the soluble components are in equilibrium with the natriphosphate double salt.

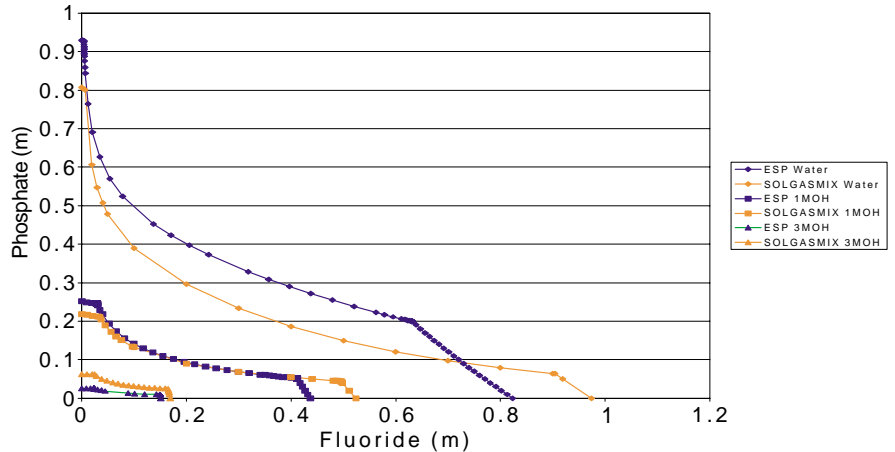


FIGURE 11. ESP and SOLGASMIX calculations for Natrophosphate, 25°C.⁷

Two of the three molecular components associated with the solubility curves are of concern in waste transfers. Trisodium phosphate forms long needle like crystals and the natrophosphate double salt (DS) forms large crystals that may lead to pipe plugging. The trisodium phosphate has been implicated in plug formation at Hanford.⁷ The ability to accurately predict the presence of these two molecules, based on model calculations from baseline data (such as the Best basis Inventory), is, of course, a function of the quality of the fundamental thermodynamic data. Whereas the data shown in Figure 11 is in qualitative agreement with regard to decreased solubility with increasing hydroxide levels, the reversal of the predictions in going from water to 1-M, and then to 3-M hydroxide indicates that the data employed for one or both of the calculations should be examined. An experimental project was developed to obtain additional data on this system and also to examine SLE behavior at elevated temperatures.

Only a handful of measurements have been reported on the Na-F-PO₄-OH system. Previous experimental data was evaluated in the Dissertation by Webber and will not be repeated here.⁸ Problems

encountered in previous studies included inaccurate predictions of the time needed to reach thermodynamic equilibrium and a lack of crystal identification.

Initial sample concentrations were based on the theoretical predictions as shown in Figure 12. Solutions were prepared in water, 1-M, and 3-M hydroxide, dissolved at elevated temperatures, and then allowed to equilibrate for a period of not less than two weeks. Temperatures of 25, 35, and 50°C were selected. Following equilibration the samples were sequentially removed from the constant temperature water bath or oven and filtered. Solids were reserved for polarizing light microscopy (PLM) analysis. The filtrate was diluted to coincide with the response of the ion chromatograph (IC) for fluoride or phosphate anions. The IC was calibrated during each run using standards traceable to NIST. Diluted aliquots of the samples and the calibration standards were placed in sample vials for the IC auto sampler.

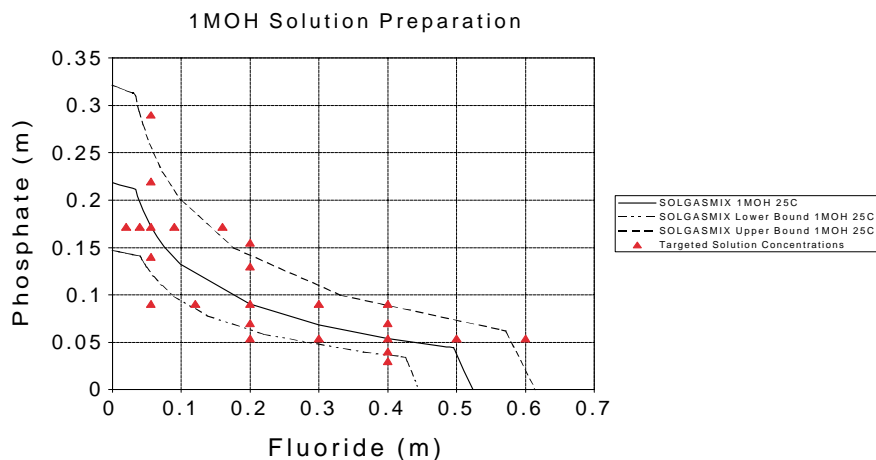


FIGURE 12. SOLGASMIX calculations and selection of the experimental concentrations for the 25°C 1-m hydroxide compositions.

It should be noted that specifying the initial sample concentrations based on the theoretical predictions is only sufficient when the predictions are available and accurate. Problems were encountered with the 3-M hydroxide compositions at both 35 and 50°C. These equilibrated solutions did not produce a sufficient amount of DS crystals and, consequently, these experiments, along with the ESP predictions are being repeated.

The data obtained from the experiments in 1-M hydroxide at 25°C are collected in Figure 13. The theoretical predictions are shown as lines and the red triangles denote the results from the IC analysis. The solid black triangles are the original concentrations based on the theoretical predictions (as in Fig. 12). The experimental data is seen to fall slightly below the ESP and average SOLGASMIX predictions and tend to the lower bound SOLGASMIX prediction. The upper and lower bound curves for the latter calculations were based on the spread of the chosen thermodynamic data employed. Data that did not form solids following the equilibrium period are denoted by open red triangles. In all cases, except for the one data point low in phosphate and low in fluoride concentration, the compositions where solids were not predicted to form were consistent with the compositions at fluoride and phosphate concentrations lower than those associated with the SLE predictions.

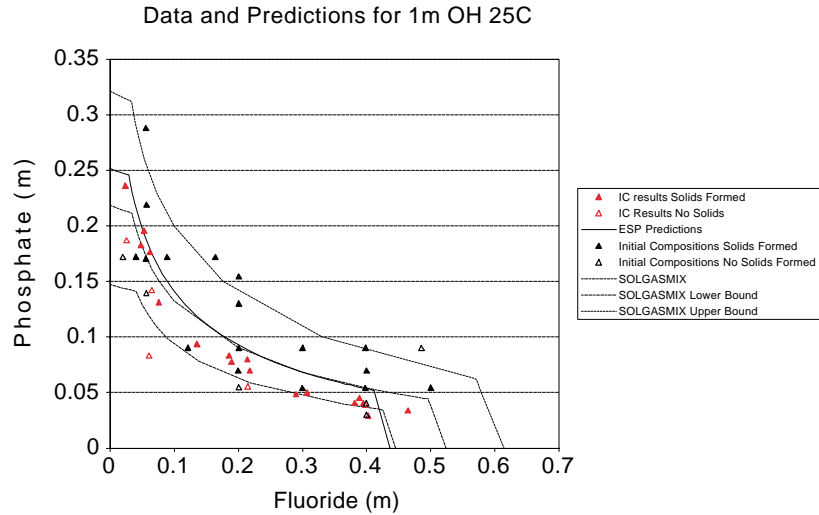


FIGURE 13. Experimental results for the data from Figure 12 compared to the theoretical predictions.

The data provided in Figure 13 only designate solids formation for those particular compositions but not different crystal type. PLM images were obtained for all of the solids found in this work. These were then correlated to the compositions as given in Figure 14. A shelf should be observed at both low and high fluoride concentrations; however, determination of the location of the transitions from the trisodium phosphate to the double salt and the double salt to sodium fluoride requires compositions in a restricted concentration range. To date, only one shelf has been observed for trisodium phosphate in 3-M hydroxide at 25°C, and these results will be discussed in a later report.

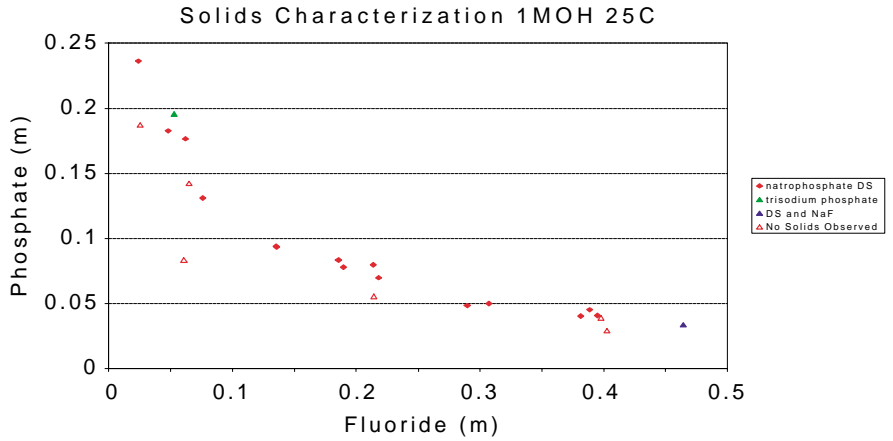


FIGURE 14. Solids compositions from the data in Figure 13.

Data for the 1-M hydroxide compositions are plotted at different temperatures along with the theoretical predictions in Figure 15. Increasing the temperature results in increased solubility. The data at 35°C is separated from that at 25°C although the change in solubility is small. An increase in the scatter of the data is observed in going to 50°C. The source for this behavior has not been determined; however, it should be noted that these experiments are somewhat more difficult to perform; all of the equipment necessary to isolate the solids from the filtrate must be kept at the elevated temperature.

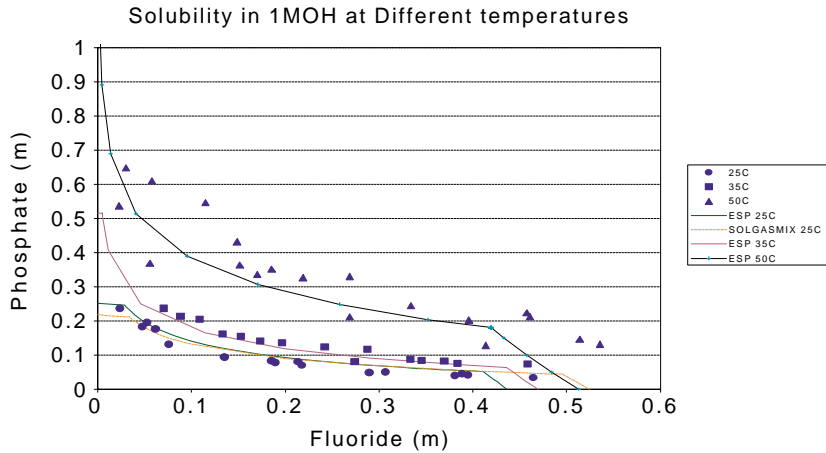


FIGURE 15. Temperature dependence of the solubilities for the Na-F-PO₄-OH system.

SOLGASMIX predictions are only available at 25, 60, and 80°C. The data appear to coincide with the (lower bound) SOLGASMIX predictions at the lowest temperature, to be roughly equivalent to the ESP prediction at 35°C and to be above the ESP prediction at 50°C. This indicates that the ESP model is not predicting the data quantitatively. This finding, and the data for the water and 3-M hydroxide solutions will be forwarded to OLI Inc. for the development of a database. Once completed the model predictions will be repeated and compared again with the SOLGASMIX calculations and the experimental results.

Conclusions

Initial results for the determination of the solid liquid equilibria for the Na-F-PO₄-OH system have been reported. The data for the 1-M hydroxide compositions are in good agreement with the predictions of the SOLGASMIX calculations performed by Webber at 25°C and with ESP predictions at 35°C. Increased solubilities were

observed in the experimental results as compared to ESP calculations at 50°C. Additional experiments are in progress.

Project Status

Work on experimental determinations of solubilities will continue and experiments have begun to establish the SLE behavior of the Na-CO₃-OH system at different temperatures and hydroxide concentrations. Literature studies revealed only a few articles on the carbonate system at elevated hydroxide loadings. Modeling of the dissolution behavior of saltcake for tank 241-TX-113 has been initiated. Studies on feed stability from this tank are in progress at RL and will be compared to model calculations.

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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 immedi-

ate, 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 two 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. Taking these considerations into account, 0.1 inch is a reasonable estimate of the depth resolution for the concrete scabbling application.

Work Accomplished

We have transferred the technology, equipment documentation, and all project data and supplies due to a personnel change.

Work Planned

We will complete the internal technology transfer and continue the work already planned.

Pipe Decontamination

Gary Boudreaux

Introduction

The Department of Energy has radioactive and hazardous contamination inside many of its process piping and duct systems. Contaminants remain in these systems after liquid is drained from them, adsorbing onto metal and other surfaces or depositing as residual liquids 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 Mississippi 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 secondary 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 High Voltage Lab has continued testing of the IGBT electronic modules in the original power modulator cabinet. Several of the electronic controls for these modules were redesigned and tested.

The demonstration with National Heat Exchange Company has been tentatively scheduled for late January 2000. We will be cleaning one-inch diameter tubes in an off-line heat exchanger. The tip that propels the acoustic pulse forward and potentially unclogs pipes was designed and the materials to build this tip have been ordered. We will use this tip at the National Heat Exchange demonstration.

We talked with Ingalls Shipbuilding about a potential application for the pipe cleaner.

Work Planned

The new, improved Pulsed Acoustic Pipe Cleaner is soon to be completed at DIAL. The electronics to control the solid state switch will undergo further testing. We will build the applicator tip that propels the acoustic pulse forward and may unclog pipes. We will also perform the demonstration with National Heat Exchange. Pipes with different types of fouling will be cleaned with the 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.

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 nonintrusive 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, nonintrusive 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 have documented the laboratory setup and data collection procedures due to a personnel change. The new personnel were put in touch with Military Technologies (Miltec) to continue the commercialization of the technology.

Work Planned

We will continue to transfer the technology internally to the new personnel. We will then continue building the statistical database looking for similarities and differences between drum lids by manufacturer and lot. We will continue to seek a commercial partner and re-submit as SBIR type proposal. We also plan to convert the mechanical filtering unit to a software-designed filter. This will be necessary to design a smaller hand-held instrument.

Plasma Treatment of VOCs and Other Off-gas Components by Pulsed Micro Hollow Cathode Plasma Array

George P. 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 to approximately 100 microns in diameter.⁹ 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 flows.

There are several advantages of this technique. It is simple and inexpensive to develop and can be operated at a high gas temperature. It can also be built to the size required.

Experimental Arrangement and 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 CCl₄ 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 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

(C₂HCl₃ 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



This is ideal since HCl and Cl₂ are easily removed from the gas stream by a water spray (or bubbling). H₂ and CO₂ 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 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

The objective of the project is to build and evaluate a micro hollow cathode array for the treatment of VOCs, using TCE as an example.

Work Accomplished

All major components have arrived with the exception of the power. The lack of a graduate student continues to hinder progress.

Work Planned

Assembly and testing of the system will begin, subject to time restraints and hardware delivery.

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Laser-induced Breakdown Spectroscopy

H. Zhang, F. Y. Yueh and J. P. Singh

Introduction

This technical task has been focused on the development and application of laser induced breakdown spectroscopy (LIBS) to monitor RCRA metals from thermal treatment processing facilities. LIBS is a laser based, nonintrusive, and sensitive optical diagnostic technique for measuring the concentration of various atomic and molecular species in test media.^{10,11} 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. LIBS has successfully demonstrated its real time monitoring capability in various field tests.¹²⁻¹⁸

Work Accomplished

LIBS technique require the laser spark generated at the sample medium. Through a beam delivery system, we can send the laser

beam to the desired location and perform remote measurement with an optical fiber. However, this method is limited by the available space and safety issues. It is more convenient to use optical fiber to transmit laser beam and collect the emission signal from the laser plasma. Recently, researchers have successfully transmitted the high power laser beam via optic fiber. It is now possible to design an all-optical fiber LIBS probe which can perform remote measurements in the harsh and hazardous environments.

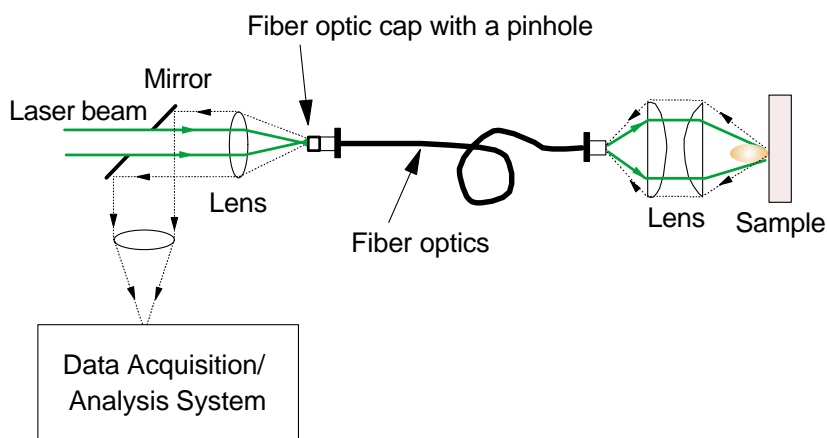


FIGURE 16. Schematic of the optical fiber LIBS system.

During this work period, an all-optical fiber LIBS probe for glass measurement was designed, constructed and tested. The schematic of the fiber optic LIBS system is shown in Figure 16. The most difficult task in designing an optical-fiber LIBS probe is to couple the high pulse energy laser beam to an optical fiber without damaging the fiber. To transmit enough laser energy through the fiber optic cable and below the damage threshold of fiber optic cable, laser beam was focused ~ 3 mm before the fiber tip via a 10-cm focal length lens. We placed a cap with a 0.8-mm pinhole on the fiber input end to avoid the possibility of damage the core and cladding of the fiber.¹⁸ The laser beam transmitted through the optic fiber was collimated with a 10-cm

focal length lens and then focused on the sample with a 2.5-cm focal length lens. The emission from the laser induced plasma was collected through the same lenses and optic fiber. A mirror with a hole on the center was used to send the LIBS signal to the detection system.

In practical application, the optical fiber LIBS probe needs to be operated for an extended time without the damage of the optic fiber. A long term duration test was therefore conducted by measuring the laser energy from the output end of the optical fiber. Figure 17 shows the result of this test. The measured laser energy from the fiber output is gradually decreased over the test period. The observed lower output from the fiber is not due to the fiber transmission loss over test time. It only reflects the performance of the laser system used in the test.

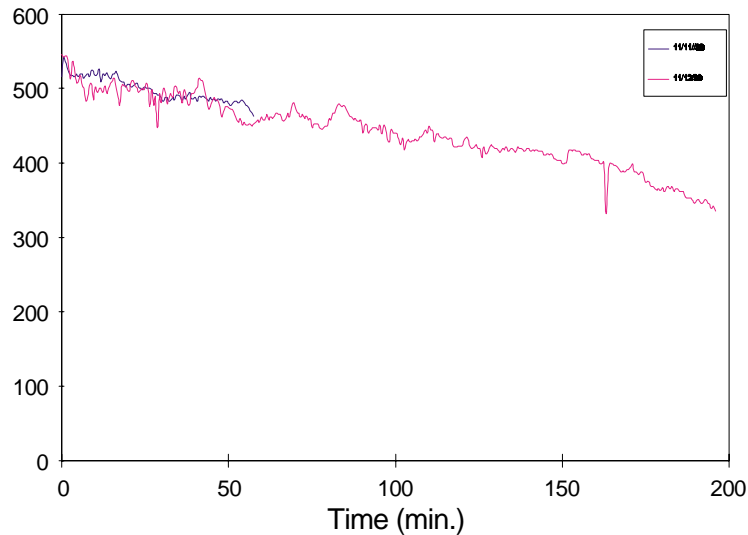


FIGURE 17. Results of the long-term durability test for a 1-mm core diameter UV fiber. The laser pulse energy is fixed to 19.5 mJ.

To evaluate the performance of the fiber optic LIBS system, LIBS measurements of solid sample were made using this optical fiber LIBS probe. Figure 18 shows a LIBS spectrum of a stainless steel tube. Laser energy, delay time and gate width used in the experiment was 19.5 mJ, 10 μ s and 40 μ s, respectively.

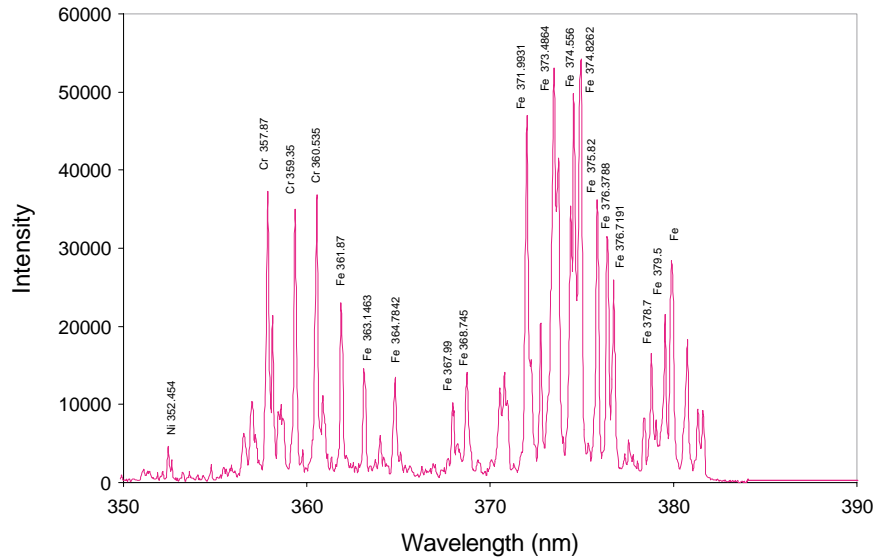


FIGURE 18. LIBS spectrum of a stainless steel tube obtained with the fiber optic LIBS probe.

Work Planned

Test of the optic fiber LIBS probe will continue. The study of the effects of gas stream conditions to LIBS measurement will be conducted in DIAL test stand.

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