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

**Quarterly Technical Progress Report
for the period
October 1, 2001 - December 31, 2001**

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**On-line isotopic monitoring and analytical protocol development for uranium and other actinides.** CRDS efforts during this quarter focused on training a new graduate student, installing and testing new data acquisition software, and initiating the construction of a piezoelectric mounting system for the optical cavity. The student completed radioactive materials safety training and began to learn the operation and maintenance of the laser and plasma systems. The new data acquisition system dramatically improves data acquisition speed by allowing direct access to computer memory and avoiding long communication times with the oscilloscope. The new piezoelectric mount will be used to modulate the length of the optical cavity to achieve resonance between the cavity and the diode laser wavelength.

The LIF group has placed an order for a moderately high-resolution dye laser system, which was finally delivered at the beginning of January. This dye laser system is required to enable us to have the required spectral resolution and not have to rely upon when we can borrow the CRDS group's laser. Two new graduate students completed radiation safety training and began their instruction in laboratory safety and practices. The results of our LIF and spectral imaging

study of the detection of uranium were reported at an international conference during this quarter.

The majority of the IC instrument time has been used in support of local industry needs for very low level (> 10 ppb) anions. This was satisfactorily accomplished using a 10 times the normal sample loop. Peak shapes were very good up to 1.5 ppm with this loop. Detection limits ranged from 2 ppb for F and Cl to 5 ppb for $PO_4$ and $SO_4$. The IC was also retrofitted for Cr (VI) analyses. Detection limits were in the 50 ppb range using diphenylcarbazide as a post column derivatization compound. This method is specific for hexavalent chromium.

**Laser probe for technetium monitor.** Work on evaluating the signal enhancing technique that uses double pulse excitation continued. During this work period, we completed the experimental setup for double pulse LIBS experiment. Initial experiments shows a 16-times enhancement in sensitivity when data were obtained from the jet of 5-ppm magnesium solution with a 2-microsecond interpulse interval with 4-microsecond gate delay from the first laser pulse. The optimum condition for LIBS experiment with the double pulse excitation was then determined. The LIBS spectra of aqueous solution of magnesium, chromium and rhenium are being recorded under the optimum condition. LIBS spectra of various concentrations of each element in aqueous solution were used to obtain the calibration curve and limit of detection in the presence of double pulse excitation. The limit of detection of magnesium was found to improve by nearly an order of magnitude under the double pulse excitation.

## *Development of Tools for Long-term Monitoring*

**Monitor plant physiological status in contaminated environments by high-resolution spectral imaging.** During this quarter, we studied the phytoremediation process of zinc by potted barley (*Hordeum vulgare*) plants using visible and near-infrared diffuse reflectance spectrometry. Bar-

ley was grown in pots and treated with Zn at different, selected concentration levels. Diffuse reflectance spectra of plant canopies recorded with laboratory illumination and with solar irradiation were used to monitor growth and metal treatment processes. The plants have been harvested; the plant shoots were dried and prepared for metal concentration analysis. Spectral and chemical analysis will begin in January. Spectra of barley plants treated with 50-millimolar Zn solution reveal in the near IR region systematic differences from the spectra of untreated plants. The second group of barley plants was treated with 500-micromolar Zn solution; the reflectance spectra of this group of plants are similar to the spectra of the untreated group because of the low Zn concentration applied.

We have also finished a study of potted *Brassica juncea* during this quarter. The growth of potted plants of *Brassica juncea* was slower than during the first experiment period because the plants were grown out of season in Starkville, Mississippi. The plants have been treated with different concentrations of Zn and Cd solutions. Visible and near IR diffuse reflectance spectra have been collected during the metal treatment process. Spectral analysis and chemical analysis of the harvested plant shoots have begun.

**Moisture fiber-optic diode laser sensor.** The aim of this project is to achieve a fiber optic relative humidity sensor for long term monitoring. In this period we have been successful in: (1) achieving a method to make the bent probe more sensitive; (2) testing the bent probe for long term monitoring; and (3) achieving ways to protect the sensitive coating.

**Application of imaging techniques.** System calibration and software modification have been completed for the thermal imaging system that utilize the newly selected spectral region, the insertion probe optical access, and the SONY XC-75 camera system. For the NIR InGaAs camera, the development of a false-color image display based on assigned intensity (12-bit) temperature bins has been com-

pleted. System calibration using a standard temperature source will continue. Work also will continue on system calibration and software modification with the newly selected spectral regions for various camera systems.

The development of FTP imaging analysis software utilizing the new system drivers has been completed. Also completed is the software development of a computer-controlled precision range finder. This device will provide critical distance information that is required in FTP profile rendering. Construction of a grid-pattern projector for the WVNS melter inspection is underway. Necessary optical components have been ordered.

Work continued on FTP measurements with high-slope surfaces, which exist in the WVNS melter. Initial results indicate that the horizontal surface can be utilized for system reference. Further investigation of the melter's internal surface profiling will continue. For the system in-house measurement/verification, manufacture of a WVNS melter mock-up system (with exact interior dimensions) is in progress.

The spectral imaging group ordered and received an acousto-optical tunable filter (AOTF) video adapter that provides us with the ability to rapidly select any arbitrary wavelength region in the visible and near-infrared. During the next quarter, we will develop software to control the AOTF and integrate that software with our image acquisition and processing software package. We have completed the LabView image acquisition/processing software package for use with a filter wheel system.

The information sifting effort validated software for spectral selection using principal component analysis and available EPA reference spectra. AgentBuilder software has been received, installed, and its capabilities investigated. Two papers have been accepted for presentation at international conferences.

## *Hanford Tank Waste Chemistry*

**Saltcake dissolution.** During this quarter, significant progress was made in the effort to expand the thermodynamic data basis for double salt chemistry within the ESP program. ESP predictions for the sodium-sulfate-carbonate-hydroxide system were revised using ESP V6.5, and a comparison with SOLGASMIX predictions was completed. Experimental solubility measurements of this system also progressed well, with the laboratory studies completed for this system at 25 C and 50 C and in aqueous, 1-m caustic and 3-m caustic solutions.

Experimental solubility measurements for the sodium-fluoride-nitrate-hydroxide system were completed. Regression of these data to obtain interaction parameters was completed and the obtained parameters have been used to refine predictions of the solubility envelopes for this system.

Regression of experimental solubility data for the sodium-fluoride-sulfate-hydroxide system has been completed and efforts are underway to revise earlier saltcake dissolution simulations to determine the impact of these new data on the earlier predictions of saltcake dissolution.

D. Herting provided experimental results for saltcake dissolution experiments on saltcakes from tanks BY-109, S-110, and U-107 during this past quarter. ESP predictions of saltcake dissolution are compared with these experimental results. Identification of residual solids during BY-109 cascade dissolution studies indicated that cryolite ($Na_3AlF_6$) was present and persisted through all stages of the cascade dissolution. Comparison of the solids predicted by ESP to those identified experimentally was completed. Available literature data for cryolite was regressed, incorporated into a database and this database used to revise predictions for BY-109 saltcake dissolution.

**Feed stability and transport: solids formation.** Results are presented describing experiments aimed at unblocking plugs of sodium phosphate dodecahydrate. Unplugging experiments in water indicated that the plug structure did not depend on the Reynolds number at which the plug formed and that the longer the residence time of the plug the faster it can be unplugged. Experiments using carbonate solutions indicated rapid plug dissolution. The time necessary to dissolve the plug using a 0.9-M carbonate solution was 1100 seconds as compared to 6700 seconds for the same operation with water. ESP calculations predicted the reaction of the dodecahydrate crystal with the carbonate anion.

Details of the development of a laboratory-scale saltcake dissolution experiment are given. The emphasis of subsequent test runs will be to determine the chemistry occurring during the dissolution process and compare the results to the predictions of the ESP model and to obtain data on the parameters that govern transport of flow in the porous media. An experimental design is provided.

## *Process Monitoring and Control of Toxic Organics*

**Sampling system for dioxins, furans and other semi-volatile products of incomplete combustion and characterization.** The formation of dioxins and furans during combustion processes has become a significant focus of concern over the past few years. EPA has initiated an intensive effort to characterize the different sources of dioxins in the US and to reduce the overall annual rates of emissions. The 1999 MACT for hazardous waste combustors establishes an emission limit for dioxins and furans that will be technically difficult to achieve. Large strides to controlling dioxin and furan emissions from combustion processes will most easily come from an enhanced understanding of their mechanisms of formation. The work being conducted by DIAL will seek to reduce uncertainties associated with the locus of forma-

tion of these compounds and factors that contribute to their formation.

**Toxic organic compound monitoring using cavity ringdown spectroscopy.** Extensive data analysis was carried out during this quarter for the diode laser cavity ringdown experiments as part of thesis preparation for a master's level chemistry graduate student. Remarkable improvement in reproducibility is evident in the data after reanalysis using updated mathematical procedures described in earlier reports. For example, the variability in absorption cross-section measurements for benzene has dropped from approximately ± 15% to better than ± 1% due to the improved mathematical treatment of the ringdown waveforms. This is indicative of a greatly improved reproducibility.

Work on the slit-jet cavity ringdown experiments was delayed due to shipping damage on the system vacuum pump. However, repairs were completed and the vacuum system has been assembled and leak tested and is working well. The system vacuum chamber has been installed on a frame along with a gate valve and diffusion and mechanical vacuum pumps.

# Characterization of Heavy Metals and Radionuclides

## On-line Isotopic Monitoring and Analytical Protocol Development for Uranium and Other Actinides

*D. L. Monts, Yi Su, C. B. Winstead, and Thomas Meaker*

### Introduction

Many DOE applications would significantly benefit from the availability of robust and convenient instrumentation for trace-level actinide monitoring and analysis. This project focuses on developing new instrumentation for on-line or at-line monitoring for actinides with isotopic analysis capability. In addition, analytical protocols for a novel concentration method for actinides are being investigated. These efforts focus on demonstrating these techniques using uranium. In addition to its value in the analytical laboratory, the combination of a simple concentration technique with a robust isotopic monitor could provide a powerful method for addressing a number of outstanding DOE needs. Potential applications include monitors for waste water and sewage treatment systems influent and effluent, and the ability to determine the isotopic content of transuranic species in low-activity waste fractions for waste classification and product acceptance. For example, the need for improved monitoring for uranium, plutonium, and americium in treatment plant influent is clearly identified in need

RF-ER11. With some additional sample pretreatment, such technology could also impact materials characterization needs by providing on-site isotopic analyses in a system that is smaller and significantly less complex than inductively coupled plasma mass spectrometry (ICP-MS).

The development of at-line or on-line monitors for uranium with isotopic analysis capability focuses on the evaluation of two laser techniques, laser-induced fluorescence (LIF) and cavity ringdown spectroscopy (CRDS), in combination with an inductively coupled plasma (ICP). The ICP serves as a sample atomization source, providing free uranium atoms and ions for LIF and CRDS measurements. For LIF, typical limits of detection (LODs) are on the order of parts-per-million (ppm) to parts-per-trillion (ppt), depending on the oscillator strength of the transition.[1] Thus, LIF has the required sensitivity to detect radionuclides at low concentrations. High-resolution laser spectroscopy permits isotopic species to be differentiated from other isotopes of the same element. Because of the mass difference, the energy levels (and hence the absorption/emission wavelengths) of different isotopes are slightly shifted from one another. Combined with an optimized ICP source, LIF will address a DOE need for a rapid determination of concentrations and isotopic abundances of long-lived radionuclides in order to assure process control and product acceptance.

CRDS is a relatively new spectroscopic technique based on measurement of the decay time for laser light trapped in a stable optical cavity.[2] The presence of an absorbing species (such as uranium) in the cavity will reduce this decay time by absorbing some of the light propagating in the cavity. CRDS efforts toward isotopic uranium monitoring focus on the construction of a small CRDS unit using diode lasers. These small lasers are available for some wavelengths in the blue region of the spectrum and most wavelengths in the red to near-infrared spectral region. They also possess an extremely narrow line width easily capable of isotopic resolution. Our previous CRDS

efforts using a narrow-line width pulsed dye laser have demonstrated isotopic resolution of mercury in an ICP, quantifying isotopic abundance features separated by as little as 1.1 ppm.[3] These results suggest that a small, sensitive, and isotopically selective CRDS monitor is feasible. Our typical CRDS solution detection limits achieved thus far range from approximately 1 part-per-billion (ppb) for lead to 20 ppb for mercury.[3,4]

One need currently identified by DOE is the analysis of alpha emitters (U, Pu, Am, etc.) in waste water effluents in the 10-n Ci/mL range. This is typically done with either ICP-MS or alpha scintillation counting (ASC). An ICP-MS can cost several hundred thousand dollars and cannot distinguish between isotopes with similar masses (e.g., Pu-238 and U-238). ASC may require long counting times in order to detect isotopes with low disintegration energies. Reaching detection limits of the caliber of ICP-MS on a low-cost instrument (50,000 to 75,000 dollars) could be greatly facilitated using efficient concentration mechanisms. Currently, materials are available that can extract uranium and other actinides from water matrices. After extraction, actinides are eluted from the concentration media via concentrated acids (ranging from a couple of weight percent to 3 M). The concentration media are typically in the form of coated particles that are mixed with a volume of sample (1 - 2 L) and filtered prior to eluting with acid. These concentration methods are not particularly user friendly. The 3M Company has developed concentration disks for the extraction of transition metals and radioactive Cs, Sr and Tc. They are currently working on extraction disks for actinides. By using extraction disks, a volume of sample can be passed through the disk similar to filtration. Although this eliminates one step from the coated particle concentration scenario, the ultimate concentration method would simply contact the sample with an extraction "tool" that would double as an injection device similar to solid phase micro-extraction (SPME) on GC/MS. These preconcentration methods will be evaluated using LIF or CRDS techniques as well.

**Work Accomplished**

*Laser-induced Fluorescence Spectrometry*

The LIF group has placed an order for a moderately high-resolution dye laser system, which was finally delivered at the beginning of January 2002. This dye laser system is required to enable us to have the required spectral resolution and not have to rely upon when we can borrow the CRDS group's laser. Two new graduate students completed radiation safety training and began their instruction in laboratory safety and practices. The results of our LIF and spectral imaging study of the detection of uranium were reported at an international conference during this quarter.[5]

*Cavity Ringdown Spectroscopy*

CRDS efforts during this quarter included the training of a new graduate student, the installation and testing of new data acquisition software, and the design and initial construction of a piezoelectric optical mounting system for the optical cavity. Very importantly, the student completed radioactive materials and laser safety training and is learning the operation and maintenance of the laser system in preparation for upcoming experiments. In addition, data acquisition software developed in-house by an electrical engineering graduate student was installed, modified, and tested. The new data acquisition system is based on a high-speed, high-resolution (100 MHz sampling rate at 12-bit resolution) analog-to-digital converter card rather than a digital oscilloscope. This dramatically improves data acquisition speed by allowing direct access to computer memory and avoiding long communication times with the oscilloscope. This improved acquisition speed will allow for better signal-to-noise and resolution in the isotopically resolved data in addition to shorter data acquisition times.

A new piezoelectric optical mounting system is under development for the CRDS isotopic measurement effort. One of the easiest approaches to performing high-resolution spectroscopy using diode laser CRDS is to modulate the length of the optical cavity to achieve resonance between the cavity and the laser wavelength. Specifications for a piezoelectric mount and driver were developed and a system was purchased. In addition, recalibration of the pulsed dye laser used for isotopic measurements was initiated. This recalibration was necessary after changing the grating in the dye laser to achieve longer lasing wavelengths. The pulsed dye laser will be used for obtaining initial isotopic data for a red-wavelength uranium transition. This will be followed by expected improvements obtained using a diode laser to probe the same transition.

### *Analytical Method Development*

The majority of the IC instrument time has been used in support of local industry needs for very low level (> 10 ppb) anions. This was satisfactorily accomplished using a 10 times the normal sample loop. Peak shapes were very good up to 1.5 ppm with this loop. Detection limits ranged from 2 ppb for F and Cl to 5 ppb for $PO_4$ and $SO_4$. The IC was also retrofitted for Cr (VI) analyses. Detection limits were in the 50-ppb range using diphenylcarbazide as a post column derivatization compound. This method is specific for hexavalent chromium.

## Work Planned

### *Laser-induced Fluorescence Spectrometry*

Installation of the new moderate-resolution dye laser system is expected early in the next quarter. This will enable us to perform experiments without having to rely upon the CRDS groups' laser. Using the new laser system, we will continue our exploration of a variety of excitation/emission transition pairs in order to select the optimum excitation wavelength for isotopic abundance determina-

tions. Efforts to purchase a spectrometer and intensified charged-cou-
pled device (ICCD) detector for high-resolution detection of the
uranium fluorescence have begun.

### *Cavity Ringdown Spectroscopy*

Upcoming CRDS work will focus on evaluating the detection
limits and isotopic resolution achievable using our pulsed dye laser to
probe a red wavelength uranium transition. Our original research plan
called for using a blue-wavelength uranium transition as the initial
target for a diode laser cavity ringdown system for isotopic analysis.
However, as described in our last quarterly report, several consider-
ations, including the cost, availability, and quality of cavity mirrors
and laser sources, have caused us to reconsider this initial plan. A sys-
tem operating on a red-wavelength transition would ultimately be
much less expensive to construct while likely sacrificing little sensi-
tivity.

### *Analytical Method Development*

The next quarter experiments are planned to assess compatible
mobile phases for rare earth elements. These will first be attempted
with large volume injections. Continued method development on che-
lation chromatography will continue using transition metals.

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## *Laser Probe for Technetium Monitor*

*V. N. Rai, F. Y. Yueh and J. P. Singh*

### Introduction

Technetium is a product of the nuclear power cycle. The most stable Tc isotope is $^{99}$Tc. It has a half-life of 2.1 x 10$^5$ years and decays via β-emission. Due to the long half-life and the relatively high yield from uranium decay, DOE desires to separate technetium from non-radioactive and short life components of tank waste. They plan to isolate it with other long life radionuclides in a geologically stable waste form for long term safe storage. An on-line monitor for technetium is needed for this waste processing. On-line monitoring during waste processing will ensure Tc is properly removed from the processed effluent. The on-line Tc monitor should be able to measure Tc below the 100-µg/L level. The technique should achieve at least a 10% confidence interval at 1000 µg/L.

This technical task focuses on the development and application of laser-induced breakdown spectroscopy (LIBS) to monitor Tc in the effluent of a Tc processing waste facility. LIBS is a laser-based, non-

intrusive, and sensitive optical diagnostic technique for measuring the concentration of various atomic and molecular species in test media.[6,7] 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.[8-15] However, it is well known that the detection limit and precision achievable with LIBS cannot yet surpass those of other analytical techniques. Various attempts have been made to improve the analytical performance of LIBS. We will evaluate various techniques which can improve LIBS' sensitivity for Tc measurements.

**Work Performed**

The use of multiple laser pulses for producing more intense and sustained plasma emission in various experiments has been found useful in improving the signal to noise ratio. This double pulse technique has been used to study solid as well as liquid samples.[16-20] The double pulse excitation was first used to facilitate the bulk analysis of transparent liquids.[16] After this, it was used for the analysis of solids immersed in liquids.[17,18] It was found that the laser spark generated by focusing the laser inside the liquid was confined by its surroundings, and the plasma radiation was quenched strongly at the plasma liquid boundary leading to a shorter lived atomic emission than the plasma formed in the gaseous environment. The high thermal conductivity of hydrogen present in the plasma when analyzing the aqueous solution or organic liquid, was also a cause of the short plasma life time. In contrast, a double pulse scheme enables an expanding plasma plume or gases formed with the help of the first pulse, whereas the second pulse a few microseconds later excites the expanding plasma plume or gas and helps in the analysis of the liquid sample. The liquid jet

technique has been reported to be more sensitive in the analysis of aqueous solutions than the bulk. Nakamura[20] has utilized two sequential laser pulses focused on the liquid jet to determine the concentration level of iron suspension in boiler water from a thermal power plant. He reported an improvement in the detection limit to 16 ppb from 600 ppb.

During this reporting period, we utilized the double pulse LIBS technique to improve the sensitivity of this system for the study of the aqueous solution of Mg, Cr and Re, which are surrogates to the technetium, a radioactive element of the nuclear fuel cycle.

The present experimental set-up utilizes two Nd:YAG lasers converted to second harmonics operating at a wavelength of 532 nm. The lasers were able to deliver up to a maximum energy of ~ 200 mJ. Both the lasers were synchronized using a delay generator, which can control the time delay in the arrival of both the laser pulses at the sample target. The lasers were made collinear with the help of mirrors and a thin film polarizer. The thin film polarizer plays an important role in making both the orthogonal polarized laser beams collinear. The optical ray diagram has been reported in the previous report. The collinear laser beams were focused on the liquid jet using a 20-cm focal length lens. The emission from the laser-induced plasma was collected and focused onto the optical fiber, which transmitted it to a spectrometer through which we recorded the dispersed spectra. The spectra obtained at the exit slit of the spectrometer was recorded using a gated intensified CCD camera and then analyzed.

Figure 1 shows the LIBS spectra of aqueous solution of magnesium recorded using double laser pulse excitation techniques where the interpulse delays between the two lasers were 0 and 3 μs. One can see here that both the strong emission lines of magnesium ions show enhancement in the case of double pulse excitation in comparison to single pulse. Neutral line intensity is very weak and the background is high, because the gate delay for recording spectra was 4 μs. The

enhancement was nearly similar for ionic as well as neutral lines. The extent of enhancement in the signal was found to be dependent on the concentration of the solution as well as on the delay between the laser pulses. A maximum increase of five times in emission intensity was noted for a 5-ppm solution, when the delays between both lasers were set to ~ 2 - 3 μs. It was observed that emission intensity increases up to ~ 2.5 μs as the delay between both the lasers. Any further increase in the delay between lasers decreases the emission intensity. The enhancement in emission intensity in the double pulse excitation technique seems to be due to better heating of the preformed plasma by the second laser beam. The time delay between the lasers makes the effective volume of the emitting plasma increase. The volume of the emitting plasma first increases with an increase in the time delay and reaches maximum when the delay is ~ 2.5 μs. Any further increase in the delay probably depletes the number density of emitting elements (Mg) in the plasma plume generated by the first laser, which ultimately leads toward a decrease in the signal at a higher time delay.
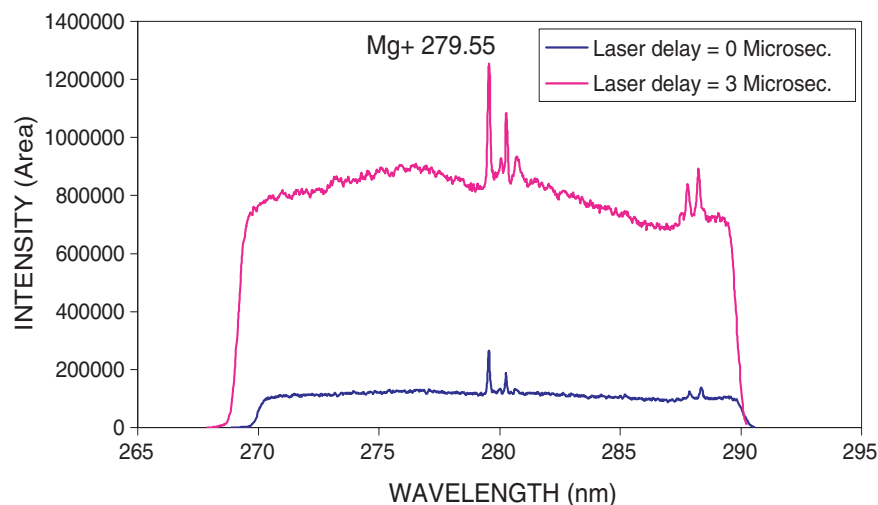


**FIGURE 1.  Double pulse LIBS spectra of aqueous solution of magnesium.**

Figure 2 shows the calibration curve of magnesium obtained under the double pulse excitation in aqueous solution. The concentration of the solution was changed from 100 ppb to 10 ppm. The LIBS signal increases linearly up to 1 ppm and then shows saturation beyond this concentration. The limit of detection for magnesium was calculated to be 61 ppb in comparison to 570 ppb obtained in single pulse LIBS.
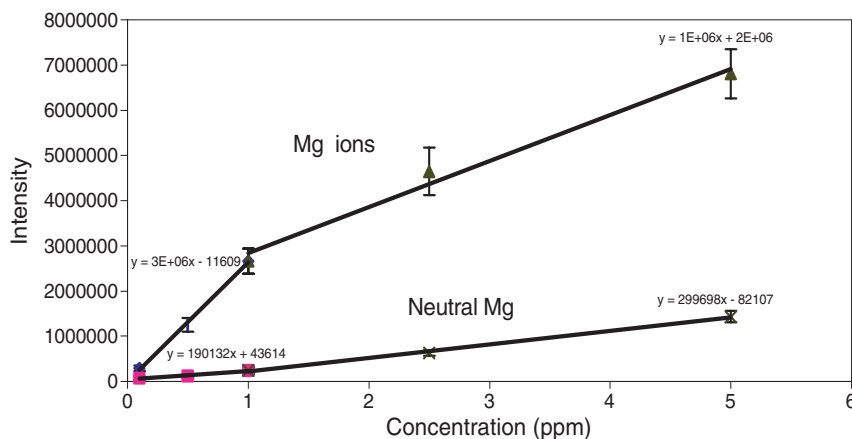


**FIGURE 2. Calibration curve for aqueous solution of magnesium under double pulse excitation. Delay between the lasers was 2.5 $\mu$s.**

**Work Planned**

The combination of magnetic field and double pulse excitation will be tested after completion of the double pulse experiment, which is in progress.

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### *Monitor Plant Physiological Status in Contaminated Environments by High-resolution Spectral Imaging*

*Yi Su and David Monts*

## Introduction

### *Purpose*

The goal of this project is to use remotely sensed data to monitor the physiological status of plants growing on contaminated DOE sites. The physiological status will be used as an indicator of the presence of pollutants, such as heavy metals or radioactive species, in the growing environment. This capability will enhance DOE's capability for cost-effective long-term monitoring of contaminated sites.

Plant reflectance is governed by leaf surface properties and internal structure, as well as by the concentration and distribution of biochemical components, and thus remote analysis of reflected light can be used to assess both the biomass and the physiological status of a plant. Particular spectral bands and band combinations (often referred as reflectance indices) for monitoring crop stress resulting from nitrogen deficiency, water deficiency, etc. have been reported using remote

sensing. We propose to monitor the impact of contamination, such as by heavy metals, on plant physiological status. A computerized spectral imaging system will be applied to take images of plants growing in a controlled environment with known concentrations of heavy metal contamination. Spatial and temporally distributed information extracted from images of different spectral bands will be part of this plant physiology study. The focus of this project is to search for indices (signatures) that indicate the impact and the content of heavy metals in the leaves and canopies of live plants. This ground-level study will also help to determine whether the physiological reflectance signals are stronger than disturbances introduced by factors such as the position of the sun, heterogeneity of the landscape, or atmospheric interference. The resulting information will be essential to determine whether remote sensing technology can be used for long-term monitoring of the spread of pollutants at some of the DOE closed sites.

### *Methodology*

A portable spectroradiometer system and a spectral imaging system will be applied to monitor plant physiological status in contaminated environment. The spectroradiometer will be used to record reflectance spectra from the plant throughout the growing process. The spectral analysis will provide us the impact of the contamination on the plant physiology, and also will help determine the key spectral band(s) (signature) related to specific contamination. A spectral imaging system, which is based on the outcome of Task 3.2, On-Line Multispectral Imaging of Thermal Treatment Process, of last year's Cooperative Agreement, will provide the spatial analysis. The spectral imaging system will help us overcome problems related to mixtures in the field of view, such as soil, dry leaves, stems, and shadows. The information extracted from spectral images will also be used to study plant canopy structure change during the growing process.

This is a multi-year project. First year will be devoted to a laboratory study: a laboratory-size plant bed will be used to study the

impact of selected metal species on plant physiology status. The second and third years will be devoted to study plants grown under a controlled natural environment for conditions similar to those that pertain to selected DOE sites; the plants affected by contamination will be studied in a potted-plant growing facility in a natural environment. The following years will be devoted to DOE site-specific studies.

## Work Accomplished

During this quarter, we studied the phytoremediation process of zinc by potted barley (*Hordeum vulgare*) plants using visible and near-infrared diffuse reflectance spectrometry. Barley was grown in pots and treated with Zn at different, selected concentration levels. Diffuse reflectance spectra of plant canopies recorded with laboratory illumination and with solar irradiation were used to monitor growth and metal treatment processes. The plants have been harvested; the plant shoots were dried and prepared for metal concentration analysis. Results from spectral and chemical analysis will be presented in the next quarterly report.

We have also finished a second study of potted *Brassica juncea* during this quarter. The growth of potted plants of *Brassica juncea* was slower than during the first experiment period because the plants were grown out of season in Starkville, Mississippi, that is, under cooler conditions. Spectral analysis and chemical analysis of the harvested plant shoots have begun.

During this quarter, we finished spectral and chemical analysis of the first study of phytoremediation of Zn and Cd by potted Indian mustard (*Brassica juncea*); the experiment was conducted during the previous reporting period (from July to September 2001). Analytical chemistry results on harvested plant shoots show a significant amount of Zn and Cd accumulation for the groups treated with metal solutions. Spectral analysis reveals that the near-infrared reflectance spec-

tra from metal treated plants are systematically different from those of untreated plants. Figure 3 shows the diffuse reflectance spectra of Indian mustard plants from the untreated group and the ZnT1group (treated with 100-mM Zn solution). The spectra were taken on the sixth and ninth days of the metal treatment process. As can be seen from Figure 3, not only is the near-IR plateau (approximately from 780 to 920 nm) from the Zn-treated plants significantly lower than that from the untreated plants, but also the spectra from the two groups are characteristically different throughout the near-IR region from 750 nm to 1350 nm. Notice that the height of the 1110-nm peak relative to the plateau from 780 to 920 nm is significantly different for treated and untreated plants. To overcome individual variability among barley plants, the reflectance spectra were averaged within each of the subgroups for a given day and given illumination conditions. As a result, each spectrum presented here is the average of reflectance spectra of 16 individual plants recorded on the same day under the same lighting conditions. From the fourth day of Zn treatment, the spectra of the ZnT1 group consistently exhibit differences from the spectra of the untreated group in the near IR region (from 750 nm to 1350 nm). Further in-depth spectral analysis shows that the band ratio of the spectral reflectance at 1110 nm and to that at 810 nm might be used as an indicator of metal accumulation in plant shoots. Figure 4 shows plots of the band ratio R1110/R810 for three subgroups [T0 (untreated), ZnT1, and Cd + Zn] during the metal treatment process. This band ratio clearly distinguishes the three subgroups.
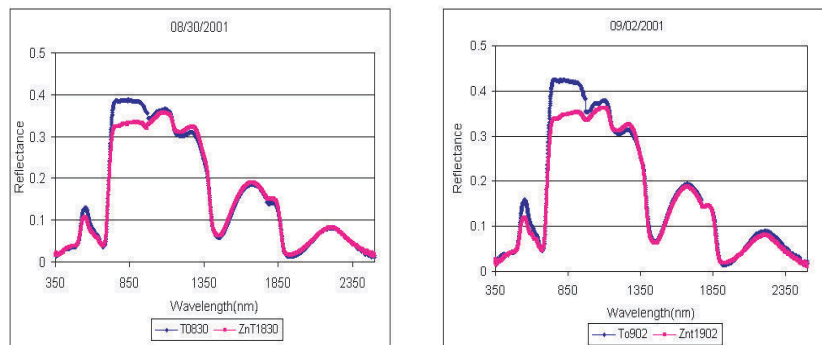
**FIGURE 3.** **Diffuse reflectance spectra of Indian mustard plants from untreated (T0) and Zn treated (ZnT1) groups on the sixth and ninth days of Zn treatment.**
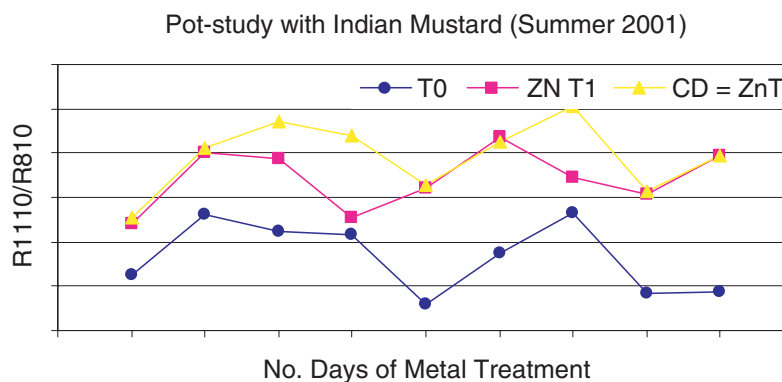


**FIGURE 4.** **Band ratio R1110/R810 of three subgroups [T0 (untreated), ZnT1, and Cd + Zn] during the metal treatment process.**

## Work Planned

We have already started another study of phytoremediation of zinc and cadmium by potted barley (*Hordeum vulgare*). A larger number of subgroups with different metal treatment concentrations will be used to investigate the correlation of near-IR reflectance spec-

tra to metal accumulations in plant shoots. The same spectral monitoring procedure and analytical chemistry tests described above will be employed on this new batch of plants. Also during the next reporting period, we will perform chemical and spectral analysis on the data and harvested plants from the previous two pot studies that we finished at the end of year 2001.

## *Design, Fabrication and Development of a Portable Miniature Ion Trap Mass Spectrometer*

*T. Meaker*

### Introduction

Current research performed by the principle investigator has successfully reduced the size of a mass spectrometer to a few millimeters in diameter. This accomplishment has eliminated the need for large rf voltages associated with ion traps (IT). Furthermore, the vacuum manifold needed for the mini-IT is significantly reduced, requiring considerably less power demands to maintain a suitable vacuum. The short-term goal revolves around incorporating these two major advancements of miniaturization into the design and fabrication of an ITMS. This would allow for a portable instrument to be in place within 12 to 18 months. The long-term objective would continue to improve on the prototype by further reducing electrical energy demands by incorporating a field emitter array as the ionization source. To further reduce the overall size and power needs, we would assess the potential use of Fourier transform (FT). This, if successful, would effectively allow the elimination of electron multiplier detection devices. The FT of a time domain signal will produce a frequency spectrum that can easily be correlated to mass. This would have a two-fold affect. First, this would eliminate the external electronics of the electron multiplier, further miniaturizing the instru-

ment. Second, it would allow for the non-destructive analyses of a particular sample, allowing for significantly lower detection limits. Current IT technology uses a mass selective instability scan to eject ions out of the trap to an electron multiplier. Once the electrons are ejected, they are lost (and only one-half of the ions reach the detector). Using FT, all ions are analyzed and the signal can be integrated for extremely long times, effectively lowering detection limits.

## Work Accomplished

No new progress to report. Currently, laboratory space has not been identified for the undertaking of this task.

## Work Planned

Identify available space in laboratory wing to house instrumentation package. Proceed with procurement of turbo pump and data station.

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## *Moisture Fiber-optic Diode Laser Sensor*

*R. Jindal, S. Tao and J. P. Singh*

## Introduction

Moisture fiber optic sensors can be used for monitoring of the harsh environment such as down hole drill, factories with electromagnetic noise unacceptable for regular capacitance-based moisture gages, radioactive waste storage places etc. Several U.S. DOE waste tank storage sites such as Hanford site has needs to monitor water in subsurface rear storage. The main purpose of this study is to prove the concept of the sensor, make preliminary samples as well as experi-

mentally find a way for improvements of their performance. The present study of the sensor is based on the absorption of the evanescent tail of the light propagating in fiber.[21,22] To increase the interaction with the light propagating in the fiber a bent probe was tried and found to give very desirable results. In this period the bent probe was tried for long term monitoring and was found to be stable for more then a month's period and should be easily stable over longer periods of time.

**Work Accomplished**

The non-linear behavior that was obtained for initial bent probes seems to be inherent and do not seems to be removable, but should not be a worry if we could calibrate the probe. In fact a few probes were tried and calibrated and it was found that the over all behavior of the sensor is non-linear but can be easily calibrated using a second-degree polynomial. Another observation made was that the different probes leads to a similar behavior (Fig. 5), which is a good indication for the mass production of the sensor. A long term monitoring of the probe was also tried and it was found that sensor response remains stable for tests done over a period of a month. For the optimization of performance, several bent probes were tried during this period and it was found that smaller bent diameter probes are more sensitive (Fig. 6). Also smaller diameter fibers were found to be more sensitive too. But in both cases the fiber probe more fragile and thus can break more easily. The insertion loss of the probe also increases in both cases. So we have to keep a good balance in sensitivity and the loss and stability.
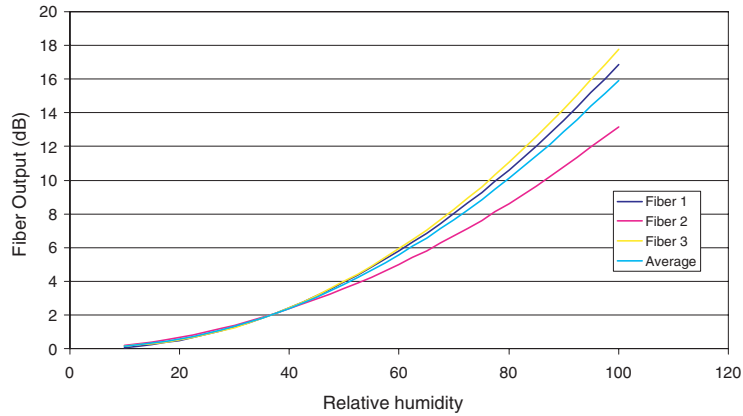
**FIGURE 5.** **Comparison curve for 200-μ bent probe.**
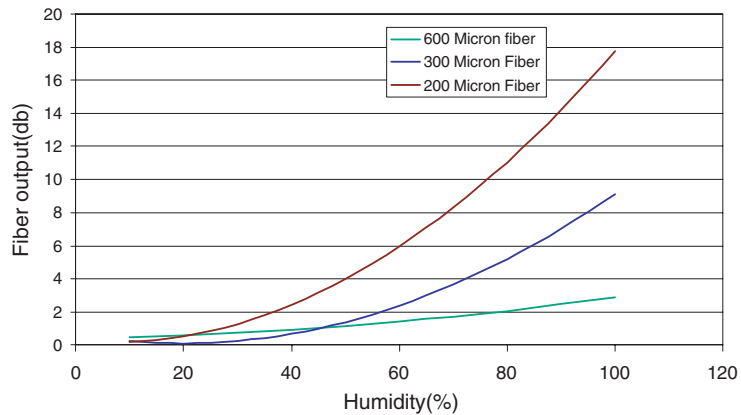


**FIGURE 6.** **Comparison of 600, 300 and 200-μ fiber responses to humidity.**

The coating on probe was tested for high humidity for long time and also the stability of it when put in water. It was found that in fact the coating of sensor comes off when put in water for some time; this is because of the property of PVA as it dissolves in water (PVA was used as a support material for $CoCl_2$ which is actual moisture indicator). So it was decided that a protective coating needs to be put on

original coating to stop a direct interaction of PVA with water, this is necessary to make the probe working in real conditions where it can rain or can have other adverse conditions. For that first the bent probe was coated with PVA and $CoCl_2$ solution and then a coating of Silicon rubber solution. It was found that the sensor does work even after dipping in the water for few minutes (which otherwise used to take off the PVA + $CoCl_2$ coating and thus making sensor not respond at all). The only problem that comes is that the response time of the sensor becomes very slow, in the order of few minutes. So other coatings are also being tried. Also an effort is started in terms of packaging the bent probe so that it can be used under soil.

### Work Planned

The primary requirement in this period is to find the effective protective so the sensor works even after being exposed to water. Also an effort would be made to package the fiber optic probe and test it in soil to monitor soil moisture content.

### Reference

21.  A.P. Russell and K.S. Fletcher. 1985. Optical sensor for determination of moisture. *Analytica Chimia* 170:209-216.

22.  S.K. Khijwania and B.D. Gupta. 1999. Fiber optic evanescent field absorption sensor: effect of fiber parameters and geometry of the probe. *Optical and Quantum Electronics* 31:625-636.

## *Application of Imaging Techniques*

*David Monts, Yi Su, Ping-Rey Jang, and Thomas Philip*

### Introduction

#### *Purpose*

Imaging techniques can be utilized to provide solutions to a wide variety of issues facing DOE, ranging from process control to off-line melter inspection to long-term monitoring. This effort will develop the techniques and instrumentation needed to address these needs.

Spectral images are obtained by positioning a narrow-bandwidth bandpass filter in front of a camera. The bandpass spectral region of the filter is selected to coincide with the emission of an atomic or molecular species of interest or to coincide with regions of the spectrum containing only blackbody emission. By proper selection of wavelengths, information about the spatial distribution of species present or about temperature distribution can be derived from these images. Spectral and thermal imaging can provide DOE with information crucial to its decision-making processes.

There is a commonality to the data collection hardware, data and analysis software, and to the data sifting techniques necessary for applying imaging techniques. This effort expands on existing expertise to develop imaging collection and analysis systems that address a wide variety of DOE's needs. Our efforts this grant year concentrate on (but will not be limited to) inspection of off-line Joule-heated melters to determine where and how much exceptional wear occurred, and also to determine where deposits are located, how big the deposits are, and a preliminary identification of the materials deposited.

*Methodology*

Our efforts will concentrate on DOE needs for inspection of off-line Joule-heated melters to determine wear patterns and the location and composition of deposits; this information can be utilized in the design of the next generation of HLW melters. Narrow bandpass filters will be combined with block cameras to enable spectral imaging within the melter. DIAL's imaging capability will be extended to the near-infrared spectral region. Diffuse reflectance spectroscopy will permit selection of proper observation wavelengths. Means of quantitative determining the extent of wear or amount of deposition will also be developed based on two techniques: Fourier transform profilometry (FTP) and stereovision. DIAL has previously demonstrated that its FTP system can quantitatively determine the volume and depth of removed material to high accuracy. Improvements will include: (1) improvement of the fringe pattern projection system; and (2) improvement of the phase unwrapping algorithm - this upgrade will resolve the $2\pi$-phase discontinuity associated with abrupt changes in surface height. A second imaging technique, stereovision, will also be developed as a means of determining the depths/heights of surface features. Stereovision provides determinations of depths/heights by combining images simultaneously recorded by two cameras. Knowledge gained from and techniques developed for characterization of off-line melters can also be applied to characterization of on-line melters. A collaborative arrangement has been established with SRS's DWPF facility to inspect their melter at an appropriate time. Efforts are underway to establish a similar relationship with West Valley.

Techniques have been developed to detect hot spots, thermal distribution, characterization of vegetation, detection of uneven surfaces, etc. from imaging data. This year's effort also aims at enhancing the techniques already developed here and to develop new techniques and capabilities utilizing statistical as well as intelligent system approaches. While statistical methods provide linear relationships,

artificial neural networks are apt to deal with non-linear relationships inherent in the data. Besides these, rule-based techniques would derive heuristic relationships. The existing capabilities will be extended to characterize soil, melters, and vegetation from uni- and multi-spectral images. This will enable long-term monitoring to detect the presence and variation of trace elements, especially hazardous ones in plants. The ability to classify regions of interesting characteristics will provide valuable information regarding contamination in soil and other media. One of the objectives of this effort is to go beyond typical data analysis methods in pursuit of discovering new relationships and thereby sifting information hidden in the data.

## Work Accomplished

### *Profilometry*

Development of FTP imaging analysis software utilizing the new system drivers has been completed. Also completed was software development of a computer-controlled precision range finder. As shown in Figure 7, the software control window displays the important communication parameters during the device measurement and returns the measurement results.
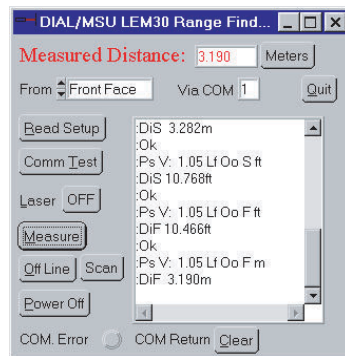


**FIGURE 7. Computer-controlled LEM30 range finder.**

This device will provide critical distance information that is required for FTP profile rendering. The design of a compact projector has been completed. The projector optical system (shown in Fig. 8) has been designed using the WVNS melter dimensions. Construction of this grid pattern projector is underway.
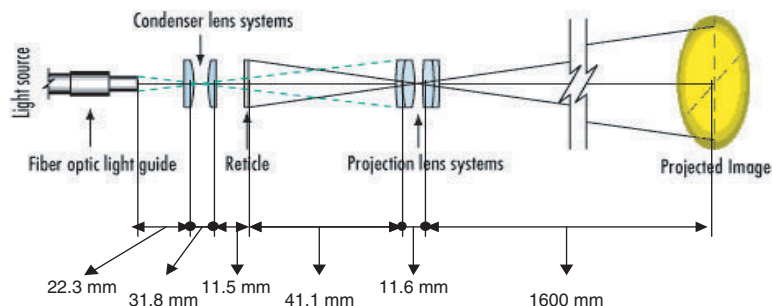


**FIGURE 8. Design of a compact projector system for FTP measurement in WVNS melter.**

Work continued on FTP measurement of high-slope surfaces, which exist in the WVNS melter. For system in-house measurement/verification, construction of a WVNS melter mock-up system (with exact interior dimensions) is in progress. Initial results indicate that the horizontal surface of the WVNS melter can be utilized for system reference. Further FTP profiling investigations for the melter's internal surfaces will continue.

### Thermal Imaging

System calibration and system software modification have been completed for the thermal imaging system that utilized the newly selected spectral region, the insertion probe optical access, and the SONY XC-75 camera system. A camera system with better quantum efficiency and better exposure-time control has been located. Calibration for this new system will be performed.

For the NIR InGaAs camera, as shown in Figures 9 and 10, the development of a false-color image display based on the assigned intensity (12 bits) temperature bins has been completed. With a properly calibrated system response function, temperature profiles can be easily monitored in near real time.
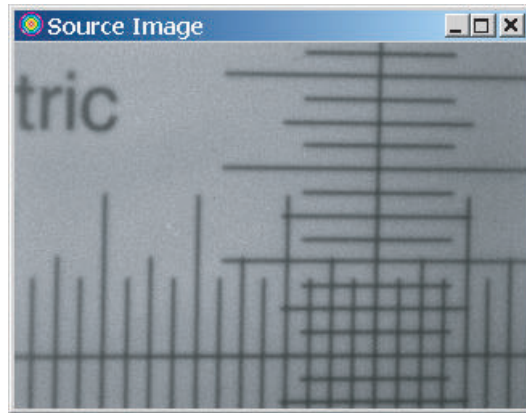


**FIGURE 9. Twelve-bit monochrome raw image from InGaAs camera**.
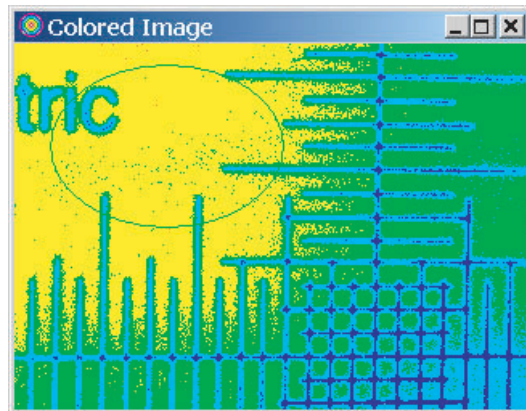


**FIGURE 10. False-color image display based on the assigned 12-bit intensity-temperature bins.**

System calibration against a standard temperature source for the InGaAs camera continued. Work also continued on system calibration and software modification with the newly selected spectral regions in various camera systems.

### *Spectral Imaging*

The spectral imaging effort ordered and received an acousto-optical tunable filter (AOTF) video adapter that provides us with the ability to rapidly select any arbitrary wavelength region between 500 nm and 1000 nm. During the next quarter, we will develop software to control the AOTF and integrate that software with our image acquisition and processing software package. We have completed the LabView image acquisition/processing software package for use with a filter wheel system.

### *Information Sifting*

The information sifting effort validated software for spectral selection using principal component analysis and available EPA reference spectra. AgentBuilder software has been received, installed, and its capabilities investigated. Investigation of the effect of the level of data reduction on identification speed and reliability has begun. Two papers based on work for this project have been accepted for presentation at international conferences.[23,24]

## Work Planned

### *Profilometry*

Work will continue on study of phase unwrapping algorithms[25,26] for target areas that have large height discontinuities and/or surface isolations. Efforts will also continue on construction of the mock-up system and the optical system control/delivery. FTP measurements of simulated surfaces inside WVNS melter will also continue.

### Thermal Imaging

A new camera system, SONY XC-T50, has been identified. This camera system has better quantum efficiency and allows the camera exposure time (or electronic shutter speed) to be controlled by an external trigger pulse width. System development of the control scheme and thermal calibration will be undertaken. For the NIR InGaAs camera, system calibration against a blackbody radiation source will be performed. The software module for reading parameters within PNG image files will be integrated into the current imaging system so exact interpretation of acquired images can be achieved. We will continue our efforts on thermal calibration and system software modification for the new thermal imaging system with newly selected spectral regions and with the high-resolution camera.

### Spectral Imaging

During the next quarter, we will develop software to control the AOTF and integrate that software with our image acquisition and processing software package. We will continue our efforts to develop and optimize the data acquisition and analysis software. As part of the WVNS melter autopsy effort, we begin acquisition of radiation-hardened block cameras and related equipment.

### Information Sifting

We plan to apply the principal component analysis technique that we have tested using EPA data to spectral data collected from plants. The objective is to demonstrate how well the technique works with data collected at DIAL. Also, we plan to classify the plant data based on specific nutrients in the plants, using an artificial intelligence (AI) approach.

## References

23.     Prashant Copra, Thomas Philip, Yi Su, and David Monts. 2002. Autonomous agents in prediction of element concentration: real-time fuzzy classification paradigms. Proceedings of First International Congress on Autonomous Intelligent Agent Systems (ICAIS 2002), Geelong, Australia.

24.     Thomas Philip, Yi Su, and David L. Monts. 2002. Characterizing thermal devices by identifying spectra using principal component analysis. Proceedings of 2002 Computers and the Applications Conference (CATA 2002), San Francisco, CA.

25.     D.C. Ghiglia and M.D. Pritt. 1998. *Two-dimensional phase unwrapping.* John Wiley & Sons, Inc.

26.     Yosuke Takahashi, Mitsuo Takeda, Masaya Kinoshita, Quan Gu, and Hideaki Takai. 1997. Frequency-multiplex Fourier-transform profilometry: a single shot three-dimensional shape measurement of objects with large height discontinuities and/or surface isolations. *Applied Optics* 36:22:5347-5354.

## Acronyms

| | |
|---|---|
| CCD | charge-coupled device |
| DWPF | Defense Waste Processing Facility |
| EPA | Environmental Protection Agency |
| FTP | Fourier-transform profilometry |
| ICP | inductively coupled plasma |
| InGaAs | indium gallium arsenide |
| NIR | near infrared |

PCA        principal component analysis

PNG        Portable Network Graphics

ROI        region of interest

SRS        Savannah River Site

WVNS       West Valley Nuclear Services

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## *Saltcake Dissolution*

*R. Toghiani, J. Lindner, V. Phillips, and D. Selvaraj*

### Introduction

This project is a continuation of the work previously reported on the dissolution of Hanford waste saltcakes. A main portion of the work is to continually validate and upgrade a thermodynamic equilibrium model, the Environmental Simulation Program (ESP) as applied to the Hanford wastes. Toward this end, a number of significant accomplishments have been reported previously.[27-31] These include the evaluation of the code for the dissolution of saltcakes varying in composition through a comparison of model predictions with experimental results on core samples performed at the site, the use of the model to aid in the development of remediation strategies for Hanford tank 241-SY-101, an evaluation of data preprocessing, and the experimental determination of the solubility of natrophosphate, a double salt observed in the tank wastes.

A main focus is in bolstering the predictions of the code through comparison with experimental data and with other thermodynamic models such as SOLGASMIX. Accurate data called by the model are

an essential requirement for quantitative code predictions; however, it must be noted that evaluation of the thermodynamic interactions between all of the species existing in the waste streams is not possible. The path, therefore, has been to concentrate on those anions such as nitrate, nitrite, hydroxide, sulfate, phosphate, fluoride, oxalate, carbonate, and cations such as sodium, aluminum, calcium, nickel, uranium, etc., and the associate solids from these species that comprise the majority of the waste composition. Once assured that the code predictions accurately reflect the thermodynamics of these systems, it becomes possible to further upgrade the model to include other species of considerably lower concentration. The project is divided into three tasks as summarized below.

### *Task 1. Comparison of ESP to Other Thermodynamic Equilibrium Codes*

The model has been shown to provide agreement with literature data for the solid liquid equilibrium behavior of many of the saltcake constituents at both high and low ionic strengths. Nonetheless questions will remain on the application of the model to situations where the ionic strength is high owing to the extrapolation of fundamental electrolyte theory to regions of high ionic strength. Theoretical calculations for sodium nitrate, the most prevalent solid in the waste, will be performed at high ionic strength and compared to an alternate model developed by M. Ally at ORNL. Comparisons with the SOL-GASMIX model, in collaboration with C. F. Weber (ORNL) will be performed for the sodium-fluoride-sulfate system. Companion solubility experiments will be made on this system to improve the ESP database (Task 3).

### *Task 2. Comparison of ESP Predictions to Saltcake Dissolution Experiments*

Previous work has characterized saltcakes with roughly four typical compositions as anticipated in the Hanford tank wastes. These

studies have indicated that ESP can be used to predict the dissolution behavior of the majority of the solids present. An exhaustive search for other types of saltcake compositions was conducted recently by D. L. Herting of Fluor Hanford resulting in the identification of two additional tanks with different composition distributions. A sample from tank TX-113 will be evaluated this year. In addition, recent interest in pretreatment and retrieval operations has indicated that there may be some concern when supernates from different waste streams are combined. ESP will be used to examine the propensity of solids formation under expected operating conditions. Predictions will be compared with on-going experimental work at the site.

A conference on the dissolution of saltcake will be organized and this forum will provide for extended discussions on the progress and results of the work and on future programmatic directions. Reports on the saltcake dissolution studies and on the outcomes of the saltcake dissolution conference will be provided.

### *Task 3. Improvements and User Documentation for the ESP Model*

Some deficiencies have been shown to exist within the ESP data-banks.[27] Of high interest is the determination of solubility data for double salts. Solubility studies for $Na_3FSO_4$ will be conducted and compared to the results of the prior literature and the calculations performed in Task 1. Additional studies on the extent of hydration as a function of ionic strength will be performed for $Na_2CO_3$ and $Na_3PO_4$.[32] Experiments are also planned for NaF at elevated ionic strength and in the presence of $NaNO_3$.

Considerable effort has been expended in learning the most appropriate ways in which to develop and run ESP simulations. These will be documented and forwarded to customers at Hanford for incorporation in the ESP User Manual.

**Work Accomplished**

*Saltcake Dissolution – Modeling of Experimental Saltcake Dissolution*

ESP predictions for saltcake dissolution of FY 01 saltcakes were presented in a previous quarterly report for experiments conducted at 21 C. Experimental results for dissolutions of FY 01 saltcakes conducted at 21 C became available during this quarter. Solids characterization of BY-109 saltcakes as a function of diluent addition also became available.
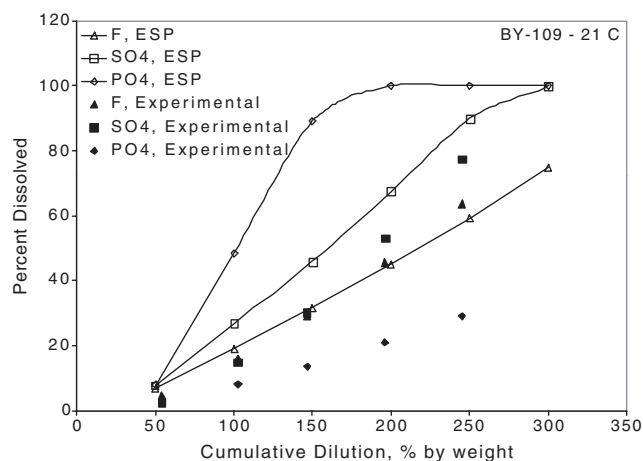


**FIGURE 11. Dissolution profiles for fluoride, phosphate, and sulfate anions from saltcake BY-109 at 21 C.**

Dissolution profiles for BY-109 saltcake at 21 C are shown for phosphate, fluoride, and sulfate in Figure 11. Experimental data on the percent of a given anion in the original saltcake dissolved as a function of cumulative diluent addition. Similar profiles are shown in Figure 12 for dissolution experiments conducted at 50 C. It is apparent from comparison of the plots that, while the prediction of fluoride dissolution at both temperatures is in good agreement with experi-

mental data; predictions of both sulfate and phosphate differ greatly from experimental data.
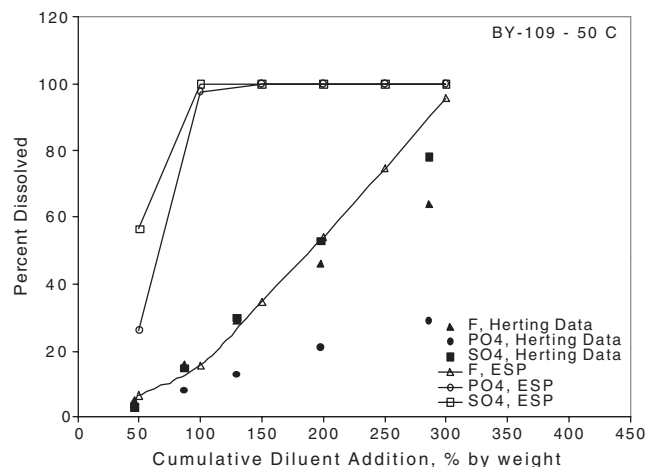


**FIGURE 12. Dissolution profiles for fluoride, phosphate, and sulfate anions from saltcake BY-109 at 50 C.**

At 21 C, ESP predictions of the solid phase indicate that $Na_3FSO_4$, $Na_7F(PO_4)_2 \cdot 19H_2O$, and NaF are present in the solid phase (in order of decreasing percent by weight). As diluent is added at 21 C, natrophosphate [$Na_7F(PO_4)_2 \cdot 19H_2O$] is predicted to dissolve to a greater degree than either NaF or $Na_3FSO_4$. ESP predictions of solid phase speciation are shown in Figure 13 for 21 C. Similar data for 50 C are shown in Figure 14. At 21 C, ESP predicts that the sulfate is partitioned into $Na_3FSO_4$, while at 50 C, it is partitioned into burkeite [$Na_6(SO_4)_2CO_3$] and anhydrous sodium sulfate [$Na_2SO_4$]. This partitioning is due to the temperature limits placed on the formation of these species by the ESP Public database. $Na_3FSO_4$ can only be predicted to form when the temperature is in the range of 20 C to 40 C, while $Na_6(SO_4)_2CO_3$ can only be predicted to form when the temperature is in the range of 30 C to 150 C.
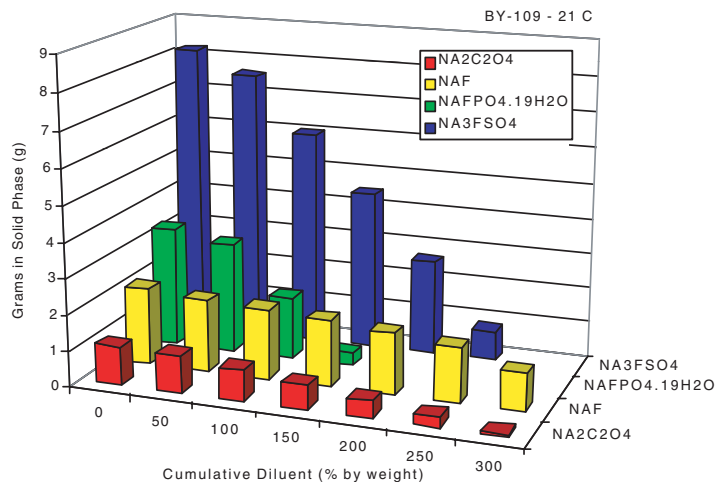
**FIGURE 13. Distribution of solid phase species with dissolution at 21 C for saltcake BY-109.**
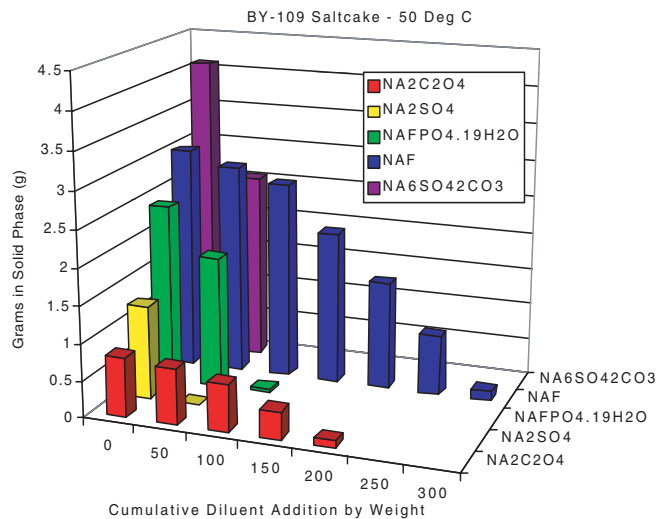


**FIGURE 14. Distribution of solid phase species with dissolution at 50 C for saltcake BY-109.**

Experimental measurements of the solubility of $Na_3FSO_4$ in aqueous, 1-m caustic and 3-m caustic solutions have yielded crystals of $Na_3FSO_4$ in the equilibrated solid phase at 50 C. Examination of the percent dissolved curves for sulfate at 21 C and at 50 C indicate that ESP predicts much greater dissolution of sulfate at 50 C than is experimentally realized. The partitioning of the sulfate into burkeite rather than $Na_3FSO_4$ is, in part, responsible for this behavior in the predictions. ESP predicts that the sulfate will be almost entirely dissolved by 100% cumulative dilution by weight, while experimental measurements indicate just less than 80% of the sulfate has dissolved by 300% cumulative dilution by weight. Even greater evidence that the sulfate present in the solid phase may be in the form of $Na_3FSO_4$ at 50 C is the close tracking of the experimental sulfate dissolution profile with that of fluoride. For both temperatures, 21 C and 50 C, the fluoride, sulfate, and phosphate experimental data show a slow increase as the cumulative diluent addition by weight increases. The experimental data for fluoride are predicted fairly well at the lower temperature, but at 50 C, ESP significantly overestimates the amount of fluoride dissolved at 300% by weight cumulative diluent addition.

Herting has conducted solids characterization of BY-109 saltcake as a function of diluent addition.[33] Major constituents of the solid phase in the undissolved BY-109 saltcake identified by PLM were $Na_3FSO_4$, $Na_7F(PO_4)_2 \cdot 19H_2O$, $Na_2C_2O_4$. NaF was also identified by XRD. In the ESP predictions for 21 C, these were also the major species identifies in the solid phase, comprising almost 90% of the solid phase by weight. In the solids identification by Herting, cryolite ($Na_3AlF_6$) was identified even after contact with diluent. The persistence of NaF in the solid phase is consistent with this finding. Cryolite is not an entity in the ESP databases, but it is an incongruent double salt. Previous experience with ESP predictions for an incongruent salt [$NaNO_3 \cdot Na_2SO_4 \cdot H_2O$] indicate that ESP predictions for the solubility envelope for such a species is predicted fairly well when thermodynamic data are available for the individual salts, even when no data are available within ESP for the double salt.

### *Comparative Calculations*

ESP predictions of the solubility of burkeite [$Na_6(SO_4)_2CO_3$] were revised using version 6.5 of ESP. The thermodynamic information available within the PUBLIC database for ESP is based on available literature and as a result, the temperature range over which ESP can predict the presence of this species in the solid phase is restricted to temperatures above 30 C. At temperatures below 30 C, either $Na_2CO_3 \cdot 10H_2O$ or $Na_2SO_4 \cdot 10H_2O$ precipitate from solution depending on the overall concentration of carbonate and sulfate in the aqueous solution. In the presence of caustic, the temperature at which the transition from sodium carbonate decahydrate to sodium carbonate monohydrate is depressed and in solutions containing 1-m hydroxide and 3-m hydroxide, the carbonate will precipitate as the monohydrate at 25 C. Similar behavior is present in the sodium sulfate system, with the depression of the transition temperature for the sodium sulfate decahydrate to anhydrous sodium sulfate with increasing concentration. Thus, it is reasonable to expect that the formation of burkeite may occur at temperatures below 30 C in the presence of hydroxide.

SOLGASMIX predictions of the sodium-sulfate-carbonate-hydroxide system were completed by C. F. Weber at ORNL. Two sets of predictions at 25 C were completed: one set assuming that burkeite was prohibited from forming at 25 C; and one set allowing the formation of burkeite in caustic solutions. At 50 C, only a single set of predictions were completed, those allowing the formation of burkeite. Comparisons with the ESP predictions are given in Figures 15 and 16. One item of note is that the speciation of carbonate in the solid phase differs in the ESP calculations and the SOLGASMIX calculations at 25 C, in 3-m hydroxide solution. SOLGASMIX predicts the decahydrate of sodium carbonate to be the stable phase, while ESP predicts the heptahydrate. These differences will be resolved once the experimental laboratory data for the sodium-carbonate-sulfate-hydroxide system have been regressed and incorporated into ESP.
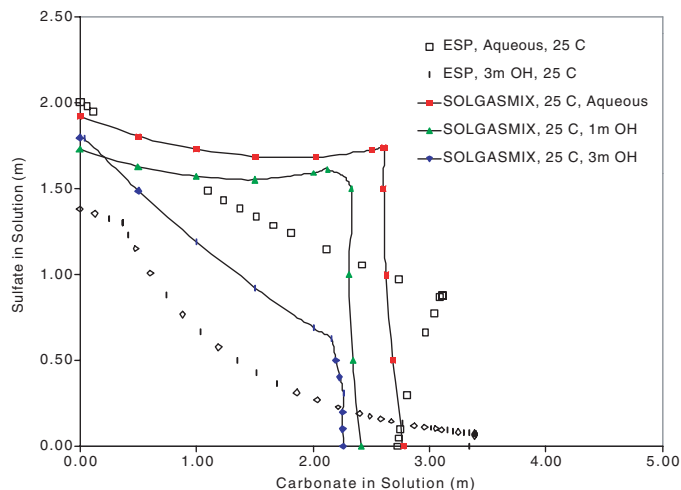
**FIGURE 15. Sodium-carbonate-sulfate-hydroxide system at 25 C. Comparison of ESP model predictions with SOLGASMIX predictions and with literature data.**
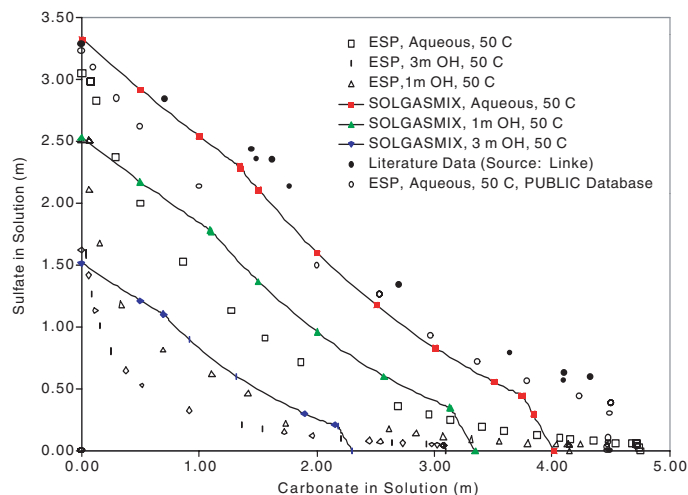


**FIGURE 16. Sodium-carbonate-sulfate-hydroxide system at 50 C. Comparison of ESP model predictions with SOLGASMIX predictions and with literature data.**

### *Laboratory Measurements for Double Salt Systems*

Experimental measurements for the solubility envelope in the sodium-fluoride-nitrate-hydroxide system and in the sodium-phosphate-nitrate-hydroxide system have been completed. These data have been regressed and incorporation of the regression fit into ESP is underway.

Experimental measurements for the solubility envelope in the sodium-carbonate-sulfate-hydroxide system are nearing completion and preliminary regression of the data has been initiated.

### Conclusion

Comparison of ESP predictions with saltcake dissolution experiments for the FY 01 tanks have reconfirmed the deficiencies in ESP with respect to fluoride, phosphate, sulfate, and carbonate partitioning. These deficiencies were previously identified in simulations of TX-113 saltcake dissolution during FY 00. Experimental efforts have been focused on addressing the deficiencies in the ESP databases. These experimental data have been or, are in the process of being, regressed and will be incorporated into ESP.

### Work Planned

Regression of available laboratory data will continue and compilation of regression results into a user-supplied database should be accomplished by the end of the first quarter of 2002. Revision of earlier predictions of saltcake dissolution will provide a point of comparison and reveal whether deficiencies previously noted are reduced and/or eliminated with use of the newly available data.

Laboratory measurements of the solubility for the sodium-fluoride-phosphate-nitrate-hydroxide system are underway and will pro-

vide additional data on the behavior of natrophosphate in high ionic strength solutions.

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## *Feed Stability and Transport: Solids Formation*

*J. S. Lindner, T. Durve, V. Raju, and R. K. Toghiani*

### Introduction

Tank farm operations at Hanford include the interim stabilization program where the supernate and interstitial liquor in the single-shell tanks is reduced. Benefits from this process include the minimization of leakage from aging tanks, thereby limiting migration of waste into the soil, and the temporary reduction of waste within the tank. The process consists of jet-pumping the liquid in a given tank, obtained through a screen or salt well to a double-shell holding tank and then to an evaporator. Dilution water is added at the pump head. Recently, solids formation and plugging have been noted during transfers from tanks 241-SX-104, 241-U-103, and 241-BY-102.[34] The primary solid responsible for the plugs from the first two tank wastes has been tentatively assigned, through experiments conducted on the waste liquid in the laboratory, as $Na_3PO_4 \cdot 12H_2O$. The plug formed during salt well pumping of BY-102 was believed to arise from sodium carbonate.

Other solids may participate in the plug formation process and this will largely depend on the solid-liquid equilibrium of the species contained in the waste stream. Little information, aside from the laboratory screening experiments is known regarding the mechanisms of plug formation and, more importantly, the required change in pressure that would indicate the beginning of plug formation. From operations measured records, the time needed for a plug can be determined and by knowing the pressures and flow rates the approximate location of the plug can be estimated; however, prevention of inadvertent plugs may be possible based on a suitable engineering tool that will allow operators to tailor waste transfers.

Long-term site operations will involve the dissolution of saltcake in the single-shell tanks and the removal of the salt liquor. Site plans are currently in progress for the retrieval of all of the salt in Hanford tank 241-S-112. Diluent will be added to the top of the saltcake followed by dissolution and permeation of the supernatant through the saltcake to the saltwell pump already located in the tank. Thus, some of the same problems that have already been addressed regarding the transport of high concentration phosphate solutions will remain. In addition, questions involve the rate and mechanisms associated with the saltcake dissolution process. These include the distribution of chemical species as retrieval proceeds (dissolution, dilution, and re-precipitation) and the physical characteristics of the saltcake bed, such as the porosity and permeability, which govern the rate at which the tank can be emptied. Work has started in this area with the development of an experimental approach that can provide the necessary information.

## Work Accomplished

### Salt Well Pumping Flow Loop Experiments

#### Unplugging

Details of the saltwell pumping flow loop and the experiments aimed at understanding the conditions under which sodium phosphate dodecahydrate crystals form has been described previously.[35,36] In most of these reports emphasis has been placed on identifying the processes and conditions that lead to plug formation. Additional work has been carried out to investigate the remediation of a plug once formed.[37] As noted earlier, many of the remaining single-shell tanks that have not yet undergone interim stabilization contain high phosphate loadings.[35,36] The possibility for additional site plugs based on phosphate remains. Consequently any method that may be available for the remediation of a phosphate plug could result in significant cost savings.

At the request of the TFA Pretreatment technical integration manager studies were begun to try and find suitable reagents that could aid in the removal/destruction of sodium phosphate dodecahydrate plugs. Initial baseline experiments, Figure 17, were conducted with warm (50 C) water. In brief the plugs were formed at different Reynolds numbers and allowed to remain in the channel of the flow loop for a specified length of time. The water was then applied to the plug at the pressure head of the pump. Corresponding pressures and temperatures were recorded until the pressure decreased signifying destruction of the plug. Data obtained indicates that the time necessary to unplug the channel depends on the plug standing time. The result indicates that the structure of the plug, once formed, depends on the time and this effect has been ascribed to Oswaltd ripening. This process, not well understood, involves the growth of larger crystals at the expense of the smaller ones. The results indicate that the plug becomes easier to dislodge or destroy if allowed to remain in the pipe.
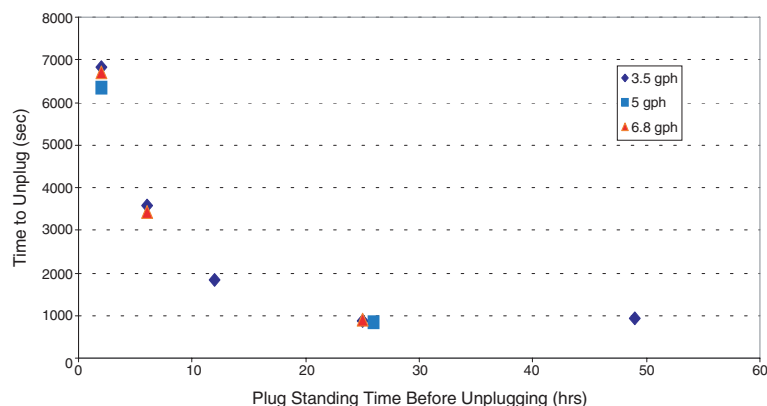


**FIGURE 17. Effect of plug standing time on plug destruction using water.**

Only one citation was found describing reaction of the sodium phosphate dodecahydrate crystals. Belton, et al., observed the forma-

tion of $NaHCO_3$ and $Na_2HPO_4 \cdot 7H_2O$ when carbon dioxide was added to the dodecahydrate ($Na_3PO_4 \cdot 12H_2O \cdot 0.25NaOH$).[38] The reaction was of interest from the fact that one crystal forms two when a gas was added. In practice the gas will convert to the carbonate anion from which the reaction proceeds. Experiments were then undertaken on the flow loop to investigate the potential of carbonate anion on plug destruction. Additional calculations were also carried out with the Environmental Simulation Program (ESP).

Plugs were formed from the same baseline surrogate composition (SX-104) as in the previous experiments. The flow rate of the surrogate was maintained at 3.5 gph and the plug, once formed, was allowed to remain in the channel for a period of two hours. A sodium carbonate solution of specific concentration was prepared, heated to 50 C and then applied to the plug at the pressure head of the pump. The results of the experiments are collected in Figure 18 where the data point at a carbonate concentration of 0 mol/L was averaged from the data for the two-hour period shown in Figure 17. A substantial decrease in the time necessary to clear the channel is observed with carbonate solutions as compared to water alone.
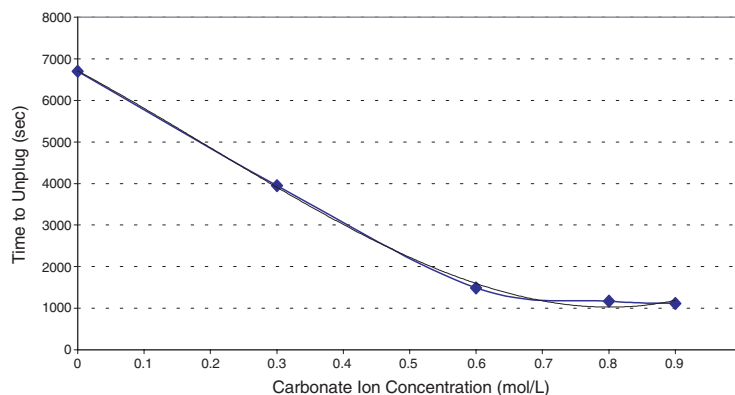


**FIGURE 18. Effect of the addition of sodium carbonate solution on unplugging.**

ESP calculations indicate the destruction of sodium phosphate dodecahydrate either with the addition of sodium carbonate or with carbon dioxide. $CO_2$ will rapidly oxidize to $CO_3^{-2}$ anion under the basic conditions of Hanford waste streams. Experiments using $CO_{2(g)}$ are under consideration. The selection of which reagent to employ at the site will require a safety review as well as a consideration of the implication of the addition on downstream process chemistry.

### *Support of 241-S-112 Saltcake Retrieval*

#### *Background and Experimental Design*

Porosity and permeability are expected to influence the rate at which the waste in the single shell tanks can be retrieved through the transport of the liquor through the saltcake to the saltwell pump. The Blake-Kozeny equation is one representation for the change in pressure, $\Delta P$, over some distance, $l$, through a material of porosity, $\varepsilon$,

$$\Delta P/l = (Q/A)(150\mu/D_p^2)((1-\varepsilon)^2/\varepsilon^3) \qquad \textbf{(EQ 1)}$$

here $Q$ is the volumetric flow rate, $A$ is the cross-sectional area of the column, $\mu$ is the liquid viscosity, and $D_p$ is the particle diameter.[39] The permeability, $k$, is related to the porosity through Darcy's law

$$Q/A = -(k/\mu)\Delta P \qquad \textbf{(EQ 2)}$$

Equation 1 provides a vehicle for the development of the experimental system.[40]

Preliminary sensitivity calculations were performed to understand the inter-relationships between the pertinent variables of Equation 1. Assuming that the flow rate is known or can be measured the carrier fluid viscosity, the average particle diameter, and the porosity will dictate the change in pressure. For example, a 1% increase in the flow rate or a 1% increase in the carrier fluid viscosity will correspond to a 1% increase in $\Delta P$. A 1% increase in the average particle diameter

corresponds to a 2% decrease in $\Delta P$. Finally, a 1% increase in the porosity corresponds to a 4% decrease in the change in pressure.

The parameters $\mu$, $D_p$, and $\varepsilon$ are expected to change during dissolution. Of these three variables, the viscosity of the effluent can be measured following the experiment and is calculated using the Environmental Simulation Program (ESP). Initial estimates are that the particle size distribution will not change significantly during the first stages of dissolution. Specifically, the dissolution process proceeds from the top of the column to the bottom. Consideration of the mass of the solids that initially undergo dissolution and the total number of like particles in the sample does not indicate a significant shift in the PSD. The distribution will, however, change as the salts are selectively dissolved. Experiments to determine changes in the average particle size will rely on running the column for select diluent additions followed by sampling. This same approach will be used to assess the saltcake structure by mercury intrusion porosimetry.
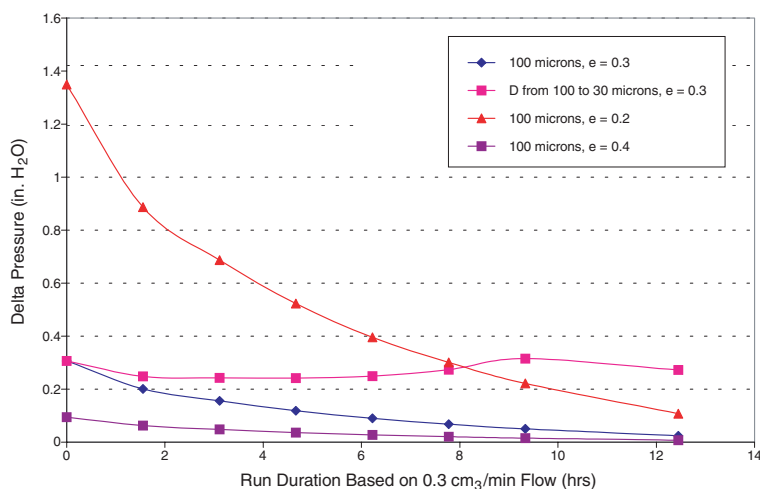


**FIGURE 19. Estimated $\Delta P$ values from Eq. 1 assuming carrier fluid viscosities calculated using ESP.**

The experiments to be performed are guided by the maximum flow rate of 8-gal/min. that can be attained in retrieving the saltcake liquor from the 75-ft diameter tank at the site. Using a 3-in. diameter column the corresponding laboratory flow rate is 0.3-ml/min. Using this value and estimates for the porosity and the particle diameter along with predicted viscosities from ESP at various stages of dilution the change in pressure was calculated, Figure 19. Here the initial composition of the surrogate was supplied by R. Hunt at ORNL, Table 1.

**TABLE 1. Composition of the saltcake base solution.**

| Constituent | mol |
|---|---|
| $Al(NO_3)_3*9H_2O$ | 0.967 |
| $Na_2CO_3$ | 0.813 |
| Na | 12.161 |
| $NaNO_2$ | 1.409 |
| $NaNO_3$ | 4.942 |
| NaOH | 5.762 |
| $Na_3PO_4*12H_2O*^1/_4NaOH$ | 0.313 |
| $Na_2SO_4$ | 0.189 |
| $H_2O$ | 55.509 |

This solution was processed in ESP by heating to about 130 C to evaporate water and then cooling. The final saltcake consisted of various salts, predominately sodium nitrate (> 50% by wt.) and sodium phosphate dodecahydrate and sodium carbonate in the carrier fluid. The total water loading was 15% by weight.

The viscosity was taken of that in the effluent and depends on the volume of diluent added. A given diluent volume relates to the duration of the run at the nominal 0.3-ml/min. flow rate. The initial viscosity of the liquid in the surrogate saltcake was calculated as 17 cp,

while the viscosity at the end of the simulation was determined as 6 cp (non-linear with diluent addition).

The data given in Figure 19 encompass a dilution range of from 0 - 100% by weight of the original saltcake mass (~ 230 g) used in the calculations. The diameter of the column, the flow rate, and reasonable assumptions for the porosity and the particle diameter indicate that the pressure drop across the column can be measured.

### *Saltcake Dissolution Flow Module (SDFM)*

A block diagram of the one-column version of the Saltcake Dissolution Flow Module (SDFM) is given in Figure 20. The 3-in. i.d. column is also 3 in. high and is packed with the surrogate saltcake. Diluent (water or caustic or sequential additions of both depending on model predictions) from the controllable peristaltic pump is delivered to the column at a flow rate not to exceed 0.3-ml/min. through stainless steel fittings.
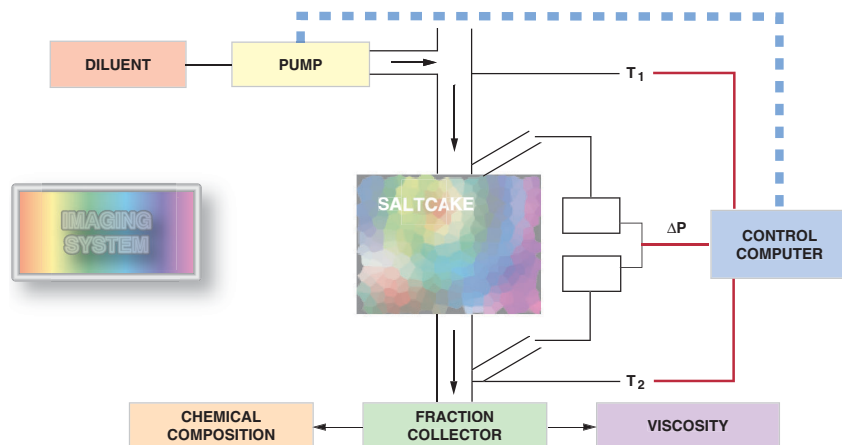


**FIGURE 20. Base configuration of the saltcake dissolution flow module.**

The system will be instrumented with thermocouples (to assess the endothermic or exothermic nature of the dissolution process) and with a differential pressure transducer. Signals from the sensors will be logged on the existing Camile® laboratory control system. In the preferred embodiment of the SDFM the pressure will be maintained at a constant value by controlling the flow rate from the peristaltic pump. This data, along with the measured viscosities will allow calculation of the Darcy permeability, Equation 2. The porosity of the saltcake as a function of dissolution can also be obtained through either the assumption of the average particle size or through the microscopic analysis described above.

The base system configuration will allow for the assignment of bed bridging through radical changes in the pressure. Analysis of solids re-precipitation will require a series of two columns with provisions for sampling the effluent from the first column.

The experiments are expected to provide chemical information relating to the dissolution of the various salts in the column along with an understanding of the effects of the fundamental parameters on the transport of the saltcake liquor trough the bed. Liquid fractions will be analyzed for ionic constituents using ion chromatography and for aluminum using ICP. Measurements of the viscosities of the fractions will be performed and compared to the ESP predictions and used in evaluation of the permeability and porosity. Solids formed will be characterized and sized using the polarized light microscope. Pressures, flow rates, and viscosities will be used to determine the permeability and using the Blake-Kozeny equation or a similar expression to determine the factors controlling the saltcake dissolution process.

The above data will allow for the determination of effluent composition over time and for evaluation of permeability/porosity as a function of time/bed height and an assessment of re-precipitation process that are occurring. Determination of feed stability and transfer-

water dilution requirements is a direct result of the chemical composition studies.

At present most all of the components of the SDFM have been obtained. The acrylic column has been machined in the DIAL shops and system assembly is in progress. The saltcake from the recipe given in Table 1 has been made in the laboratory. The material was observed to flow easily into a standard 100-mL burette indicating that packing the 3-in. column is not expected to be difficult. A small amount of saltcake was filtered and dried and submitted for mercury intrusion porosimetry. The resulting porosity of 58% was somewhat surprising based on an initial literature review and probably reflects the packing of the rod-like sodium phosphate dodecahydrate crystal with the smaller carbonate crystals and the regular sodium nitrate crystals. If needed a longer column will be manufactured if it turns out that the porosities determined in the SDFM are considerably larger that anticipated.

**Project Status**

Work is continuing both on saltwell pumping and pipe unplugging and on the scaling experiments for 241-S-112 retrieval. Additional CFD calculations to further define slurry transfer operating envelopes are in progress.

**Conclusions**

A significant effect on the unplugging of blockages comprised of sodium phosphate dodecahydrate has been observed. Addition of a low concentration sodium carbonate solution to the plug results in faster destruction of the plug. An experiment has been designed which will allow for determining the chemistry associated with saltcake dissolution and for understanding of the various properties that effect the retrieval process.

## Work Planned

Assembly and completion of the SDFM will continue followed by experiments on the saltcake simulant provided by ORNL. Discussions with Hanford customers will be initiated regarding carbon dioxide or carbonate injection for remediation of phosphate plugs.

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*Environmental Control Device Testing*

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### *Evaluation of HEPA Filter Performance*

*J. A. Etheridge*

**Introduction**

In 2000, the U.S. Department of Energy (DOE) and the Environmental Protection Agency (EPA) signed a Memorandum of Understanding to combine research efforts to the maximum extent possible to resolve important questions of common interest. One of these revolved around the issue of assuring the performance of HEPA filters used in off-gas systems. As a result, this Technical Working Group was chartered to provide methodology to ensure that HEPA filters provided adequate protection throughout their service life. The work proposed here is a direct result of the efforts of the NTW.

One of the major parts of this project is a survey of what has already been done, what is currently being done, and what the priorities are for additional work that needs to completed. At present there is a lot confusion and misinformation concerning HEPA filters, filter testing, and filter applications. There appears to be a strong need for a HEPA filter test bed for the purposes of challenging the filter medium as well as for development of instrumentation. We plan to construct a

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filter test bed (HEPA Filter Challenge Facility). It will be capable of DOP/PAO testing as well as handling a variety of other challenge agents including water, smoke, heat, and particles from particle generators. It will be instrumented and monitored in much the same way as the combustion test stand and will also be useful for instrument development and CEM testing. Modeling of the results of specific types of failures will also be done along with testing, where practical, to verify that the model is useful. This is important for understanding both DOP testing and online failure of HEPA filters.

One of the major needs related to HEPA filters is the need for a "break through" detector. Testing of the cavity ring down system for possible use as a break through detector is also planned. It is also proposed to acquire an "electrostatic impactor" (ELPI) for use as both a measure of input challenge agents and for measuring after the HEPA filters. If this unit is successful in measuring very low particle concentrations (or low mass loading) it will allow us to test the limits of detection of other particle measuring techniques.

The scope of this project could be amended depending upon the results of the NTW's review of our Data Quality Objectives and the evolution of the NTW's HEPA Filter Performance position paper. However, it is believed that the activities described below accurately represent the magnitude of the effort, and the equipment and supplies required for the program.

**Work Accomplished**

The HEPA Test Plan was peer reviewed by the ASME on October 2, 2001, in Boise, Idaho. The review went well and was helpful to us for formulating the balance of the Test Plan (Failure Mode and Source Term Testing). The results of the peer review along with the Work Group's response are included on the MWFA web site.

Several of the particle size/classifier instruments, as well as other support instrumentation, have been ordered. These include an ELPI (electric low pressure impactor) and a DMA-CPC, or SMPS. The design for the test stand to be used for filter/CEM evaluation has been completed and most of its support instrumentation has been ordered.

Two conference presentations describing this project are currently being written. One for the Waste Management Symposium in Tucson has already been submitted and one to be presented at the Incineration Conference in New Orleans in not yet complete.

Conference calls involving several members of the NTW continue at about two-week intervals to finalize many of the details of the project.

We will continue work on preparing a laboratory for use as space for the calibration portion of the project. The lab is currently be cleaned and air filtration equipment is being evaluated for maintaining a low ambient particle level.

### Sampling System for Dioxins, Furans and Other Semi-volatile Products of Incomplete Combustion and Characterization

#### Introduction

Selected congeners of the families of dioxins and furans (D/F) are potentially some of the most carcinogenic compounds known to exist. Recognition of the potential risk to the U.S. population spurred the conduction of a national inventory of D/F sources. A significant outcome of this initiative has been the establishment of a strategy to reduce emissions in a targeted fashion. One of the centerpieces of the D/F reduction strategy is the Maximum Achievable Control Technology (MACT) standard just issued for hazardous waste combustors (HWC). Each of the DOE hazardous or mixed waste incinerators falls subject to this new standard and there are stringent emission levels that will need to be met in the near future.

The 0.2 ng/dsm$^3$ emission standard called for under the HWC-MACT stresses the technical limits of operational control and emissions testing. Uncertainties associated with US EPA reference method stack sampling accuracy and method quantification limits for

the 17 D/F congeners that have non-zero toxicity equivalence factors invite skeptical review of the measurements that will be made by facilities to demonstrate compliance with this new standard.

Of the six needs listed on the DOE EM-Needs web page related to dioxin/furan problems, three (ID-3.2.32, ID-S.1.02, and SR00-1021) recognize the lack of knowledge associated with the specific locus of D/F formation, the distribution of D/F congeners between adsorbed and gaseous phases at temperature, and/or the behavior of these classes of compounds in the sampling train. This lack of knowledge is an impediment to minimizing emissions by process control or design/operation of pollution control devices. Additionally, a much fuller understanding of the phase behavior in off-gases is essential to development of a functional continuous emission monitor or verifying the accuracy of extractive sampling methodologies. Finally, a clearer picture of the gas phase chemistry is the best hope of identifying a dependable analytical surrogate, if one exists.

Intensive research has been undertaken throughout the past two decades to gain a more complete understanding of the mechanism(s) of dioxin/furan formation in combustion processes. The majority of controlled mechanistic studies of D/F formation tend to be carried out using bench top and micro-scale apparati. A significant body of data has also been accumulated from off-gas samples collected from solid waste incinerators and industrial processes. However, the large number of variables associated with fuel feed and operational history of incinerators makes it difficult to extrapolate from bench to full scale. A series of studies is proposed to take advantage of bench scale results and, in a two-stage manner, extend these investigations to pilot scale.

The primary focus of this effort will be to determine the behavior of D/Fs associated with fly ash particulates in an isothermal off-gas environment for the temperature range of 300 to 800 F. This will include analysis of samples for D/F homologues to determine the

extent of formation, destruction, and dechlorination under test conditions.

All of the results from these investigations will be utilized, along with literature information, in the initial development and evaluation of a hybrid artificial intelligence system (combination neural network-expert system) to project D/F formation, identify areas of needed research, and search for analytical surrogates.

**Work Accomplished**

This quarter has been productive in terms of reaching a point of functionality for the sampling system. A temperature profile for the flight tube of the test stand was developed to help determine the feasibility of maintaining a constant sample temperature throughout the length of the sampling system. Equipment needed for the sampling system has been acquired and tested. At this point almost all of the pieces are in place and are in the process of being tested to ensure that the parts selected are all appropriate and sufficient. Most of the development this quarter has involved the physical assembly of the system itself, but also included a fair amount of testing.

The list of newly acquired pieces includes valves for the process. After a very difficult search, valves that seem to fulfill the needs of the project were selected and placed in the system. The valve chosen is an all-metal ball valve manufactured by Whitey, with Graphoil seats and seals. The next step is to select a heating method for the valve, so that the sample does not suffer any thermal losses. It does not fit within the oven and the first attempt at using heating tape was not as successful as anticipated, however, this is not a serious problem. Two all-metal 1/8-inch valves have been obtained for the inlet and outlets to the analyte trap. There is a temperature limitation with the valves currently in use, but a more expensive variety of this same valve will solve that problem when it is determined conclusively that these valves are sufficient for the application.

To determine additional information involving a potential need for extra heating elements or insulation, a temperature profile for the flight tube of the test stand was developed. From the information gathered in this experiment, it was determined that the amount of the sampling system exposed to the ambient air needs to be minimized. Heating tape has been acquired and tested for portions of the system. Temperature controllers have also been selected to maintain temperatures in several different locations. It was also determined that an additional heating unit will be necessary for the flight tube.

A power supply has been selected to drive the peltier coolers used in this application. There are four 156-W peltier coolers used to cool the trap. Two coolers per side of the trap, measuring 50 mm x 100 mm. The heat given off by the peltiers is removed through the water flowing through a hollow block of copper, serving as a water jacket. There are two sets of two peltier coolers and water jacket that fit one on either side of the analyte trap. Tests have been conducted to determine the efficiency of the cooling setup in maintaining the temperature of the trap at a desired level. It is possible that a trap with a greater surface area for cooling will need to be constructed pending further testing.

The temperature controllers, along with the power supply, the oven, the heaters along the flight tube of the test stand, the flow rates of both the fuel and the air supplied to the combustor are all under the control of a computer software program. That program also records temperature data from five locations with in the system, and has the capability of adding ten more data points of input. The goal is to eventually be able to control every aspect of the sampling system from one computer.

**Work Planned**

DIAL will continue to develop its small-scale test stand for D/F research and the evaluation of its isokinetic and isothermal sampling

system. During the next three months emphasis will be placed on completion of the assembly of the sampling system components with respect to thermal and flow properties. Testing will begin to ensure that the entire system functions as desired, considering both temperature and flow requirements. The system will then be sent to Restek to be coated with the inerting material. Other issues that need to be addressed include reducing the carrier gas flow rate for the particle feeder to a level that is functional with regard to particle transport and nominal with regard to perturbing the off gas chemistry and temperature profile in the region downstream of particle injection.

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## Toxic Organic Compound Monitoring Using Cavity Ringdown Spectroscopy

*C. B. Winstead*

### Introduction

Several US DOE science and technology needs are based upon the need for high-sensitivity and robust monitoring devices for various organic species. For example, the following needs are all related to the monitoring of volatile or semi-volatile organic compounds (VOCs or SVOCs) in combustion or thermal treatment systems:

- Continuous Emissions Monitor for Offgas Analysis (ID-2.1.18, Priority 1)
- Develop Thermal Treatment Unit Offgas CEM Monitors. (ID-3.2.32, Priority 2)
- Volatile Organic Compound Monitoring and Detection (ORHY-04, Priority 3)

The effort reported here is a continuation and combination of two separate tasks from DIAL's previous cooperative agreement (Task 1.1 *Volatile Organic Compound Monitors Using Diode Lasers* and Task 1.3 *Sensitive Detection of Toxic Chlorinated Compounds*). Together, these projects have demonstrated the first sensitive detection of VOCs such as benzene and chlorobenzene using diode laser CRDS and obtained the first CRDS spectra for dioxin (an SVOC). While the emission of dioxins and furans are important risk and regulatory drivers, significant research will be required prior to full development of a dioxin/furan continuous emission monitor (CEM). Questions such as how dioxin is partitioned in the gas stream between gas and particulate phases must be investigated and appropriate sampling systems developed before truly quantitative analysis can be carried out on-line. In addition, monitoring dioxin precursor or indicator molecules

such as chlorobenzene may prove to be a viable alternative to dioxin monitoring.[1] Thus, it is beneficial for the development of VOC or SVOC monitors for thermal applications to be coupled with an over-all investigation of formation and monitoring of dioxin. Such instru-ments likely will have value in research efforts to understand dioxin formation well before reaching a level associated with an industrial CEM, a role that may ultimately prove more important for reducing dioxin emissions than a commercial CEM.

The approach taken here includes continuing the development of advanced CRDS techniques using both ultraviolet pulsed and near-infrared diode lasers for the detection of VOCs and SVOCs at atmo-spheric or reduced pressures. CRDS is based upon the measurement of the time required for light to decay in a stable optical cavity.[2] This light may be injected into the cavity using either pulsed or continuous wave lasers. A small quantity of an absorbing species present in the optical cavity will absorb and thus remove some light from the cavity, reducing the decay time. This change in ringdown time can be directly related to the number density of absorbing atoms or mole-cules in the cavity. The extreme sensitivity of the CRDS techniques is achieved due to the extremely long effective pathlength (up to several kilometers) for the light recirculating in the cavity to interact with a sample gas.

The efforts described here are focused on improving the sensitiv-ity and selectivity of our previous measurements and participating in collaborative efforts to develop appropriate sampling systems for dioxin species. Slit jet expansion techniques will be incorporated with CRDS to cause narrowing of molecular spectra by decreasing the population in excited vibrational and rotational energy levels.[3] This narrowing will reduce the spectral overlap between different VOCs or SVOCs, thus enhancing detection selectivity. The slit jet expansion will initially be tested with VOCs prior to a demonstration of the detection of dioxin. The expansion cooled spectra will be directly compared to our other room temperature dioxin data to quan-

tify the change in detection limit due to the expansion. These efforts are designed to be complementary to those underway by EPA researchers who are using resonantly enhanced multiphoton ionization (REMPI) for dioxin detection.[4] Continued development of CRDS should ultimately provide a technology complementary to the REMPI system. CRDS sensitivity should not be strongly impacted by increasing chlorination of dioxin molecules, in contrast to expected sensitivity reductions for REMPI.

Finally, small yet ultra sensitive sensor systems could no doubt play a significant role in monitoring and/or process control for a number of remediation activities related to clean-up of volatile organics. For example, a number of subsurface and ground-water remediation efforts could benefit from on-line "process" monitoring for VOCs. These include efforts utilizing soil heating, in-well vapor stripping, passive soil vapor extraction, and other in-situ clean-up technologies where simple, real-time VOC monitoring could be used to indicate or monitor system performance. Low-power sensing technologies for VOC monitoring will be required for long-term monitoring efforts both for atmospheric and subsurface monitors, e.g. for continuous monitoring of subsurface reactive barriers or VOC plumes. Systems have already been demonstrated that utilize underground piping to collect soil gas and transport it to a surface monitoring system.[5] For long-term monitoring, diode-based VOC monitoring systems could significantly simplify the analytical equipment required for monitoring while reducing power consumption, features important for use in remote locations. Our continued development of diode laser CRDS may impact these areas in addition to thermal or combustion system monitoring.

**Work Accomplished**

Extensive data analysis was carried out during this quarter for the diode laser cavity ringdown experiments as part of thesis preparation for a master's level chemistry graduate student. The experimental

data obtained to date have been reanalyzed using an improved three-parameter exponential fit described in the preceding quarter's report. Remarkable improvement in reproducibility is evident in the data after reanalysis using this updated procedure. In most cases, the variability in absorption cross-section measurements has dropped from approximately ± 15% to better than ± 1% due to the improved mathematical treatment of the ringdown waveforms. For example, at a wavelength of 1656.11 nm, analysis of data from five separate experimental series resulted in a cross-section measurement of 0.777

($\forall$0.004) x $10^{-21}$ cm$^{-2}$ for benzene, a standard error of less than 0.5%. This is representative of most results and is indicative of a greatly improved day to day measurement reproducibility. At present using a distributed feedback diode laser operating at 1656.11 nm, system detection limits for benzene, chlorobenzene, and toluene equivalent to 480, 140, 530 ppb are typical. By tuning to the maximum absorption wavelength using an external cavity diode laser, the detection limits improve several fold.

Work on the slit-jet cavity ringdown experiments was delayed due to shipping damage on the system vacuum pump. However, repairs were completed and the vacuum system has been assembled and leak tested and is working well. The system vacuum chamber has been installed on a frame along with a gate valve and diffusion and mechanical vacuum pumps.

**Work Planned**

With student thesis work and the vacuum chamber for the slit jet expansion system nearly completed, installation of the gas valve for the expansion should begin shortly. When completed, this will allow for testing of the valve and the beginning of experiments aimed at coordinating the ringdown data acquisition with the valve firing. Several more experiments are planned for the present diode laser ringdown system to complete the acquisition of spectra using the external

cavity diode laser. However, most effort will soon be transferring to the slit jet expansion system.

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