
Technology Demonstration and Verification Research

**Quarterly Technical Progress Report
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Table of Contents

Executive Summary	1
Task 1. Verification Monitors for Thermal Treatment.	1
Task 2. Deactivation and Decommissioning Technology Support	2
Task 3. Technical Data to Support Cleanup Decisions	4
Task 4. Product Acceptance Support.	5
Task 5. Advanced Cleanup Support: Robust Immobilization Devices	6
TASK 1 Verification Monitors for Thermal Treatment	9
Subtask 1.1. Monitors for Thermal Treatment Processes	9
Air Plasma Off-gas Emission Monitor	10
Laser-induced Breakdown Spectroscopy	17
Subtask 1.2. Mercury Absorber Technology	22
Subtask 1.3. Feature Extraction from Digital Images of Thermal Treatment Source(s)	23
TASK 2 Deactivation and Decommissioning Technology Support	25
Subtask 2.1. Pipe Decontamination	25
Subtask 2.2. Wall Removal Monitor	29
TASK 3 Technical Data to Support Cleanup Decisions	33
Subtask 3.1. Dioxins/Furans in Incinerator Burners	33
Dioxin Tests	34

Detection of Chlorinated Organics by Cavity Ring-down Spectroscopy	35
Subtask 3.2. Dissolution of Hanford Salt	39
TASK 4 Product Acceptance Support	64
Subtask 4.1. Monitors for Idaho Law Stream	64
Subtask 4.2. Pressure in Drums	70
TASK 5 Advanced Cleanup Support: Robust Immobilization Devices	74
Subtask 5.1. Hybrid Plasma Induction Cold Crucible Melter	74
Subtask 5.2. Hollow-electrode DC Arc Furnace for Mixed-waste Treatment	83

List of Figures

Figure 1. APO-GEM schematic diagram	12
Figure 2. LIBS experimental setup	18
Figure 3. Pb signal at different gas temperatures	20
Figure 4. Signal-to-noise ratio of LIBS data at different gas temperatures	20
Figure 5. Low resolution spectrum of 1,4-dichlorobenzene in the region of the origin band of the $S_1 \leftarrow S_0$ system	37
Figure 6. Ring-down waveforms for 1,4 dichlorobenzene at the peak of the origin band and at the baseline to the blue of the peak	37
Figure 7. ESP flowsheet for the crust remediation simulations	47
Figure 8. Block diagram of the crust level growth remediation	47
Figure 9. Gas released from the crust as a function of water added	52
Figure 10. Selected crust solids dissolution behavior for the 3-layer model at 458 C	53
Figure 11. Configuration information for SY-101 following the transfer of 100,000 gallons of waste liquid and subsequent dilution of the 3-layer crust	56
Figure 12. Solids loadings for the three layer crust model at different diluent temperatures	59
Figure 13. Waste elevations and percentage of the original crust gas released for a 400,000-liter dilution of the crust at the indicated temperatures	60
Figure 14. Schematic of cavity-ringdown spectroscopy technique	66

Figure 15. Schematic of the laser-induced fluorescence spectrometry technique 67

Figure 16. Schematic of isotopic energy shifts and the associated LIF spectrum 67

Figure 17. Schematic of hybrid plasma induction cold crucible melter 76

Figure 18. Average temperature vs. input power 81

List of Tables

Table 1. Detection limits for the APO-GEM for various metals . . .	15
Table 2. Relative accuracy of DIAL Air-ICP data	16
Table 3. Temperature settings used in the experiments.	19
Table 4. Simulated crust layer configurations assumed for the 3-layer model calculations	45
Table 5. Solids distributions from ESP and from Person	49
Table 6. Final crust (all layers) compositions following dilution with water at 458 C	51
Table 7. Final crust solids distribution, 3-layer model at 458 C . .	54
Table 8. Final configuration for SY-101 following crust dilution, 3-layer model, 458 C	55
Table 9. Effect of water addition temperature on crust layer solids dissolution with 400,000 L of water added and the crust at 458 C	58
Table 10. Final configuration of SY-101 for the elevated temperature experiments.	59

Executive Summary

Task 1. Verification Monitors for Thermal Treatment

Subtask 1.1. Monitors for Thermal Treatment Processes

Air Plasma Off-gas Emission Monitor (APO-GEM). Three presentations were made and one publication issued. Discussions are proceeding with two companies with respect to possible commercialization of the instrument. Another company has expressed interest in evaluating APO-GEM for use in measuring uranium concentration. Experimental progress continues to be significantly impacted due to the manpower shortfall. The focus in the next quarter will be on the completion and submission of several papers for publication.

Laser-induced Breakdown Spectroscopy. A series of studies were conducted in a simulated system to study the effects of gas stream parameters on LIBS calibration. LIBS spectra were recorded with and without fly ash and under several gas temperatures. We found that the calibration slope for measurements with fly ash is higher than that without fly ash. It might be due to the enhancement of the laser spark with the presence of fly ash in the gas stream. Experiments also showed that the measurement precision degraded as the gas temperature increased. This is due to a weaker signal from the lower density hot gas.

Subtask 1.2. Hg Absorber

Project deferred.

Subtask 1.3. Feature Extraction from Digital Images of Thermal Treatment Source(s)

The goal of this project is to extract information about species and objects of environmental concern from images of the primary chamber of a thermal treatment system. We have demonstrated the feasibility of determining the concentration and spatial distribution of selected species (including mercury, sodium and potassium) in laboratory flames. Using a two-camera system, we simultaneously determined the spatial distributions of sodium and potassium in laboratory flames; sodium and potassium were chosen for this study because they are strongly emitting species that are safe to work with. The presence of potassium alters the calibration curve for sodium. Efforts are continuing to develop a calibration method that takes this “matrix effect” into account. We have applied different visualization techniques to the images acquired from DIAL’s plasma torch hearth, so that the species emission intensity and its local distribution can be visualized in the formats of two-dimensional intensity contour and three-dimensional surface. Studies are on-going to determine if information extracted from digital images of the plasma torch can be utilized for process control of the plasma torch.

Task 2. Deactivation and Decommissioning Technology Support

Subtask 2.1. Pipecleaning Technology

The Department of Energy has radioactive and hazardous contamination inside many of its process piping and duct systems. Con-

taminants remain in these systems after liquid is drained from them, adsorbing onto metal and other surfaces or depositing as residual liquids or solids. Many of the piping systems are not directly accessible because parts of them are buried underground or under concrete floors. A tube cleaning system (TCS) has been developed at Mississippi State University (MSU) in collaboration with the Tennessee Valley Authority (TVA) and the Southwest Research Institute (SwRI). The TCS utilizes repetitive high-voltage electrical discharges in water or other fluids to produce acoustic shock waves which are effective in removing scale, silt, and other fluid-saturated deposits from tube inner surfaces. This method is a noncontact, nonchemical method for removing these deposits. The arc-discharge applicator tip is mounted on a coaxial cable which can be deployed in excess of one hundred feet long. The pulsed acoustic shock wave successively removes accumulated scale and other deposits as the arc discharge source is moved down the tube by the TCS operator. Foreign matter scrubbed from the wall by the shock impulse and cavitation is ejected from the wall into the water. Microscopic particles remain in suspension, where they may be removed from the water via conventional means. The TCS minimizes the generation of secondary waste while at the same time minimizing worker exposure to radiation.

Subtask 2.2. Wall Removal Monitor

In support of the DOE decontamination and decommissioning (D&D) of concrete structures, DIAL has developed a technology for monitoring scabbling operations. To D&D a concrete structure the thin (~.5 inch) layer of contaminated concrete is removed by a process called scabbling. Current technology requires a surveying crew to measure points on the structure at one-foot intervals. After the survey is completed the scabbling contractor performs the removal operation, and then the surveying crew comes back to make measurements. This process is time consuming and complicated, and if the contractor does not remove the required amount of material, additional cost and time is required to correct and re-measure the results.

The wall removal monitor runs in real time providing information about the amount of material removed while the scabbling operation is occurring. In tests, the system was placed ~30 feet from the wall (well out of the way of operating machinery) and measured 145 square feet at a time. Data collection took only seconds, and set-up required only 30 minutes. The wall removal monitor developed by DIAL is described in *Wall Removal Monitor* (DIAL Technical Memo WRM 1198).

Task 3. Technical Data to Support Cleanup Decisions

Subtask 3.1. Dioxins/Furans in Incinerator Burners

Dioxin Tests. Thermal treatment processes (incinerators, melters) typically emit toxic metals (esp. mercury), volatile and semi-volatile organic materials (esp. dioxins and furans), and particulate matter during processing. While the levels from DOE facilities meet current regulatory limits, the EPA is in the process of promulgating new rules (the so-called “MACT” rules) with much lower limits. As was discussed at the National Technical Working Group pre-meeting on November 4, 1997, preliminary data indicate that the Consolidated Incinerator Facility at SRS may not be able to meet the very stringent MACT rules for dioxin. Based on preliminary testing, Savannah River personnel suspect that the fuel oil burner used in the incinerator may be an important contributor to the problem. Installing additional control devices on the CIF would be expensive, and difficult to accomplish in a radioactive environment. As a result, SRS and the other DOE incinerator operators require additional testing to confirm that the incinerator’s burner is the source of the dioxins/furans. DIAL will expand the scope of testing to be performed for a commercial burner manufacturer to include determination of the concentration of dioxins/furans produced as a function of burner operating conditions. DIAL will take its instrumentation to the burner manufacturer. Dioxin/furan contents in the effluents will be determined as a func-

tion of burner operating conditions. As a result, DIAL may be able to provide a window of burner operating conditions which could avoid the need for additional control devices. An engineer from DOE's Consolidated Incinerator Facility will work with DIAL on this effort. He will assist by ensuring that testing adequately reflects conditions in the CIF, and by reviewing test plans and test reports. The objective of this task is to determine dioxin/furan production from a fuel oil burner.

Detection of Chlorinated Organics by Cavity Ring-Down Spectroscopy. This project is concerned with developing cavity ring-down spectroscopy for sensitive detection of chlorinated organic compounds of environmental concern. Since the submission the previous report, we have recorded the cavity ring-down spectra of chlorinated volatile organic compounds (VOCs) with a tunable ultraviolet laser.

Task 4. Product Acceptance Support

Subtask 4.1. Monitors for Idaho LAW Stream

DIAL is developing two techniques for on-line determination of isotopic abundances of long-lived radionuclides (particularly the transuranic (TRU) elements) present at ultra-sensitive levels: these techniques are cavity ringdown spectroscopy (CRDS) and laser-induced fluorescence (LIF) spectrometry. Mississippi State University and hence DIAL currently do not have a license to work with actinides. The essential monitoring equipment has been ordered and is expected to arrive in mid-January. The university radiation safety officer has begun the process to acquire the appropriate calibration standards and other needed materials and supplies. The university expects to reopen negotiations with the state regulatory agency by the end of January. It is currently anticipated that the university will have the appropriate regulatory license by March 1999. Thereafter, we will be able to work with uranium. Consequently, our efforts have been

stalled pending issuance of this license. Efforts on surrogate materials continue. It is anticipated that in the coming year, the CRDS detection limit measurements will be finalized for TRU elements. The process of purchasing an ICP atomization system for LIF has begun, with delivery anticipated before the end of March 1999. During the next quarter, the LIF group expects an opportunity to use the new moderately high resolution dye laser system owned by DIAL's CRDS group in order to determine whether or not such a system has sufficient resolution to isotopically resolve uranium.

Subtask 4.2. Pressure in Drums

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

Task 5. Advanced Cleanup Support: Robust Immobilization Devices

Subtask 5.1. Hybrid Plasma Induction Cold Crucible Melter

The Diagnostic Instrumentation and Analysis Laboratory (DIAL) at Mississippi State University has begun evaluation of a hybrid plasma induction cold crucible melter (PICCM) for its potential success in processing spent nuclear fuel and other heterogeneous, metal containing waste. The hybrid plasma induction cold crucible melter

was developed at the Russian Institute of Chemical Technology in Moscow. Though originally designed for producing chemically active, high purity metals, it was brought to the United States for research in treating radioactive wastes containing metal. The PICCM combines plasma heating for the non-metal portion of the waste and inductive heating for the metallic portion. Processing yields distinct layers providing the ability to remove the metal layer as an ingot for reuse or for disposal as a low level waste with the radioactive components concentrating in the upper glassy slag layer. The cold crucible design nullifies the problem of selecting/creating a refractory that can withstand glass and metal environments in high temperature processing. The PICCM, fabricated in Russia in 1994, was received at DIAL in May 1998 after a brief installation at Georgia Tech during 1996. Two technical exchanges between the Russian developers and DIAL followed the PICCM arrival in June and September/October 1998. The close of the second technical exchange between Russian scientists, Dr. Vitality Gotovchikov and Naum Gurvitch, and DIAL produced a successful installation. The functional aspects of the melter operation have been identified through the three tests performed during the international exchange and subsequent tests. Thermal imaging was in place for the later melts. Troubleshooting, repair and maintenance, as well as testing have allowed DIAL personnel to become very familiar with the individual components of the induction melter. At the end of the reporting period, several significant parameter values were established. It appears that the maximum melt height for the batch operating mode is 220 mm. For these late runs, the largest portion of the melt volume as glass was 30% or approximately 2.27 kg, produced as a homogeneous layer within about 20 minutes. The remainder of the melt was primarily ductile and cast iron, approximately 35 kg. Thermal imaging indicated the best yet operation of the melter with a clear view of the expected induction stirring action due to the pattern of magnetic flux in a multi-turn coil. Formulation of acceptable simulated spent nuclear fuel feed stock is in progress to provide DIAL with the resources for determining the feasibility of employing the PICCM for this type remediation.

Subtask 5.2. Hollow-electrode DC Arc Furnace for Mixed-waste Treatment

Project deferred.

Subtask 1.1. Monitors for Thermal Treatment Processes

Thermal treatment processes (incinerators, melters) typically emit toxic metals (esp. mercury), volatile and semi-volatile organic materials (esp. dioxins and furans), and particulate matter during processing. While the levels from DOE facilities meet current regulatory limits, the EPA is in the process of promulgating new rules (the so-called “MACT” rules) with much lower limits. Based on limited test data, some of DOE’s thermal treatment facilities will require continuous emissions monitoring of process effluents in order to comply with this rule. Currently, several such monitors are under development, but, as yet, there are no accepted monitors for this use.

During the first year of the Cooperative Agreement, DIAL will test monitors for toxic metal effluents in its combustion test facility. DIAL will contact users, developers, and other stakeholders, and with their assistance, develop detailed test specifications for toxic metals monitors. Monitors will be brought to DIAL’s test beds for extended testing. At the completion of testing, a report will be drafted, reviewed by all parties, revised, and issued. This report will detail the results of testing, and compare the performance of each of the monitors against the specifications.

Personnel from the major thermal treatment process operators in the DOE complex (the TSCA incinerator at Oak Ridge, the CIF at Savannah River, the WERF at Idaho, and the DWPf at Savannah River) will assist in developing specifications for CEMs, and in reviewing test plans and test results. DIAL will utilize DOE's *ad hoc* CEM group to guide testing and review test results, as well as the Mixed Waste Focus Area. DIAL will also test the ability of the CEMs to act as process monitors.

The objective of this subtask is to determine, through testing, whether existing CEMs meet DOE user specifications.

Air Plasma Off-gas Emission Monitor (APO-GEM)

George P. Miller

Introduction

Project Significance

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

Background

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

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

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

Methodology

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

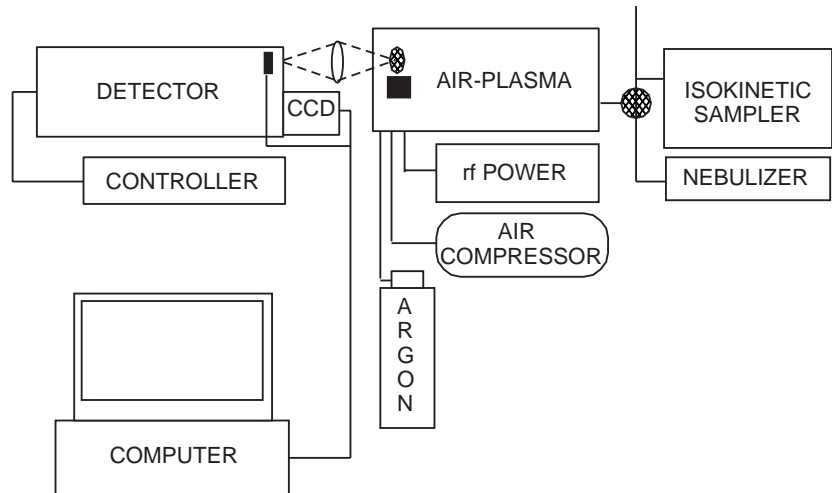


FIGURE 1. APO-GEM schematic diagram.

The APO-GEM plasma is started using argon and progressively switched over to air. Calibration is performed using an ultrasonic nebulizer. The detection system uses a 1-m monochromator, and CCD detector. This remains the largest single component of the system. It has adequate resolution but operates sequentially and is relatively large. It, nevertheless, provides the ideal platform for identifying and characterizing the spectral emissions and possible interferences arising from unidentified components making up exhaust gas emissions. (To provide simultaneous metal concentration measurements, this monochromator could be replaced by a polychromator.) In addition, we are evaluating a novel solid-state spectrometer developed for this project by Dr. David Baldwin, Ames National Laboratory. This instrument is compact, thermally and vibrationally stable. It uses a combination of an acousto-optic tunable filter and an echelle grating to provide the resolution of a 1.5-m monochromator into a 10-kg package. The successful combination of the solid-state APO-GEM and this spectrometer represents a large step forward in instrument development and will reduce the overall size and weight of the complete package substantially (from the original ~1000 kg, to the present 250 kg, then to ~150 kg) while improving the resolution, and thereby the detection limits.

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

Calibration. An important concern with any CEM is the question of calibration. In this instance, instrument calibration follows a modi-

fied standard ICP calibration procedure.¹ An ultrasonic nebulizer is used to provide metal-containing aerosols at a known concentration ($\mu\text{g}/\text{m}^3$). This concentration is determined from

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

where C_A is the aerosol concentration ($\times 10^3 \mu\text{g}/\text{m}^3$), C_s is the standard solution concentration ($\mu\text{g}/\text{g}_{\text{solv}}$), u is the solution uptake to the ultrasonic nebulizer, F is air flow rate to the plasma, and ε is nebulizer efficiency. The efficiency of the nebulizer was determined both in the laboratory and again on-site prior to the test. For the initial instrument calibration, the metal aerosol was mixed with ambient air. Instrument response was checked against standard calibration curves prepared previously. In the field, the presence of fly ash as well as variations in loading and exhaust gas composition allow the possibility of substantial matrix effects significantly impacting the results of any real-world analysis. This variation in composition between laboratory air and the exhaust gas composition renders any direct comparison of the laboratory air calibrations to the instrument off-gas response highly suspect. To circumvent this problem, we have developed a novel technique whereby the calibration standards are mixed with the exhaust off-gas at the entrance to the sampling loop while maintaining isokinetic conditions. This ensures that the standard and off-gas sample are matrix-matched. This allows recalibration and QA checks to be performed on-line under actual operating conditions.

To further improve the sensitivity of the instrument, a novel chemometric software package has been developed which by modeling background spectrum (at the spectra regions of interest) effectively reduces the background noise and thus improves the instrument sensitivity. To apply this method accurately, data from the spectral regions of interest was collected during the shakedown period prior to the test. In addition, as the instrument presently employs a sequential detection system, wavelength calibration is essential. A chemometric-

based software package was developed to check and, if necessary, correct wavelength calibration. This software checks the wavelength position with respect to the pixel position on the CCD every time the wavelength setting is changed as well as periodically checking for instrument drift.

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

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

Metal Instrument	Detection Limits ($\mu\text{g/dscm}$)
As	47
Be	0.07
Cd	2.5
Co	0.6
Cr	0.25
Hg	20
Mg	0.05
Ni	0.4
Pb	0.9
Sb	55
Sr	0.003

Metal concentrations and relative accuracy. The DOE/EPA demonstration at Raleigh was the first opportunity to check the accuracy and quality of the data provided by the APO-GEM. The relative errors with respect to EPA Method 29 are given in Table 2. Three of the five metals are within 30% for the high concentration level (75 $\mu\text{g/dscm}$). None are within that range at the low concentration level

(15 µg/dscm). These results are excellent considering the uncertainty present in the RM data at these low levels.

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

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

Work Accomplished

Dr. George Miller participated in the ASME Technical Peer Review of DOE’s CMST program in support of DIAL’s ongoing collaboration with Dr. David Baldwin at Ames Laboratory. The review panel’s recommendations regarding the development of a multi-metal continuous emissions monitor included:

- The need to meet the regulatory requirements likely to be incorporated into EPA Performance Specification 10.
- The need for development plans to include EPA Method 301(7) validations especially with regard to the accuracy and bias of Reference Method 29.
- The need to undertake of long-term testing of the instrument.

These recommendations parallel the Air Plasma Off-gas Emission Monitor (APO-GEM) program presently underway at DIAL.

All of the optic components, except the base plate, necessary to build the redesigned AOTF-echelle spectrometer have arrived. Additional components for the isokinetic sampling system have been ordered.

A post-doctoral research fellow has been interviewed and an offer will be tendered in the near future. A paper entitled “Air Plasma Off-

gas Emission Monitor” was submitted to the *Journal of Air and Waste Management*.

Work Planned

Preparations will begin for the testing, at DIAL, of the reduced pressure version air-ICP. This work is in collaboration with Ames Laboratory.

Subject to the postdoctoral fellow accepting the position offered, work will begin on bringing him up to speed as rapidly as possible. Initial work will focus on the completion of the redesigned AOTF-echelle spectrometer.

Reference

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Laser-induced Breakdown Spectroscopy

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

Introduction

Toxic metal emissions from various waste processing off-gas systems represent a significant health hazard. This technical task has been focused on the development and application of laser-induced breakdown spectroscopy (LIBS) to monitor RCRA metals from thermal treatment processing facilities. LIBS is a laser-based, nonintrusive, and sensitive optical diagnostic technique for measuring the concentration of various atomic and molecular species in test media.^{2,3} 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.⁴⁻⁹ The field test results also indicated that LIBS calibration techniques need further improvement to provide accurate quantitative measurements in various test environments. The LIBS calibration method has been tested with great success with laboratory data. However, practical environments are quite different from that of a laboratory. Transferring the LIBS calibration obtained in a laboratory to field measurement is a great challenge. The effects of gas stream conditions (temperature, particle size and density, etc.) on LIBS calibration have not been systematically studied before. A series of studies needs to be conducted in a simulated system to study the effects of gas stream parameters on LIBS calibration.

Work Performed

During this work period, the LIBS signal at different gas temperatures was studied. The setup used for the LIBS measurements is shown in Figure 2. An ultrasonic nebulizer (USN) was used to pro-

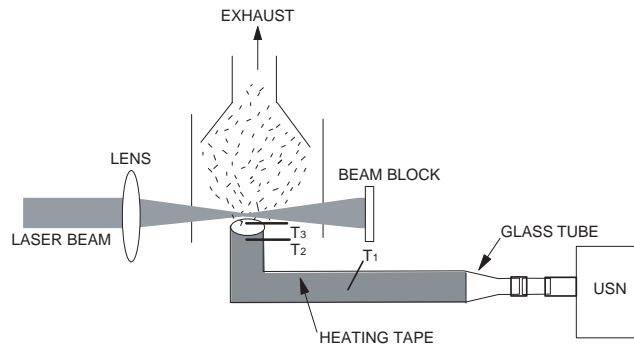


FIGURE 2. LIBS experimental setup.

duce a dry aerosol of selected metals. The dry aerosol from the USN was sent to a glass sample injection tube. The sample injection tube is enclosed in a Pyrex pipe to reduce interference from the surrounding air. The laser beam was aligned ~2 mm above the end of the tube and was focused at the center of the tube to achieve reliable calibration. In order to produce the hot aerosol in the laser focus volume, the glass sample injection tube was heated by a heating tape wrapped around it. Three thermocouples were placed near the nozzle (as indicated in Fig. 2) to measure the temperatures during the measurement. The three temperature settings used in the experiments are given in Table 3. The temperatures measured at the three locations are also given.

TABLE 3. Temperature settings used in the experiments.

Temperature Setting	T ₁ (°C) ^a	T ₂ (°C) ^b	T ₃ (°C) ^c
#1	130	90	50
#2	220	140	70
#3	370	250	100

^aT₁: Temperature measured on the glass tube.
^bT₂: Temperature measured 2 mm below the injection tube exit plane (inside the tube).
^cT₃: Temperature measured 2 mm above the injection tube exit plane.

A large temperature gradient was found around the nozzle. LIBS data were collected after the gas temperature reached equilibrium. The LIBS signal collected at different locations around the nozzle also indicated a great concentration gradient. Figure 3 shows the variation of the LIBS signal of the Pb 405.8-nm line at a measurement point at different temperatures. As shown in the figure, the LIBS signal dropped rapidly as the temperature increased to 363 K (90°C) and then slowly decreased as the temperature increased. The change in the LIBS signal did not follow the gas density change in these measurements. Figure 4 shows the variation of the LIBS signal-to-noise ratio at different temperature settings (S/N) for different metals. It is

clearly shown that the S/N ratios of different elements vary in these measurements and, except Cr, have a similar trend.

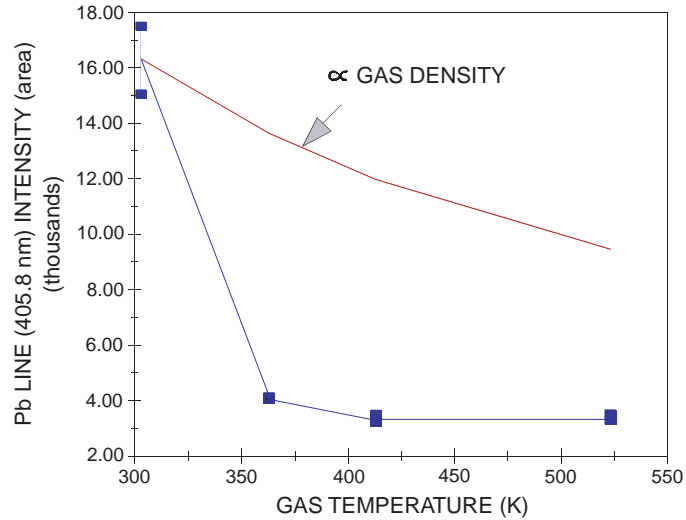


FIGURE 3. Pb signal at different gas temperatures.

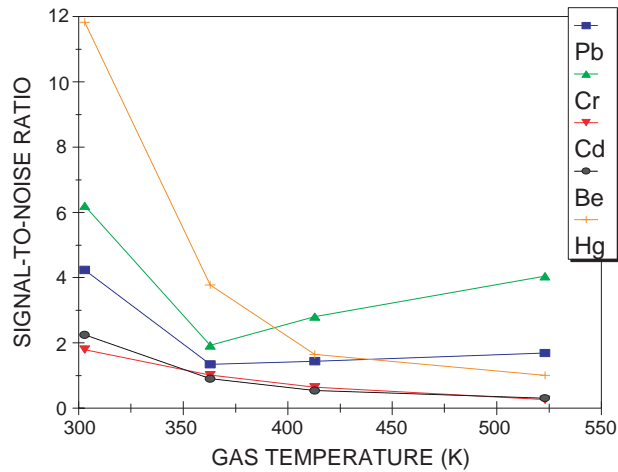


FIGURE 4. Signal-to-noise ratio of LIBS data at different gas temperatures.

In our off-gas simulation system, we can calculate the metal concentration from the head of the metal injection tube based on the gas flow rate and metal flow rate used in the experiment. However, the metal aerosols from the injection head diffuse quickly into air. It was difficult to accurately estimate the metal concentration and temperature at the measurement point. The uncertainties on gas temperature and metal concentration at the measurement points have limited us to a derived quantitative measure of the effects of gas temperature on the LIBS signal. To obtain more reliable results, a well-characterized simulated gas stream is needed to continue this study.

Work Planned

The study of the effects of gas stream conditions on the LIBS measurement will be conducted on the DIAL test stand.

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Subtask 1.2. Mercury Absorber Technology

Many of DOE's low-level wastes contain mercury. If the LLW is treated by thermal treatment processes such as incineration, the mercury will be emitted to the off-gas system and must be removed. While the levels from DOE facilities meet current regulatory limits, the EPA is in the process of promulgating new rules (the so-called "MACT" rules) with much lower limits. Based on limited test data, some of DOE's thermal treatment facilities will be unable to comply with these rules without significant capital investment.

A mercury removal technology, based on an innovative absorber, has been developed in Russia and deployed in room temperature applications there. DIAL will test this absorber because, if it proves to be effective, its use would require almost no changes to existing facilities. Key performance characteristics which will determine whether the absorber can be used in an off-gas system are the maximum temperature at which it is effective and its capacity. DIAL will utilize its test stand and off-gas systems to provide this data. The mer-

cury absorber will be installed in the off-gas system. The temperature of the off-gas hitting the material will be varied and mercury removal will be monitored. Mercury-laden off-gas will be sent past the absorber until no further removal of mercury occurs. The maximum mercury loading will be determined, as well as the maximum temperature at which the material is effective.

Representatives from the Idaho office of DOE, and from the developer of this innovative technology, will assist in developing test plans, will observe the tests, and will review test plans and test results. If initial testing is successful, stakeholders will be notified (through the Southern States Energy Board and the California EPA) and invited to participate in further performance testing.

The objective of this subtask is to determine, through testing, the maximum temperature at which the mercury absorber is effective, and the maximum loading of the material.

This project has been deferred.

Subtask 1.3. Feature Extraction from Digital Images of Thermal Treatment Source(s)

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

Introduction

Purpose

Many of the DOE waste streams, particularly those currently stored in steel barrels, are poorly characterized or even uncharacterized. Given the variety of contents that can dramatically vary from barrel to barrel, it is necessary for thermal treatment systems (TTS) to

quickly change operating parameters and/or implement divert-and-treat measures when specific species of environmental concern (such as mercury) are suddenly introduced into the TTS. It is desirable to monitor species of concern inside the primary TTS chamber in order to provide the maximum possible response time and because concentrations will be higher and hence easier to detect.

Digital images contain a wealth of information that if extracted, could be of immense value for monitoring/controlling a process. The emphasis of this project is on extending previous work to include extraction of information on concentration distributions and other parameters of use for process control of thermal treatment systems of interest to DOE. Extraction of information from the primary thermal treatment chamber will provide sufficient time for operational parameters to be changed to maintain optimum operational performance and/or to allow divert-and-treat actions to be taken for species of environmental concern. Previous work at DIAL has shown utility of digital images for visual display of thermal distribution contours and for determination of average temperatures. This project concentrates on the use of plasma arc vitrifiers as the thermal source, because such capabilities are currently available at DIAL; however, the imaging analysis capabilities developed can be readily adapted for other thermal treatment systems, such as incinerators or Joule-heated glass melters.

This project has been deferred.

Deactivation and Decommissioning Technology Support

Subtask 2.1. Pipe Decontamination

Gary Boudreaux

Introduction

The Department of Energy has radioactive and hazardous contamination inside many of its process piping and duct systems. Contaminants remain in these systems after liquid is drained from them, adsorbing onto metal and other surfaces or depositing as residual liquids or solids. Many of the piping systems are not directly accessible because parts of them are buried underground or under concrete floors. A pulsed acoustic pipe cleaner has been developed at Mississippi State University (MSU) in collaboration with the Tennessee Valley Authority (TVA) and the Southwest Research Institute (SwRI). The pulsed acoustic pipe cleaner utilizes repetitive high-voltage electrical discharges in water or other fluids to produce acoustic shock waves which are effective in removing scale, silt, and other fluid-saturated deposits from tube inner surfaces. The pulsed acoustic pipe cleaner minimizes the generation of secondary waste while at the same time minimizing worker exposure to radiation.

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

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

Work Accomplished

The design and schematics of a second pulsed acoustic pipe cleaner, being built at DIAL, have been completed. A new shield capture plate and cable adapter have been designed and built. The High Voltage Lab has completed the design of the solid-state switch and

the IGBT electronic modules have arrived. They have also developed and built a test driver circuit to test these modules.

We have discussed opportunities with National Heat Exchange Company. They are interested in jointly performing an on-site demonstration at a DOE facility (Portsmouth Gaseous Diffusion Plant).

We have now found several companies, GTS Duratek, Schlumberger, Commerce Services Corporation, Allegheny Power and Light, MTSI, and Gap-Tech, which have potential applications for the pulsed acoustic pipe cleaner. Commerce Services Corporation has agreed to send DIAL a test section of pipe to be cleaned and plan to visit our facility for a second demonstration and bring a second test pipe.

Conclusions

The pulsed acoustic pipe cleaner has been successfully demonstrated at Sequoyah Nuclear Power Plant (TVA) and the Wabash River Coal Fired Plant (Public Service of Indiana) to clean scale and other deposits from 1-in. diameter heat-exchanger tubing.^{10,11} This previously developed and demonstrated technology provides an excellent basis for further developing a system that will decontaminate radiologically contaminated surfaces. This method appears suitable for cleaning and decontaminating tubes, pipes, and other cylindrical storage containers capable of containing fluids.

There are several advantages of this technique over existing technologies. The primary advantage is that the exposure of workers to hazardous and radioactive materials is minimized. This is because the cable can be fed through a bushing into the pipe so that workers do not come into contact with the material within the pipe. Further, the generation of secondary waste is minimized, or avoided. The water in the pipes transports the scale out of the pipes. This same water can be reused to clean other pipes after the foreign matter has been separated

from it using conventional means (i.e., filtration, centrifuge, settling). Since deposits are knocked off the surface of the pipe through its interaction with the acoustic wave, the use of brushes or chemicals is avoided, further reducing the generation of secondary wastes.

Work Planned

The improved pulsed acoustic pipe cleaner will soon be completed at DIAL. The final safety features of the power modulator cabinet will be designed and tested. The solid state switch will be completed, tested using the test circuit, and then tested in the new power modulator cabinet. Pipes with different types of fouling will be cleaned with this system in order to determine the effectiveness of the pulsed acoustic pipe cleaner for different applications and to establish operating parameters. We will continue to seek a commercial partner and will schedule an on-site demonstration at a DOE facility when the initial testing of the new pipe cleaner is completed.

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Subtask 2.2. Wall Removal Monitor

Mark Henderson

Introduction

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

Another method to deal with the problem is to weigh the amount of concrete that is removed. The average depth of material removal can then be calculated by measuring the density of a small sample cut from the surface. The feedback from this technique is almost immediate, but it does not take into account variations in depth of removal or density that can occur in practice. Thus, a technique that can measure the amount of material removed over a given area and in near-real time would benefit both the agency and the contractor.

A wall removal monitor has been developed at DIAL to serve this need. The monitor uses Fourier transform profilometry (FTP), which is an imaging technique that can measure the surface profile of an

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

The system consists of a standard slide projector, a video recorder, and a computer. The projector and the video recorder are mounted on a tripod which can be placed anywhere from 2 ft to 30 ft from the surface in question. However, this distance affects the size of the area being imaged; a larger area can be imaged by setting up farther away from the surface. A grid of lines is projected onto the surface and an image is captured with the video recorder. The image is processed on the computer in order to determine the profile information. The Wall Removal Monitor can be operated in harsh environments, is easily calibrated in the field in a matter of seconds, and can currently run in near-real time.

Work Accomplished

An acoustic ceiling tile, which had random, dark flecks, was used as the test object because ceiling tile is easily modified with a knife. A rail, which sits on two tripods, was constructed to hold the camera and the projector. Tests were done on the “noisy” tile by gauging holes and sections from the tile using a knife and measuring the amount of material removed by using both FTP and a caliper.¹² The camera used in these tests was a commercial home video camera. The spatial resolution (the distance between points on the surface)

depends on the area of the surface being imaged and the resolution of surface variation. As a result, the finished profile map can be referenced to the original surface, and only the things that are different show up in the report.

A third enhancement to FTP has been developed to allow information to be collected at multiple resolving abilities concurrently. The technique uses two patterns that are projected onto the surface at the same time so that they overlap. This allows both the global picture to be seen along with the details and prevents “forest-for-the-trees” problems that can occur.

Conclusions

A system has been demonstrated that can accurately measure large areas with a high degree of precision on “noisy” surfaces. The system has been constructed for fieldwork and uses commercial parts. All necessary field measurements are quick and easy to make, and processing is in near-real time. Fourier transform profilometry fits the role of Wall Removal Monitor well, as it can measure a surface profile relative to the original surface. From the depth information gathered using FTP, it is possible to calculate volume of material removed, average depth of material removed, and point-wise depth of removal. The system can be used at the job site potentially saving the contractor and the contracting agency time and money by preventing costly re-visits and ensuring quality.

Work Planned

A demonstration of this technology is scheduled at the test facility at HCET-FIU. Modifications will be made to the configuration so that floors, ceilings, and other surfaces can be monitored. A commercial partner will be sought to commercialize the technology for this application.

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Subtask 3.1. Dioxins/Furans in Incinerator Burners

Thermal treatment processes (incinerators, melters) typically emit toxic metals (esp. mercury), volatile and semi-volatile organic materials (esp. dioxins and furans), and particulate matter during processing. While the levels from DOE facilities meet current regulatory limits, the EPA is in the process of promulgating new rules (the so-called “MACT” rules) with much lower limits. As was discussed at the National Technical Working Group “pre-meeting” on November 4, 1997, preliminary data indicate that the Consolidated Incinerator Facility at SRS may not be able to meet the very stringent MACT rules for dioxin. Based on preliminary testing, Savannah River personnel suspect that the fuel oil burner used in the incinerator may be an important contributor to the problem.

Installing additional control devices on the CIF would be expensive, and difficult to accomplish in a radioactive environment. As a result, SRS and the other DOE incinerator operators require additional testing to confirm that the incinerator’s burner is the source of the dioxins/furans. DIAL will expand the scope of testing to be performed for a commercial burner manufacturer to include determination of the concentration of dioxins/furans produced as a function of burner operating conditions. DIAL will take its instrumentation to the

burner manufacturer. Dioxin/furan contents in the effluents will be determined as a function of burner operating conditions. As a result, DIAL may be able to provide a window of burner operating conditions which could avoid the need for additional control devices.

An engineer from DOE's Consolidated Incinerator Facility will work with DIAL on this effort. He will assist by ensuring that testing adequately reflects conditions in the CIF, and by reviewing test plans and test reports.

The objective of this task is to determine dioxin/furan production from a fuel oil burner.

Dioxin Tests

John Etheridge

Introduction

Because of the concern over dioxin production in mixed waste and municipal solid waste incinerators, there is a great need for more definitive data concerning the affects of incinerator operating conditions on the production and destruction of dioxins and furans. Although there is a substantial quantity of data available, it is derived mostly from laboratory scale combustion systems that may be too small for the data to be meaningfully applied to full scale incinerators and from operating incinerators where precise control of the system parameters and repeatability of results are both problematic. DIAL's combustion test stand is large enough to produce data that is applicable to full scale incinerators, is highly controlled, and is capable of producing very repeatable operating conditions.

Work Accomplished

All support equipment, such as the fuel and off-gas systems, has been moved to the new test facility. The test stand has been reinstalled, and the control system wiring and hardware is in place. Single loop water cooled heat exchangers, which will be installed at various port locations along the combustion test stand in order to achieve the desired downstream temperature, have been designed and constructed.

Work Planned

The tests originally scheduled for December 1998 have been rescheduled for the first week of February 1999. Some of the power wiring and combustion air plumbing, along with control and monitoring system checkout, will not be completed until the end of January 1999. The first test series will be performed to determine the operating conditions and temperature requirements for fuel-bound dioxin destruction. Doing these tests first, followed by tests to determine dioxin adsorption isotherms, will hopefully allow us to finish the complete set of tests by the original target date.

Detection of Chlorinated Organics by Cavity Ring-down Spectroscopy

Ram Vasudev and William Dunsford

Introduction

The ultimate objective of this program is to develop a sensitive probe for toxic compounds, especially chlorinated organics of environmental concern. The reader is referred to previous reports and

publications for further details on our goals¹³⁻¹⁴ and the experimental setup.¹³⁻¹⁵ To achieve our goals, we are exploring the technique of cavity ring-down spectroscopy (CRDS) as a general-purpose toxic gas detector. We have shown previously that CRDS is superior to conventional laser techniques such as laser-induced fluorescence (LIF) and resonance-enhanced multiphoton ionization (REMPI) because it is unaffected by excited-state nonradiative decay due to intersystem crossing (ISC). This is especially significant for chlorinated aromatics where ISC is known to reduce fluorescence quantum-yield and photoionization efficiency.¹⁶ In the work described here, we have used a tunable ultraviolet laser to record CRD spectra of chlorinated aromatic VOCs.

Experimental

In CRDS the absorption pathlength of a pulsed laser through an absorbing sample is made very long by trapping the pulse between the mirrors of a high-finesse (low-loss) confocal/semi-confocal optical cavity containing the sample. The effective pathlength in suitable cases can be several kilometers, so very small concentrations of chemical species can be detected, being limited mainly by scattering losses and cavity mirror reflectivity. The spectrum of an absorber is obtained by analyzing the time-decay profile (the “ring-down” waveform) of the light transmitted by the cavity as a function of the laser wavelength.

Accomplishments

In the present work, a frequency-doubled dye laser, pumped by a Nd:YAG laser, is used to record the ultraviolet absorption spectrum of chlorinated aromatics. As an illustration, the spectrum 1,4-dichlorobenzene in the origin band region is shown in Figure 5. Figure 6 shows the ring-down waveforms at the peak of the origin band at the baseline just to the blue of the peak (the noise level has been reduced

since the last quarterly report). This work illustrates that CRDS is quite suitable for detecting chlorinated VOCs in the sub-ppm (~ppb) range. Further improvement in sensitivity is possible through changes in the experimental setup and data-acquisition hardware/software.

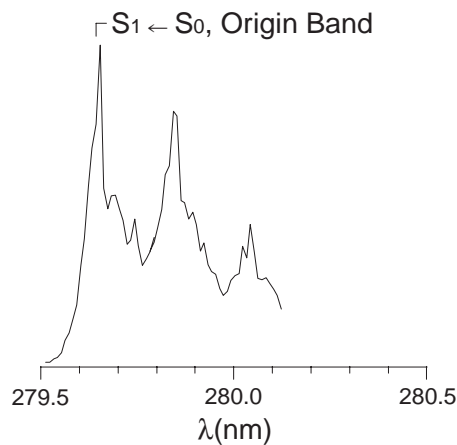


FIGURE 5. Low resolution spectrum of 1,4-dichlorobenzene in the region of the origin band of the $S_1 \leftarrow S_0$ system.

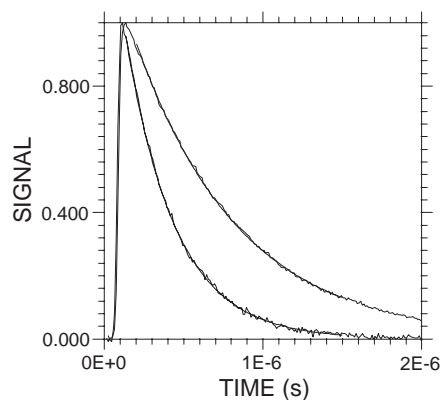


FIGURE 6. Ring-down waveforms for 1,4 dichlorobenzene at the peak of the origin band and at the baseline to the blue of the peak.

A paper describing our earlier work on CRDS of toxic compounds has been accepted for publication in *Environmental Science & Technology*.¹⁴

Future Plans

Work will continue with a number of toxic chlorinated aromatics, especially those that are good surrogates for chlorinated dioxins, as soon as safety issues (fume hood, etc.) have been taken care of. We will acquire high-quality spectra for these molecules, and improve the detection limits through improvements in the experimental setup and data acquisition.

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Subtask 3.2. Dissolution of Hanford Salt

J. S. Lindner and R. K. Toghiani

Introduction

Project Significance

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

Thermodynamic modeling of complex, multi-component electrolyte solutions at high ionic strengths and with proper consideration of solids formation is a formidable task. Workers evaluating the waste at Hanford have selected, based on initial comparisons between experimental results and an assessment of available software, the Environmental Simulation Program (ESP, OLI Inc.). The code has subsequently been used for modeling laboratory sludge leaching experiments and tank contents.¹⁷⁻¹⁹ To our knowledge, the work reported here is the first application of the model to saltcakes. The short time period in which ESP has been in use at Hanford suggests, however, that evaluation of the code for different applications is an evolving process. Thus, the work performed here is implicitly centered on model validation.

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

Background

The previous work at Hanford has indicated some limitations in the application of ESP.¹⁷⁻¹⁹ Solid-liquid equilibrium (SLE) model calculations have been found to agree with laboratory results for aqueous solutions containing most of the pertinent single salts (NaCl, Na₂C₂O₄, NaNO₃, etc.). At elevated ionic strengths, however, the solubilities from the model are less than experimental observations. Consequently, the code predicts higher solids loadings and this has potential ramifications on the privatization contract through the amounts and types of diluents used for pretreating the waste.

Other questions regarding the code concern the quality of the data used in the integral software databases, Analytical results on the tank wastes at Hanford have indicated the presence of a number of double salts such as, Na-F-PO₄, Na-F-SO₄, and Na-SO₄-CO₃.²⁰ Literature data on these systems are rare. What results are available indicate that various types of solids structures, crystals and gels, can result depending on composition. Natrophosphate, Na₇F(PO₄)₂·19H₂O, for example, has been observed to form gels.^{21,22} Sodium phosphate

$\text{Na}_3\text{PO}_4 \cdot \text{XH}_2\text{O}$ can form different crystal structures depending on the extent of hydration. Accurate modeling of the partitioning of the solids and liquid phase constituents will only be as good as the fundamental data used in the model.

Methodology

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

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

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

Different theoretical representations can be used to calculate the SLE behavior of aqueous systems. Comparison of the results from ESP with other thermodynamic models allows an independent check

on the thermodynamic framework used and may also indicate deficiencies in the ESP model or associated database.

Results

The following has been taken from a letter report on the dissolution of the crust in Hanford tank 241-SY-101.

Introduction

Application of the Environmental Simulation Program (ESP, OLI Systems Inc.) to crust remediation/mitigation options for Hanford tank 241-SY-101 was recently reported.²³⁻²⁵ The studies were motivated by a request from DOE-RL to evaluate possible mitigation options intended to address the continuing growth of the crust within the tank. In the first submission it was noted that good agreement between the code predictions and Person's 1995 analysis of a core sample collected in 1991 was obtained once the model had been tuned for both pH and TOC (oxalate/acetate) partitioning.²⁶ Results of the simulations indicated that water was more effective than 2M NaOH in dissolving the SY-101 solids.

For the transfer of supernate from SY-101 to tank 241-SY-102 (SY-102), both 100,000 and 250,000 gallon transfers were examined. Movement of the smaller volume to SY-102 followed by back dilution of SY-101 with water indicated that 62% of the solids originally present in SY-101 would still remain. This amounted to 9.2% solids by weight in the final tank configuration. Transfer of 250,000 gallons of liquid from SY-101 followed by subsequent dilution of the tank resulted in a final solid loading of about 6.8% by weight. Studies on the composition of the transfer stream and mixing of the transfer stream with the contents of SY-102, (taken from the Best Basis Inventory) were also detailed. Calculations predicted that upon mixing the transfer stream with the contents of SY-102 the solid loading in the

receiving tank would increase from ca. 3 to 4% by weight and that the vast majority of the solids within SY-102 (>60%) would be gibbsite.

The previous calculations were somewhat incomplete in that the dilute receiving tank, SY-102, routinely accepts waste supernates transferred from single shell tanks as part of the interim stabilization program.²⁷ Thus, the composition used for SY-102 was not formally correct. The pumping schedule to SY-102 has been set. Furthermore, a new core sample from SY-101 is under analysis at Numatec Hanford Corporation (NHC) in support of Lockheed Martin Hanford Corporation (LMHC).²⁸ Solids compositions, volume fractions, and densities from the LHC experiments will allow further comparisons to the ESP model. Similar comparisons have been ongoing in these laboratories with regard to of saltcake wastes.²⁵

Dissolution of the SY-101 crust following transfer of 3.78E+05 liters (100,000 gallons) of liquid to SY-102 is described below. The simulations expand on the previous work by incorporating the results from gas volume fraction determinations in the crust core segments and through the use of the average waste elevation and crust depth measurements from neutron probe experiments^{29,30} For the simulations presented, the crust has been modeled as three distinct layers.

Summary of Results

The extent of gas release is assumed to be directly proportional to the dissolution of the solids contained in the crust layers. The solids and gasses of the crust are in close physical contact. It has been noted that the crust has been formed by particulate transport within small gas bubbles generated at the lower elevations of the tank. The material is less dense than the mixed convective and loose solids layers within the tank and rises. Growth of the crust has occurred following installation of the mixer pump used to eliminate large buoyant displacement gas release events.

Some factors may limit the applicability of ESP to the estimation of crust gas release.

- First, the model is based on equilibrium thermodynamics. Incorporation of a gas phase within the model is possible; however, as soon as equilibrium is attained the gas will be partitioned according to solubility. The solubilities of the crust gasses (H_2 , N_2 , N_2O , and NH_3) in the liquid portion of the waste are minimal.
- Second, the model does not directly allow for the development of specific phase morphologies that are expected to effect gas release. The best that can be done within the ESP framework is to divide regions into approximate fractions of solid, liquid and gas and treat each layer as continuous. Gas transport mechanisms have not been considered.
- Third, the local viscosity is expected to have a large effect on the extent and rate of gas release. At present the ESP model does not predict viscosity but plans are in progress to include the calculation of this parameter in new software releases.
- Finally, the calculation results presented below do not account for the kinetics of dissolution that are a function of viscosity, morphology, local temperature, pH, ionic strength, and mixing. An estimation of the time that may be necessary to effect dissolution cannot be made. It is possible for the user to incorporate rate expressions within ESP, and such an effort is planned in connection with our continuing studies.

The presence of specific phase morphologies and local viscosity gradients, when coupled to a kinetic model, are expected to result in longer dissolution times than if the crust is modeled as a continuous layer.

Details of the developments inherent to the crust solids dissolution simulations can be found below. The gas volume fractions, neutron probe data, and geometry of the tank make it possible to calculate a total volume of gas present in each crust layer. Furthermore, through knowledge that the upper layer of the crust is dry and somewhat dense and that the density decreases in going from layer 1 to layer 2 and then to layer 3, a solids volume fraction for each layer can be assumed, Table 4.

TABLE 4. Simulated crust layer configurations assumed for the 3-layer model calculations.

CRUST LAYER	TOP CRUST LAYER	SECOND CRUST LAYER	THIRD CRUST LAYER
Liquid			
Temperature °C	45	45	45
H ₂ O kg	6.86E+04	6.03E+04	3.89E+04
Total kg	1.84E+05	1.61E+05	1.04E+05
Volume L	1.25E+05	1.10E+05	7>07E+04
Density kg/L	1.47	1.47	1.47
pH	15.2	15.2	15.2
Ionic Strength	21.58	21.58	21.58
Solids			
Total kg	1.98E+05	1.12E+05	4.26E+04
Volume L	8.68E+04	4.91E+04	1.87E+04
Density kg/L	2.28	2.28	2.28
Gas Present L	4.89E+044	1.00E+05	1.67E+05
Crust Layer Contents			
Total kg	3.82E+05	2.73E+05	1.47E+05
Volume L	2.61E+05	2.59E+05	2.56E+05
% Solids by wt.	51.83	41.03	28.98
% Solids by vol.	33.29	18.95	7.29
% Water by wt.	17.96	22.09	26.46

Neglecting the gas contribution, the solids volume fractions in the three layers are 0.41, 0.31, and 0.21, respectively. Solids speciations in each crust layer are the same as the original SY-101 composition.

The means by which water will be added to the crust layers will make a difference on the extent of crust solids dissolved. In all of the simulations reported here it is assumed that diluent will only be added to the top layer. The composition from this layer will then interact with the second layer and in a sequential manner; the first and second layer mix will interact with the third layer. In order to dissolve the solids within the crust it appears that it would be more appropriate to add diluent in this manner, especially in light of the projected (assumed) volume fraction distribution of the three layers. Measurements of solid volume fractions for each of the crust layers would be useful.

The addition of water to the second and, especially, the third, crust layers may well release large volumes of gas. It is expected, however, that there will be a tendency for direct interaction of the water with the, already saturated, higher bulk density, mixed-convective layer below the crust. The amount of “hard” crust remaining will depend on the amount of water participating in crust dissolution compared to the amount of water mixing with the tank contents below the crust.

The process flowsheet for the simulation is given in Figure 7. Water was added only to the first layer of the crust. Subsequent operations were successive with the mixed contents of one layer added to the next. Gas release was calculated after each layer mix. The composition of the diluted total crust layer was then added to the remaining solids and liquids in SY-101 and the final tank configuration determined.

The main questions addressed in the overall series of simulations relate to the effect of the composition of SY-101 before and after

crust mitigation, and the composition of SY-102 and the effect of the SY-101 transfer stream on SY-102, Figure 8.

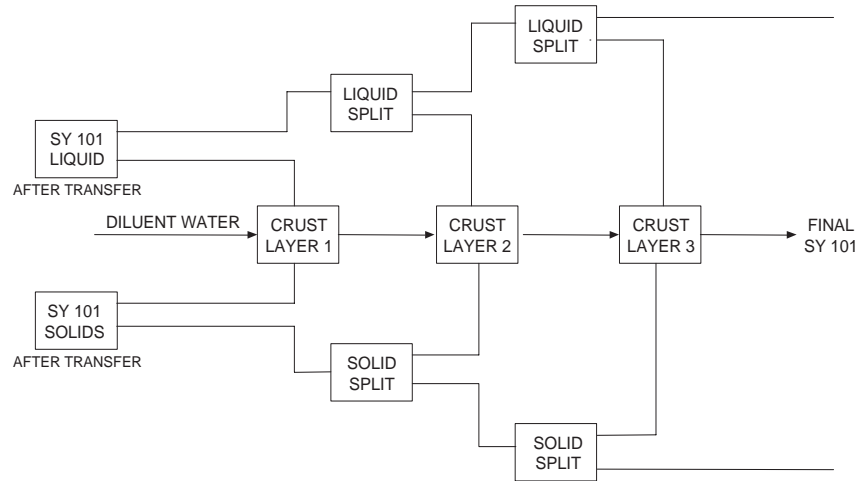


FIGURE 7. ESP flowsheet for the crust remediation simulations.

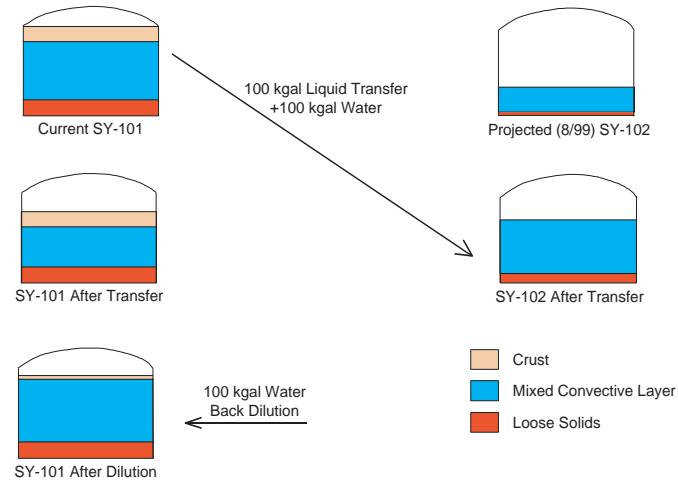


FIGURE 8. Block diagram of the crust level growth remediation.

The calculations differ from the previous efforts in that site engineers have selected the small (100,000 gallon) transfer as the first attempt to minimize or halt the growth of the crust and that water is the diluent for all operations.

The previous results were obtained with a DOS version of ESP (5.4). The data presented here are based on an augmented Windows version of ESP (6.0). Following initial receipt of the newer release it was noted that the simulation results for the base composition of SY-101 were predicted differently than that reported by Person or that obtained with version 5.4.³¹ The changes observed were mainly due to the partitioning of the NaNO_3 and NaNO_2 . For example, the new software predicted an increase of 10% in the solid weight percentage of NaNO_3 . The discrepancy was eventually traced to errors in the ESP Public database and was confirmed by OLI personnel who later supplied an additional database named Nano3. The simulations reported here relied on the thermodynamic data in the Lab, Nano3, and Public databases.

The current chemistry model includes: Al^{+3} , Ca^{+2} , Cr^{+3} , Fe^{+3} , K^{+1} , Mn^{+2} , Na^{+1} , Ni^{+2} , Pb^{+2} , Sr^{+2} , UO_2^{+2} , Zr^{+2} , and OH^{-1} , Cl^{-1} , CO_3^{-2} , F^{-1} , $\text{H}_3\text{SiO}_4^{-1}$, NO_2^{-1} , NO_3^{-1} , Acetate⁻¹, Oxalate⁻², PO_4^{-3} , SO_4^{-2} . Potassium, manganese, strontium, zirconium and silicon ions are new additions. The model contains 48 aqueous species, 169 total species and 53 solids.

Cation and anion loadings and waste volumes for the single shell tanks, and SY-102 were taken from the Best Basis Inventory (BBI).³² The data for SY-101 (also from the BBI) was the same as used previously. The temperature of SY-101 was taken as 45°C.

Recent measurements from the new core samples have indicated gas fractions of 0.19, 0.38, and 0.65, in the top three (crust) segments.²⁹ Neutron probe experiments have indicated that the elevation of the crust within SY-101 is at 429 inches.³⁰ These same experiments

found an average depth of the crust at 75 inches. Averaging the gas fractions and then assuming an average solids volume fraction for the layer will potentially underestimate the solid volume distribution that must exist in the three layers. Fewer solids will be in the top, more dense, layer where the gas fraction is low and more solids will exist in the lower density bottom crust layer where the gas fraction is high.

The three-layer model (Figure 7) was developed to provide a more accurate estimate of crust gas release. This process flowsheet neglects the prediction of the August 1999 composition of SY-102 and the interaction of the SY-101 transfer stream with the contents of SY-102. The main advantage compared to augmenting the entire process flowsheet relates to program execution. CPU time on a PC operating at 400 MHz was 20 minutes for the simulation of Figure 7 and about 45 minutes for the entire process involving the single shell tanks, all SY-102 operations, and the generation of a 1-layer crust in SY-101. An additional advantage that was observed relates to the size of the output files where the 3-layer crust model produced files as large as 400 Kbytes. The total simulation yielded files double in size.

Predictions for the dilution of the 3-layer crust model and the final composition predicted for SY-101 are given followed by simulations conducted with diluent added at elevated temperatures. The SY-101 base composition reported previously, determined with the new software, and found from laboratory measurements on the 1991 core sample are collected in Table 5.

TABLE 5. Solids distributions from ESP and from Person.²⁶ Simulation results reported in this work have been based on the modified version (6.0) of ESP.

SPECIES	ESP PREDICTION VER. 5.4	ESP PREDICTION MODIFIED VER. 6.0	PERSON ² 0
	Weight %	Weight %	Weight %
Al(OH) ₃	NR	NR	4+/-5
Ca(OH) ₂	0.40	0.40	NR

TABLE 5. Solids distributions from ESP and from Person.²⁶
Simulation results reported in this work have been based
on the modified version (6.0) of ESP.

SPECIES	ESP PREDICTION VER. 5.4	ESP PREDICTION MODIFIED VER. 6.0	PERSON ² 0
Cr(OH) ₂	4.10	3.88	5+/-1
Na ₂ C ₂ O ₄	12.10	11.42	12+/-4
Na ₂ CO ₃ ·1H ₂ O	35.50	33.51	31+/-7
Na ₂ SO ₄	NR	NR	4+/-2
Na ₆ (SO ₄) ₂ CO ₃	3.40	3.20	NR
Na ₃ PO ₄	NR	NR	4+/-2
Na ₇ F(PO ₄) ₂ ·19H ₂ O	4.10	7.08	NR
NaCl	0.10	0.16	NR
NaF	NR	0.72	NR
NaNO ₂	5.20	5.88	12+/-3
NaNO ₃	35.00	33.65	21+/-7
Ni(OH) ₂	0.20	0.14	NR
UO ₂ (OH) ₂	0.10	0.10	NR
ZrO ₂	NR	0.01	NR

The distribution obtained with the new software and the associated Nano3 database is seen to reproduce the original DOS version results. Sodium fluoride is observed in the Windows release and was not found previously. The presence of zirconium oxide was a result of adding Zr⁺² to the chemistry model. The largest difference (percentage basis) between the DOS and Windows version was observed for natrophosphate, Na₇F(PO₄)₂·19H₂O. Good agreement between the results for the new simulations and the analysis of the 1991 SY-101 core sample by Person is observed.²⁶

A 1-layer crust model is believed to result in an over estimation of the volume of crust gas released. The primary reason can be traced to the assumption involving a continuous crust layer of uniform composition. From a previous report, it appears that the top layer of the crust is somewhat dry and hard and from the gas fraction measurements the

densities decrease in the two lower layers.³³ Thus an attempt has been made to model the crust in 3-layers. One-layer crust dilution experiments are part of the Letter of Instruction sent from LMHC to NHC. These tests will provide for an average density for a homogeneous layer; however, it is not believed, as noted above, that the dilution of an average crust layer will adequately reflect the dilution of the actual crust.

Results for the final configuration for all three crust layers following the addition of water to the top layer of the crust are contained in Table 6. The entries in column 1 (with 0 liters of water added) represent averages and sums for the three layers described in Table 5. Of interest are the percent solids by weight and volume (solids volume fraction x 100). Based on the simulations it appears that a large portion of the solids within the crust have been dissolved.

TABLE 6. Final crust (all layers) compositions following dilution with water at 45°C.

Diluent Added to Layer 1							
Volume L	0.00E+00	2.00E+05	3.00E+05	4.00E+05	5.00E+05	6.00E+05	7.00E+05
Volume kgal	0.00E+00	5.28E+04	7.93E+04	1.06E+05	1.32E+05	1.59E+05	1.85E+05
Liquid							
Temperature °C	45.00	36.16	40.72	44.42	45.85	46.52	46.74
H ₂ O kg	1.68E+05	3.70E+05	4.75E+05	5.81E+05	6.84E+05	7.84E+05	8.85E+05
Total kg	4.49E+05	8.26E+05	9.63E+05	1.10E+06	1.21E+06	1.30E+06	1.40E+06
Volume L	3.06E+05	5.70E+05	6.83E+05	7.99E+05	9.00E+05	9.89E+05	1.09E+06
Density kg/L	1.47	1.45	1.41	1.38	1.34	1.31	1.28
pH	15.2	14.84	14.46	14.16	13.96	13.80	13.68
Ionic Strength	21.58	16.74	14.94	13.76	12.17	10.42	9.33
Solids							
Total kg	3.53E+05	1.74E+05	1.35E+05	9.58E+04	8.35E+04	7.84E+04	7.56E+04
Volume L	1.55E+05	7.51E+04	5.83E+04	4.04E+04	3.45E+04	3.19E+04	3.03E+04
% Solids Dissolved by Volume		51.54	62.39	73.94	77.74	79.42	80.45
Density kg/L	2.28	2.31	2.32	2.37	2.42	2.46	2.50
Gas							
Gas Evolved Layer 1		3.50E+04	3.85E+04	3.97E+04	4.01E+04	4.03E+04	4.03E+04

TABLE 6. Final crust (all layers) compositions following dilution with water at 45°C.

Gas Evolved Layer 2		1.81E+04	3.91E+04	5.89E+04	5.97E+04	5.63E+04	5.91E+04
Gas Evolved Layer 3		1.28E+04	1.14E+04	3.03E+04	4.92E+04	5.99E+04	6.15E+04
Total Gas Evolved L		6.58E+04	8.90E+04	1.29E+05	1.49E+05	1.57E+05	1.61E+05
Total Gas Remaining L	3.16E+05	2.50E+05	2.27E+05	1.87E+05	1.67E+05	1.59E+05	1.55E+05
End Crust Totals							
Total Solid + Liquid, kg	8.02E+05	1.00E+06	1.10E+06	1.20E+06	1.29E+06	1.38E+06	1.48E+06
Solid + Liquid	4.60E+05	6.45E+05	7.41E+05	8.39E+05	9.35E+05	1.02E+06	1.12E+06
Volume L							
% Solids by wt.	43.97	17.37	12.30	8.01	6.46	5.69	5.12
% Solids by vol.	33.58	11.64	7.87	4.81	3.70	3.13	2.70
% Water by wt.	20.92	37.06	43.26	48.59	52.88	56.88	59.98

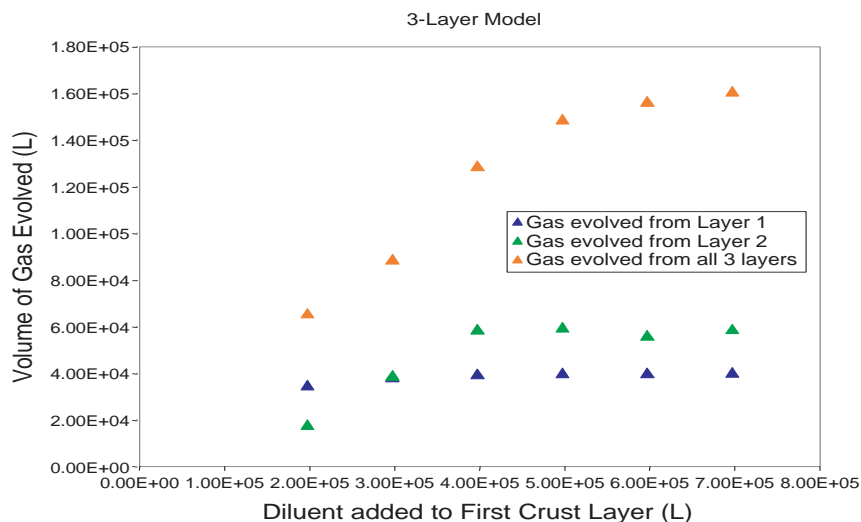


FIGURE 9. Gas released from the crust as a function of water added.

The gas predicted to be released from the first two layers of the crust and from all 3 layers of the crust (total) are plotted against the volume of added water in Figure 9. The data seem to indicate that an asymptote is approached at high dilution ratios. The percent solids by volume dissolved ranges from 51-80%. Based on the starting SY-101

solids composition, it would be expected that roughly 16% by weight of the original solids, namely $\text{Cr}(\text{OH})_2$, $\text{Ca}(\text{OH})_2$, $\text{Ni}(\text{OH})_2$, and $\text{Na}_2\text{C}_2\text{O}_4$, would not dissolve at the pH and ionic strengths encountered. At a dilution of 400,000 L, 10% of the dissolvable crust solids would remain.

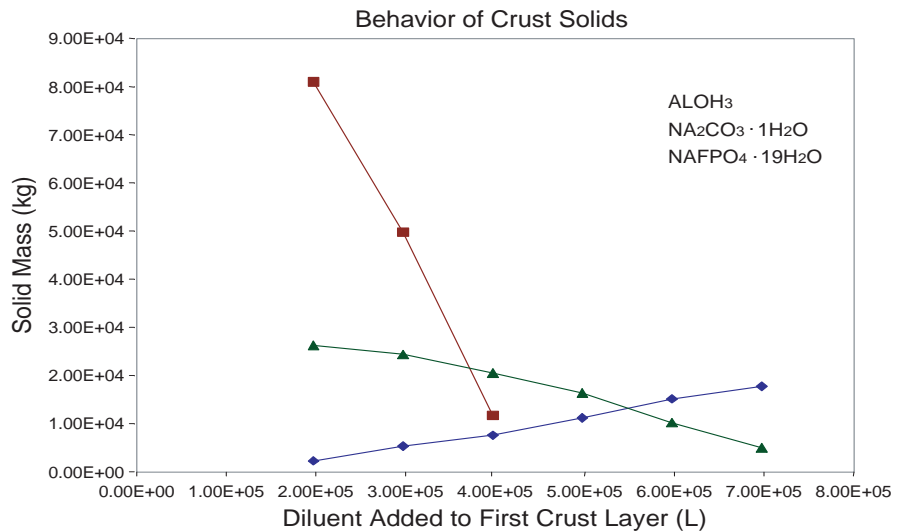


FIGURE 10. Selected crust solids dissolution behavior for the 3-layer model at 45°C.

Comments regarding the solid speciation from dilution of the crust are similar to the simulation results provided earlier.²³⁻²⁵ The effect of diluent addition on selected solids is given in Table 7 and Figure 10. The ESP model anticipates the continuing formation of $\text{Al}(\text{OH})_3$ as a function of added water. The sodium carbonate is expected to dissolve with the addition of about 500,000-L of water and some natrophosphate remains at the highest dilution ratio. Although the solids loading in the diluted crust (all 3 layers combined) decreases, somewhat continually, with the addition of water, it appears, that a dilution of between 300,000 and 400,000-L (ca.,

100,000 gallons) would minimize gibbsite formation and still allow for dissolution of the majority of sodium carbonate.

TABLE 7. Final crust solids distribution, 3-layer model at 45°C.

Diluent Added							
Volume L	0.00E+00	2.00E+05	3.00E+05	4.00E+05	5.00E+05	6.00E+05	7.00E+05
Volume kg	0.00E+00	5.28E+04	7.93E+04	1.06E+05	1.32E+05	1.59E+05	1.85E+05
Solids kg							
Al(OH) ₃		2332	5362	7663	11300	15237	17788
Ca ₃ (PO ₄) ₂				92	338	643	860
CaF ₂			1481	1410	1224	922	758
Ca(OH) ₂	1408	1407					
Cr(OH) ₃	13670	13563	13772	13882	13926	13296	13310
Mn(OH) ₂				8	61	91	106
Na ₂ C ₂ O ₄	40270	40191	40082	39931	39736	37532	37226
Na ₂ CO ₃ ·1H ₂ O	118200	81081	49840	11771			
Na ₃ FSO ₄		8220					
Na ₆ (SO ₄) ₂ CO ₃	11310						
NaCl	550						
NaF	2531						
NaFPO ₄ ·19H ₂ O	24950	26308	24432	20558	16433	10241	5072
NaNO ₂	20670						
NaNO ₃	118500						
Ni(OH) ₂	502	501	502	503	503	480	480
UO ₂ (OH) ₂	30						
ZrO ₂	1						0
Total kg	3.53E+05	1.74E+05	1.35E+05	9.58E+04	8.35E+04	7.84E+04	7.56E+04

The predicted waste configuration for SY-101 at the different dilutions of the 3-layer crust is collected in Table 8. Complete mixing of the remaining, diluted, crust contents with the solids and liquids in

the mixed convective and loose solids layers of the tank is implicitly assumed.

TABLE 8. Final configuration for SY-101 following crust dilution, 3-layer model, 45°C.*

Diluent Added to Layer 1							
Volume L	0.00E+00	2.00E+05	3.00E+05	4.00E+05	5.00E+05	6.00E+05	7.00E+05
Volume kgal	0.00E+00	5.28E+04	7.93E+04	1.06E+05	1.32E+05	1.59E+05	1.59E+05
Liquid							
Temperature C	45.00	43.40	42.85	42.29	41.73	41.98	42.63
H ₂ O kg	1.89E+06	2.09E+06	2.19E+06	2.29E+06	2.39E+06	2.48E+06	2.58E+06
Total kg	5.07E+06	5.45E+06	5.63E+06	5.80E+06	5.98E+06	6.09E+06	6.21E+06
Volume L	3.45E+06	3.72E+06	3.84E+06	3.97E+06	4.09E+06	4.18E+06	4.29E+06
Density kg/L	1.47	1.47	1.47	1.46	1.46	1.46	1.45
pH	15.20	15.16	15.13	15.11	15.08	15.02	14.94
Ionic Strength	21.58	20.73	20.25	19.84	19.48	18.95	18.39
Solid							
Total kg	9.76E+05	7.94E+05	7.18E+05	6.39E+05	5.58E+05	4.71E+05	4.48E+05
Volume L	4.28E+05	3.47E+05	3.14E+05	2.79E+05	2.44E+05	2.05E+05	1.95E+05
Density kg/L	2.28	2.29	2.29	2.29	2.29	2.29	2.29
Gas							
Total Gas Remaining L	3.16E+05	2.50E+05	2.27E+05	1.87E+05	1.67E+05	1.59E+05	1.55E+05
% Gas Released	0.00	20.89	28.16	40.82	47.15	49.68	50.95
Final SY-101 Totals							
Total kg	6.05E+06	6.25E+06	6.35E+06	6.44E+06	6.54E+06	6.56E+06	6.66E+06
Volume L	4.19E+06	4.31E+06	4.38E+06	4.44E+06	4.50E+06	4.54E+06	4.64E+06
Waste Elevation in	402.89	414.26	420.83	426.13	432.34	436.55	445.74
% Solids by wt.	16.13	12.72	11.31	9.92	8.53	7.18	6.73
% Solids by vol.	10.20	8.05	7.16	6.29	5.41	4.51	4.20
% Water by wt.	31.33	33.50	34.50	35.56	36.56	37.80	38.75
Density	1.56	1.54	1.53	1.52	1.51	1.51	1.51

* The entries at a dilution of 0 L represent SY-101 after transfer of 3.785E+05 L (100,000 gallons).

Addition of 400,000 liters of water (105,000 gallons) results in a solid loading of 10% by weight. This result is (for all practical pur-

poses) the same as that found earlier.¹⁷⁻¹⁹ Solids distributions are also similar and are not presented here.

Pertinent data is plotted in Figure 11 where it is possible to estimate the final elevation in the tank and the percentage of the original crust gas release at different water additions to the crust.

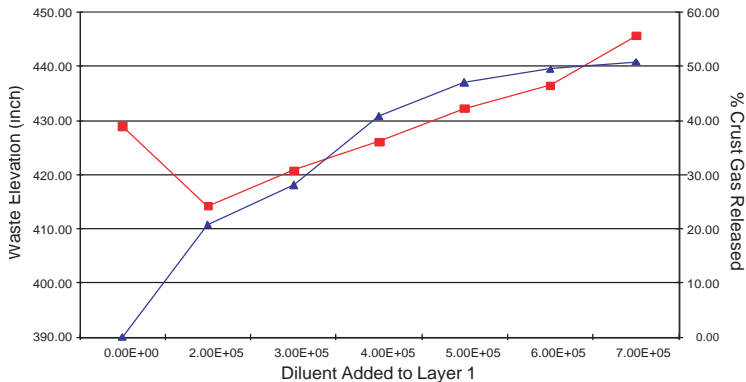


FIGURE 11. Configuration information for SY-101 following the transfer of 100,000 gallons of waste liquid and subsequent dilution of the 3-layer crust.

The waste elevation level in the tank is expected to exceed the current level of 429 inches with the addition of 500,000 liters (130,000 gallons) of water. At this point, the volume percentage of the original solids within all crust layers that are predicted to dissolve is 77% corresponding to a release of slightly greater than 40% of the total crust gas. The current model contains 88% of the total crust solids (by volume) in the top two layers. The model predicts dissolution of the majority of the solids in the first two layers. Of the total gas volume, 35% is contained in the upper 2 layers and 65% in the bottom layer. The remaining crust solids are 12% of the total (present within layer 3) and those solids, such as $\text{Cr}(\text{OH})_2$, etc., from the upper

two layers that will not dissolve. Based on the model it appears that additional gas release is possible with larger dilutions of water. This would have a tendency to raise the waste level elevation within the tank above 429 inches.

The total release of the crust gas could be under-predicted through the use of the three-layer model. The transport behavior of the gas has been explicitly neglected in the model. Currently, a portion of the gas is being retained within the crust, therefore the crust grows and gas transport is hindered. The addition of water is expected to have a tendency to redistribute the contents of the layers through solids dissolution. Thus, additional pathways for gas migration may be opened and a volume of gas released, larger than that calculated, may result. It is not expected, however, that all of the gas will be released. Other calculations using a 1-layer model and the addition of 100,000 gallons of water predicted a total gas release of 68%. This model, as noted above, is considered unrealistic and the true extent of gas release will probably lie somewhere between these two extremes. Regardless the results of the 3-layer model predict the extent of solids that can be dissolved with a given addition of water. Further tuning of the model is possible using determined solids volume fractions.

Diluent addition at different temperatures

Simulations were run with the 3-layer model to examine the effect of diluent temperature (55 - 85°C) on crust gas release and final waste level elevation. The end configurations of all 3 layers of the crust, following dilution with 400,000 l of water at the different temperatures and at the 45°C baseline condition are collected in Table 9. The results are all similar to the 45°C simulation. The solids loadings decrease as a function of increasing temperature.

TABLE 9. Effect of water addition temperature on crust layer solids dissolution with 400,000 L of water added and the crust at 45°C. Data correspond to the final crust composition.

Diluent Temperature C	45.00	55.00	65.00	75.00	85.00
Final Crust Temperature C	44.43	50.25	55.83	62.03	68.15
Liquid					
H ₂ O kg	5.82E+05	5.82E+05	5.85E+05	5.86E+05	5.83E+05
Total kg	1.10E+06	1.11E+06	1.12E+06	1.12E+06	1.12E+06
Volume L	8.00E+05	8.09E+05	8.21E+05	8.27E+05	8.29E+05
Density kg/L	1.38	1.37	1.36	1.35	1.35
pH	14.16	13.94	13.74	13.56	13.39
Ionic Strength	13.77	13.91	14.08	14.22	14.28
Solids					
Total kg	9.58E+04	8.83E+04	7.61E+04	7.15E+04	7.23E+04
Volume L	3.69E+04	3.09E+04	2.84E+04	2.87E+04	2.87E+04
Density kg/L	2.60	2.86	2.68	2.49	2.52
Gas					
Gas Remaining L	1.64E+05	1.46E+05	1.47E+05	1.51E+05	1.52E+05
% Gas Released	48.07	53.89	53.42	52.09	51.98
Crust Totals					
Total kg	1.20E+06	1.20E+06	1.20E+06	1.19E+06	1.19E+06
Solid + Liquid Volume L	8.36E+05	8.40E+05	8.49E+05	8.56E+05	8.58E+05
% Solids by wt.	7.99	7.37	6.36	6.00	6.06
% Solids by vol.	4.41	3.67	3.34	3.36	3.35
% Water by wt.	48.54	48.57	48.91	49.18	48.90

The mass of gibbsite, sodium carbonate and natrophosphate are shown at the respective diluent temperatures in Figure 12. An increase in the amount of sodium carbonate is predicted at the higher temperatures. The amounts of both gibbsite and natrophosphate are expected to decrease as the temperature is increased.

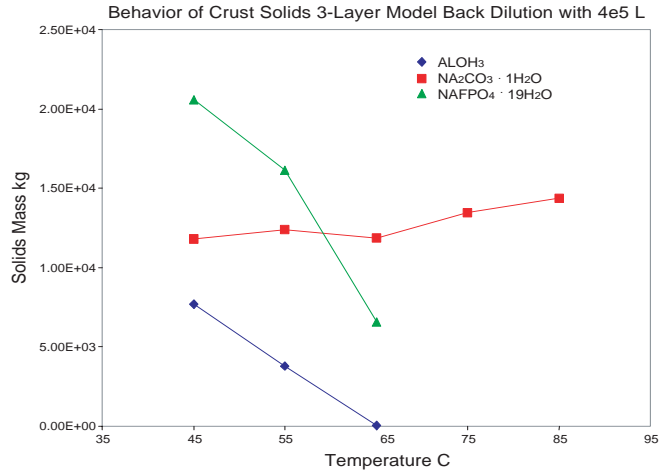


FIGURE 12. Solids loadings for the three layer crust model at different diluent temperatures.

Results determined for the final configuration of SY-101 are given in Table 10.

TABLE 10. Final configuration of SY-101 for the elevated temperature experiments.

Diluent Temperature C	45.00	55.00	65.00	75.00	85.00
Temperature C	42.29	43.25	44.20	45.14	46.07
Liquid					
H ₂ O kg	2.29E+06	2.29E+06	2.29E+06	2.29E+06	2.29E+06
Total kg	5.80E+06	5.82E+06	5.84E+06	5.86E+06	5.88E+06
Volume L	3.97E+06	3.98E+06	4.00E+06	4.01E+06	4.03E+06
Density kg/L	1.46	1.46	1.46	1.46	1.46
pH	15.11	15.08	15.05	15.02	14.99
Ionic Strength	19.84	19.96	20.08	20.20	20.33
Solids					
Total kg	6.39E+05	6.19E+05	5.99E+05	5.79E+05	5.57E+05
Volume L	2.79E+05	2.70E+05	2.61E+05	2.51E+05	2.41E+05
Density kg/L	2.29	2.29	2.30	2.31	2.31
Gas					

TABLE 10. Final configuration of SY-101 for the elevated temperature experiments.

Gas Remaining L	1.64E+05	1.46E+05	1.47E+05	1.51E+05	1.52E+05
% Gas Released	48.07	53.89	53.42	52.09	51.98
Final Configuration					
Total kg	6.44E+06	6.44E+06	6.44E+06	6.44E+06	6.44E+06
Solid + Liquid Volume L	4.24E+06	4.25E+06	4.26E+06	4.26E+06	4.27E+06
Total Volume	4.41E+06	4.40E+06	4.41E+06	4.41E+06	4.42E+06
Waste Elevation in.	423.50	422.25	423.45	423.88	424.89
% Solids by wt.	9.92	9.61	9.30	8.99	8.65
% Solids by vol.	6.58	6.35	6.12	5.89	5.65
% Water by wt.	35.57	35.56	35.56	35.56	35.58

The simulations do not forecast a direct advantage in adding water to the crust at elevated temperatures, Figure 13.

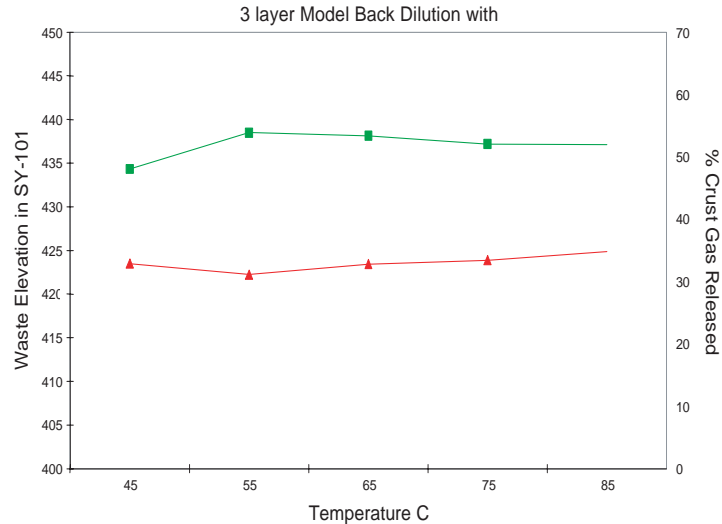


FIGURE 13. Waste elevations and percentage of the original crust gas released for a 400,000-liter dilution of the crust at the indicated temperatures.

Conclusions

The simulations described here provide estimates of those parameters that can be calculated from an equilibrium thermodynamic model. The 3-layer model is thought to be appropriate for calculating gas release. Some discrepancies may exist between data provided here and the actual mitigation and these are expected to arise from the microscopic structure of the crust and the influence of kinetics.

A further effort on coupling the chemistry contained in ESP with the associated kinetics is needed. In addition, it is expected that using ESP in conjunction with other models will allow a more detailed understanding of the release of gas from the crust.

Project Status

The 1999 Saltcake Dissolution Workshop will be held in Tennessee on May 21 and 22. Work described on this and previous reports will be discussed and customer input will be obtained. The work is on schedule.

Work Planned

Documentation of all of the simulation results for the SY-101 crust remediations are in progress. Output from the simulations will be compared to the on-going laboratory work at NHC.²⁸ Further comparisons of ESP to the saltcake dissolution experiments are also in progress. Laboratory studies will soon be augmented by the purchase of a polarizing microscope (currently on bids and purchased with TFA monies) and the addition of an ion chromatograph (also on bids and purchased with University programs monies). Solid liquid equilibrium experiments continue in the laboratory on the sodium-sulfate-carbonate and sodium, fluoride-phosphate systems. Results will be presented later.

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Subtask 4.1. Monitors for Idaho Law Stream

D. L. Monts, C. B. Winstead, G. P. Miller

Introduction***Purpose***

The Idaho National Engineering and Environmental Laboratory (INEEL) has expressed a need for monitoring of residual transuranic (TRU) elements in treated high-level waste. Specifically, a need exists for on-line monitoring of the low activity fraction of this treated waste after dissolution and partitioning of the high-level waste stream. Such a monitoring system could replace expensive off-line sampling and analysis, and hence eliminate the need for holding tanks in the Idaho high-level waste (HLW) process. Substantial savings would result because of the avoidance of expensive construction (of the holding tanks) and also due to the increased throughput, significantly reducing the time to completely process this entire waste stream. However, detecting TRU elements at ultra-sensitive levels has proven to be problematic for traditional radioactive disintegration counting methods due to the very long half-lives of these predomi-

nantly α -emitting elements. Knowledge of isotopic abundances is necessary since different isotopes can have widely differing activities.

Methodology

Two different techniques to address this need are being investigated: cavity ringdown spectroscopy and laser-induced fluorescence spectrometry.

Cavity Ringdown Spectroscopy. Cavity ringdown spectroscopy (CRDS) is a relatively new variant of absorption spectroscopy that has demonstrated extreme sensitivity in a variety of studies. The ringdown technique (Fig. 14) has been described in a number of publications, and will only be briefly summarized here. In “traditional” cavity ringdown spectroscopy, a laser pulse from a tunable pulsed laser is introduced through the end mirror of a stable optical cavity. This optical cavity is formed from two highly reflective mirrors, and serves to trap the fraction of the laser pulse that enters the cavity. The laser pulse propagates back and forth between the mirrors, where it can interact with an absorbing medium in the cavity over the course of thousands of round trips inside the cavity. Since the mirrors are not perfectly reflective, some of the laser light is transmitted through the mirrors each time the light is reflected. A photomultiplier tube is placed behind the second mirror to detect the intensity of laser light transmitted through the mirror as a function of time. The time for the pulse energy in the cavity to decay is determined by the reflectivity of the mirrors and by the absorption of the sample in the cavity. When the cavity is empty, the decay time yields a measurement of the cavity mirror reflectivities. As the absorption in the cavity increases, the decay time for the light in the cavity decreases. By inserting into the cavity an appropriate atomization source, such as an inductively coupled plasma (ICP) or graphite furnace, various chemical forms of TRU elements can be atomized and detected using CRDS.

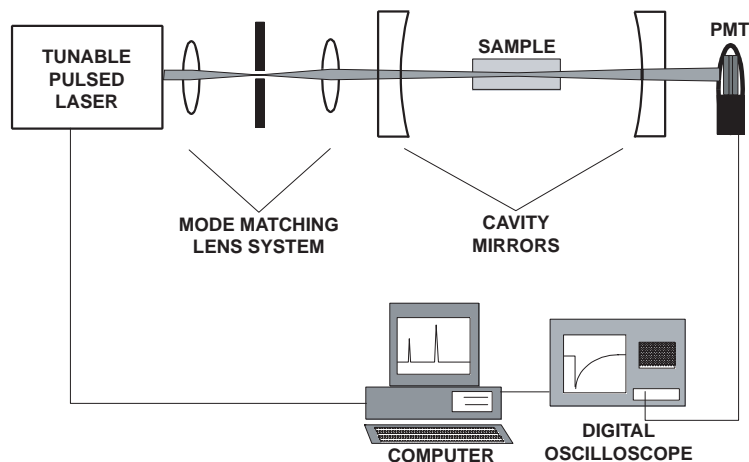


FIGURE 14. Schematic of cavity-ringdown spectroscopy technique.

Laser-induced Fluorescence Spectrometry. Laser-induced fluorescence (LIF) spectrometry is a well-established, robust technique for detecting species of interest at low concentrations. In the LIF technique (Fig. 15), an electronic state of the species of interest is excited with a tunable laser and the resulting fluorescence intensity is monitored as a function of laser wavelength. Since the mass of isotopes are different from one another, the corresponding atomic energy levels are slightly different (Fig. 16). Consequently, when a sufficiently high-resolution tunable laser is scanned across an atomic electronic transition, the resulting LIF spectrum contains a peak associated with each isotope present; the intensities of the isotopic peaks are directly related to the concentration of the isotope. Hence the isotopic abundances can readily be obtained from the LIF spectrum. In order that the individual isotopic transitions can be resolved, it is necessary that the species of interest be in the gas-phase. For the TRU elements of interest, an atomization source is required in order to volatilize and atomize the sample. A calibration curve is obtained by recording the LIF signal intensity as a function of concentration. Using the calibration curve, unknown concentrations can be determined.

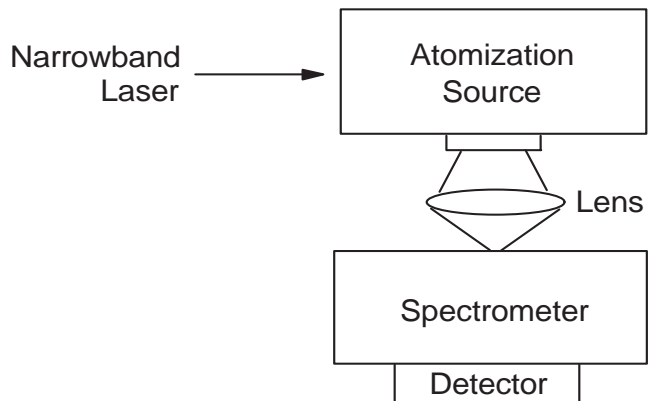


FIGURE 15. Schematic of the laser-induced fluorescence spectrometry technique.

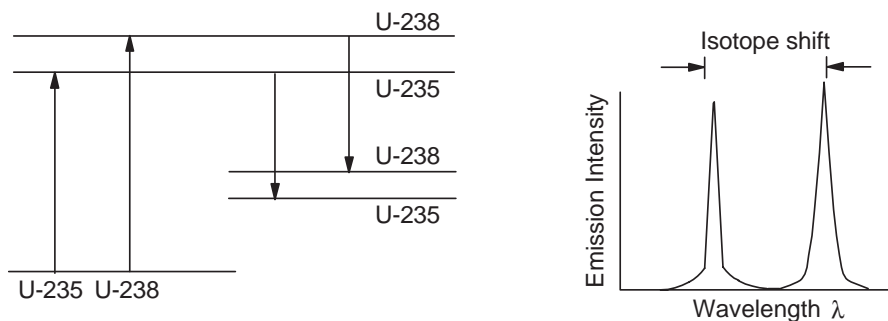


FIGURE 16. Schematic of isotopic energy shifts and the associated LIF spectrum.

Work Accomplished

Cavity Ringdown Spectroscopy

Theoretical efforts are underway to understand background losses affecting the performance of cavity ringdown spectroscopy in inductively coupled plasmas. Quantifying additional loss mechanisms in

the plasma system will provide important data for optimizing the design of the ringdown cavity and the interface between the cavity and plasma system. Various plasma scattering processes and the perturbation of the mode structure of the cavity by the plasma are being considered. In addition, experiments have been initiated to test different cavity designs for their stability and background loss at the uranium absorption wavelength (357.9 nm). These efforts allow us to carry out some optimization of the system prior to the updating of the MSU radiological license. Work with actinide species will be delayed until the updating of the license.

Laser-induced Fluorescence Spectrometry

Preparations for a laboratory capable of handling radioactive materials continue. Mississippi State University has applied to have its license extended to permit controlled usage of elements with atomic numbers in the range of 84 (Po) through 98 (Cf). It is anticipated that this license will be granted in May. Efforts have concentrated on preparing the laboratory so that radioactive work can begin as soon as regulatory permission has been obtained. Initial efforts will concentrate on uranium. As an aid toward the goal of developing rapid identification and quantification of isotopic abundances, DIAL has received a europium-doped surrogate during March and an Idaho LAW sample will be received after regulatory permission has been granted. Using standard europium solutions, we have begun familiarizing ourselves with the LIF spectrometry of europium.

Work Planned

Cavity Ringdown Spectroscopy

Surrogate waste material has been obtained from INEEL that uses europium in place of actinide elements. After completion of the cur-

rent optimization experiments, further work will be carried out to test the performance of our system with europium standards and with the surrogate waste.

Laser-induced Fluorescence Spectrometry

In order to make progress on the use of LIF for isotopic determination of TRU elements, there are three prerequisite needs that must be met. The first is that the university must have a regulatory license to work with actinides. The university is currently negotiating with the state regulatory agency and is purchasing the required monitoring equipment. It is currently anticipated that the university will have the appropriate regulatory license by May 1999. Thereafter we will be able to work with uranium rather than with surrogates. The second need is the need for a sufficiently hot atomization source. An ICP atomization source has been ordered and delivery is expected during May 1999. An ICP system capable of operating with air as the carrier gas is being purchased since many of the applications for which the LIF technique is applicable involve air. The third need is for a sufficiently narrow line widths, tunable laser system that can be reproducibly scanned. DIAL's cavity ringdown spectroscopy group will permit us to use their new moderately high-resolution dye laser system to perform some preliminary experiments on surrogates in an ICP plasma. If as expected these LIF experiments prove that such a moderately high-resolution tunable laser system has sufficient resolution for the TRU elements, then funds for purchase of a comparable dye laser system will be requested for FY2000; if the experiments indicate that even higher resolution is required, then additional funding will be sought in order to purchase an ultra-high resolution tunable laser system. In the interim our efforts to pressure scan our current dye laser will continue. A high-resolution dye laser with computer-controlled scanning mechanism would overcome all these limitations.

Nomenclature

CRDS	cavity ringdown spectroscopy
DIAL	Diagnostic Instrumentation and Analysis Laboratory
HLW	high-level waste
ICP	inductively coupled plasma
LAW	low activity waste
LIF	laser-induced fluorescence
MSU	Mississippi State University
nm	nanometer
ppm	parts-per-million
TRU	transuranic

Subtask 4.2. Pressure in Drums

Mark Henderson and R. Daniel Costley

Introduction

At many waste sites, transuranic (TRU), low-level, and mixed wastes are stored in 55-gallon drums. Many of these drums contain hazardous, organic wastes as well. Radiolysis or other physical or chemical processes may result in gaseous emissions inside these drums. When this occurs, the pressure within the drum will increase,

sometimes to unacceptable levels. In more drastic cases, these emissions may produce flammable or explosive atmospheres (e.g., hydrogen from radiolysis). Currently regulatory procedures require that each drum be individually opened and inspected for the presence of hazardous organic waste. This situation will be dangerous for workers of potential danger and greatly increase safety. Conversely, it would allow the segregation of suspect drums, and more rapidly treatment of safe drums.

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

Work Accomplished

We continue to further our understanding of how uncontrollable factors affect the measurement of pressure using modal analysis. We have completed our tests on corrosion effects and we have determined that corrosion tends to give false positives. Heavy corrosion causes the frequency of the lid resonance to increase and consequently is recognized as a higher pressure. Although a false positive is undesirable, the results of a false positive are preferable to that of a false negative where personnel would be put at risk.

Commercialization of the technology continues as we have entered into an agreement with Military Technologies (Miltec). We have proposed a Phase I SBIR for product commercialization with Miltec and will hear of the results next quarter. The test at a DOE

facility has been further delayed due to budgetary concerns at the site. We have included such tests and the funding for them in the SBIR proposal.

Conclusions

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

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

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

Work Planned

The corrosion tests will continue. Corrosion tests are inherently slow because of the nature of the process. We will continue building a statistical database looking for similarities and differences between drum lids by manufacture and lot. We will continue to seek a commercial partner, and we have a field test tentatively scheduled mid 1999.

Advanced Cleanup Support: Robust Immobilization Devices

Subtask 5.1. Hybrid Plasma Induction Cold Crucible Melter

Dana Miles

Introduction

Russian engineers have developed several melters which are more robust than current generation furnaces, and which can produce a wide variety of waste forms ranging from borosilicate glass to crystalline ceramics (Synroc). This technology potentially could be used for the orphaned spent fuel at SRS, Idaho, and Hanford. DOE has identified disposition of these materials as an “Unmet Need”. This technology appears to be a way to address this need in an expeditious manner, while also providing the capability to produce a second generation waste form in existing facilities.

As part of the Cooperative Agreement, a “hybrid” Russian melter will be installed and tested at DIAL to determine its usefulness and limitations. It is similar to the new “next generation” melter, a cold crucible design with inductive heating. This requires certain components in the glass to allow current to flow, and thus effectively heat up the glass pool. The “hybrid” melter combines the cold crucible design

with a plasma torch to initially break down waste components fed to the melter, negating the need for current inducing components in the glass feed.

Discussions continue for obtaining the next generation melter and testing it at DIAL. Future work calls for providing an appropriate control system for each system. After installation at DIAL, each melter will be tested with simulated spent nuclear fuel to determine the feasibility of producing a vitrified product (borosilicate glass) and a crystalline product (Synroc). Processing and product properties of the waste forms will be determined. Based on the testing, a recommendation will be made regarding the value of each of these systems for this application, and future testing.

The objective of this task is to determine whether the Russian melters can be used to immobilize spent nuclear fuel and selected other waste streams.

Work Accomplished

The Diagnostic Instrumentation and Analysis Laboratory (DIAL) at Mississippi State University is evaluating a hybrid plasma induction cold crucible melter (PICCM) for its potential success in processing spent nuclear fuel and other heterogeneous, metal containing waste. The hybrid plasma induction cold crucible melter was developed at the Russian Institute of Chemical Technology in Moscow. Though originally designed for producing chemically active, high purity metals, it was brought to the United States for research in treating mixed wastes at the Savannah River Site. The PICCM combines plasma heating for the non-metal portion of the waste and inductive heating for the metallic portion. A copper, water cooled crucible is loaded with waste that upon processing contains distinct separation of metal from an upper layer of slag. Radioactive components tend to concentrate in the slag phase which can be removed through an overflow spout. The metal layer can be removed as an ingot for reuse or

for disposal as a low level waste. The cold crucible design nullifies the problem of selecting/creating a refractory that can withstand glass and metal environments in high temperature processing.^{34,35} A simplified schematic is shown in Figure 17.

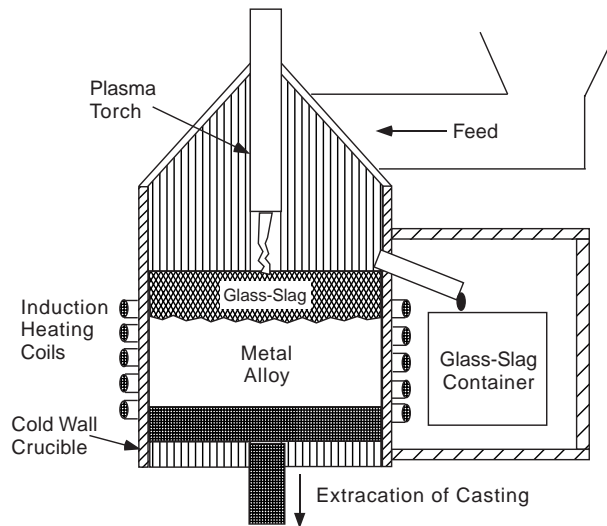


FIGURE 17. Schematic of hybrid plasma induction cold crucible melter.

The PICCM, fabricated in Russia in 1994, was received at DIAL in May 1998 after a brief installation at Georgia Tech during 1996. The potential for success in this application provides impetus for immediate short term as well as long term research opportunities for the international collaboration between the Russian developers and DIAL.

System Description

The PICCM is comprised of a melter vessel containing a 200-mm diameter, water cooled crucible with individually isolated copper segments. The crucible is designed with an overflow spout for removing the slag layer during processing. The overflow spout drains into a stainless steel bucket that is housed on one side of the vessel. The

bucket can be easily removed through a door way on the side of the vessel by rolling it on the fold out tracks. The vessel has a side port for off gas removal. Induction heating is supplied by the water cooled copper coil wrapping the crucible. The bottom of the crucible, also water cooled, is situated on a shaft that moves up or down as directed by the DC motor/controller. The shaft/crucible bottom combination is known as the ram. The melter vessel is sealed on top with a cone-shaped lid. The lid has a small, side view port and port on top to accommodate the torch; it is equipped with a rotary feeder. The feeder is activated with another DC motor/controller.

Other items include a capacitor bank with eight capacitors of which two are not used, four hydroblocks to control the delivery of water to each water cooled elements in the system, an outside coil, a draw sill, an induction power supply, a torch power supply and 70-kW torch, and an operator console. The maximum operating frequency is 2.4 kHz for the current configuration with a 480-V, 60-Hz source. The power limit for the melt operation is about 500 kW.

Summary of Previous Accomplishments

The first of two technical exchanges between DIAL personnel and Russian developers followed the PICCM arrival by approximately one month. The purpose of this meeting was to draft a plan for the unit's installation. Based on DIAL's experience with plasma torch operation, a decision was made to assemble the unit as an induction cold crucible melter (ICCM) and to explore top heating on an as-needed basis. Procurement and establishment of structural and system support equipment at the new DIAL facility filled the interim between the technical collaborations. Two Russian scientists, Dr. Vitaliy Gotovchikov and Mr. Naum Gurvitch, visited DIAL for one month (mid September to mid October 1998) to complete installation and calibration of the melter during the second technical exchange.

The individual system components were bolted to the platform; the installation of the electrical supply, water supply, emergency water supply, return water system, and off gas piping followed. A safety assessment of the facility resulted in construction of handrails, warning signs, and hard-hat only areas. The next phase of the ICCM installation was accomplished with point by point evaluations of the power supply and water supply systems. Control of the power supply would be carried out at the unit because the torch and the operator console were eliminated from the start-up assembly. The operator at the vessel would direct the power settings from the platform area. A steel cylinder, 190-mm diameter with an 8-mm wall thickness, was loaded into the crucible for a series of quick burst calibrations. The ICCM was ready to begin processing.

With the aid of the Russian scientists, the DIAL facility accomplished a tremendous amount of work to get the melter installed in a one-month period. Apart from the structural installation, several discussions and mock training sessions were held. Start-up, operating, and shutdown procedures were documented enabling DIAL personnel to operate the system once the exchange ended. In addition to trouble shooting guidelines, these procedures include the range of parameters for normal operation and upset conditions. Diagrams of the hydroblocks' water cooling service to individual components of the melter were produced as a quick reference for trouble shooting.

The three melt goal of the DIAL test plan, agreed upon by facility and test engineers prior to the arrival of the Russian visitors, was met during the technical exchange by employing a variety of feed materials and system configurations. The first melt contained 1-in. x 2-in. x 4-in. pieces of somewhat rusty carbon steel. The melt was processed with the lid open; some bridging occurred as the melting pool contacted the air at the surface. The Russian operator repeatedly pierced the skull layer with a sword-like tool to encourage the expected induction stirring action and to produce a homogeneous metal ingot. The first melt demonstrated successful installation and operation of

the system. The second melt began by heating the metal ingot from the first run and then adding 1.6 kg (3.5 lbm) borosilicate powder to the melt. The primary benefit of the second run was revealed in the documentation of start-up, operating, and shut-down procedures as well as demonstrating the two phase melting capability. The third melt again used the previous melt with the addition of carbon steel bars to the top of the glass. For this test, the melter lid was closed and the off gas vacuum was applied. The vacuum assisted somewhat in curtailing the oxidation problems experienced in the previous melts; however, the vessel had not been completely sealed. In later tests using multiple feed materials, the vessel was sealed and the oxidation of the surface metal was reduced significantly. At the close of the technical exchange, the third melt favorably verified the partitioning of the glassy slag and molten metal.

Thermal imaging was in place for the later melts. However, eruptions of powdered glass and soot from burning components prevented the ability to “see” the melt surface for extended periods. The data collected indicated that the melt was not stirring as it should. The lack of an appropriate melt volume was the cause. With continued use of the ICCM, several problems were discovered and eliminated. An indicated fault in the induction power supply was followed by water cooling leaks within this cabinet. Some communication with the Russian developers was required to eliminate the power supply fault. Once completed, the system was ready to continue testing. Though all of the data have not been evaluated, three melts of ductile and cast iron with the powdered glass, chunks of previously processed glass, and various fluxing agents were very successful at the end of the reporting period in providing picture perfect thermal images of the unit’s operation.

The functional aspects of the melter operation have been identified through the three tests performed during the international exchange and subsequent tests. Troubleshooting, repair and maintenance, as well as testing have allowed DIAL personnel to become

very familiar with the individual components of the induction melter. At the end of the reporting period, several significant parameter values were established. It appears that the maximum melt height for the batch operating mode is 220 mm. For these late runs, the largest portion of the melt volume as glass was 30% or approximately 2.27 kg, produced as a homogeneous layer within about 20 minutes. The remainder of the melt was primarily ductile and cast iron, approximately 35 kg. Thermal imaging indicated the best yet operation of the melter with a clear view of the expected induction stirring action due to the pattern of magnetic flux in a multi-turn coil.³⁶

Technical Progress

Most of this reporting period was dedicated to evaluating previous test results, preparing a topical report entitled “Installation of the Russian Hybrid Plasma Induction Cold Crucible Melter at the Diagnostic Instrumentation and Analysis Laboratory,” preparing a paper also on the melter installation for the International Conference on Incineration and Thermal Treatment Technologies to be held May 10-14, 1999, and performing a few tests. The tests confirmed the ease of operation in using the PICCM; one particular test demonstrated the technology to Mississippi State University’s Mechanical Engineering Casting and Joining Class. Melter tests produced “clean” metal ingots and homogeneous glassy slags. Some of the basic characterization parameters include records of power ramp rates for the different tests, temperature differentials of the individual cooling water routes, and a view of the average temperature increase as a function of the power as seen in Figure 18; a second order polynomial fits the data.

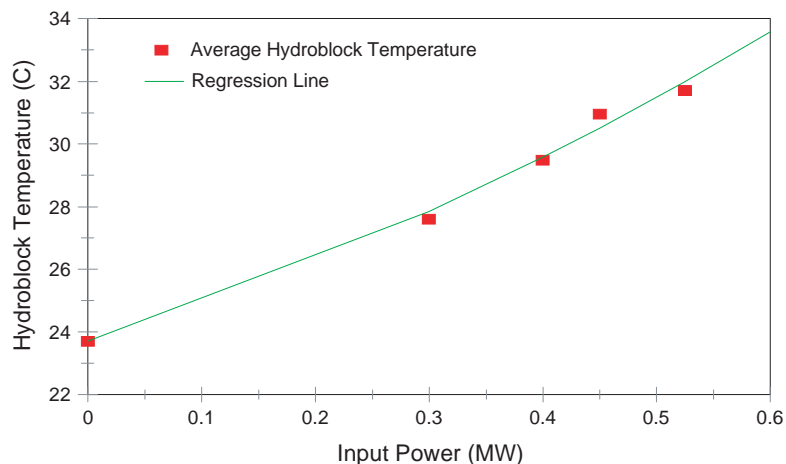


FIGURE 18. Average temperature vs. input power.

Progress was made on previously planned work in supplying modern instrumentation and data collection, finalizing the modifications for continuous operation, and outfitting the exhaust gas stream with gas analysis; all are approximately 80% complete and will be finished in the early part of the next reporting period.

Conclusion

Formulation of acceptable simulated spent nuclear fuel feed stock is near completion to provide the Diagnostic Instrumentation and Analysis Laboratory with the resources for determining the feasibility of employing the Plasma Induction Cold Crucible Melter for this type remediation. The need for the vitrification/induction technology is obvious. Over the past few months, this laboratory has performed tests using the melter with a variety of metal and glass feedstocks demonstrating the successful installation of the unit, two phase melting capability, and the partitioning of the glassy slag and molten metal. Recommendations for continued process advancement and

immediate evaluation of simulated spent nuclear fuel are based on the following:

- Vitrification has been deemed a Best Demonstrated Available Technology (BDAT) for treating High Level Waste by the United States Environmental Protection Agency.
- The process lends itself to the requirements for successful vitrification.
- The geometry and size of the unit are consistent with safe fissile material processing equipment.
- Results of preliminary tests suggest a potential for use in the United States of America, not only at Department of Energy facilities, but possibly at commercial nuclear power plants and Department of Defense locations, as well as continued international collaboration with Russia and other countries.
- Collaboration with the developers of the Plasma Induction Cold Crucible Melter during installation and testing resulted in the successful Diagnostic Instrumentation and Analysis Laboratory demonstration of the project.
- As the unit is adapted to various waste feedstocks, further instrumentation, evaluation of the vitrified and metallic products, and additional process controls can add value to the technology.

Work Planned, April 1, 1999 - June 30, 1999

- Complete previously planned work as indicated in Technical Progress section.
- Continue to develop operating procedures/historical data for various materials.
- Perform simulated spent nuclear fuel tests.

- Collaborate with Russian Research Institute of Chemical Technology for their performance of spent fuel test on “sister” unit.

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Subtask 5.2. Hollow-electrode DC Arc Furnace for Mixed-waste Treatment

Carlson C. P. Pian

Introduction

The hollow-electrode DC (HEDC) arc furnace is another advanced melter concept which is more robust than current-generation furnaces. This technology could be considered for use on the mixed wastes and orphaned spent fuel at the various DOE sites. The plasma arc technology may also be used to destroy pesticide and chemical weapon stockpiles.

The possible advantages of the hollow-electrode arc furnace for nuclear waste remediation were discussed previously.³⁷ HEDC arc furnaces are used commercially in the metals industries with demon-

strated service life of over many years without repairs. The furnace electrodes are simple, inexpensive, and easily maintained. The simple electrode replenishment procedure is extremely advantageous in the treatment of radioactive wastes since it does not expose maintenance personnel to possible radiation hazards. Another advantage of HEDC arc furnace is its ability to handle all forms of wastes. Waste feeds can be in solid, liquid, and/or gaseous forms.

This project has been deferred.

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