RECEIVED
JAN 16 1995
OSTI

DIAGNOSTIC INSTRUMENTATION AND ANALYSIS LABORATORY

APPLICATION OF MODERN DIAGNOSTIC METHODS TO ENVIRONMENTAL IMPROVEMENT

**FY 95 Annual Technical Progress Report
for the period
October 1994 through September 1995**

December 1995

**Prepared For The
United States Department Of Energy
Agreement No. DE-FG02-93CH-10575**

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

MASTER

DISCLAIMER

**Portions of this document may be illegible
in electronic image products. Images are
produced from the best available original
document.**

DIAL 10575
FY 95 Annual

APPLICATION OF MODERN DIAGNOSTIC METHODS TO ENVIRONMENTAL IMPROVEMENT

**Annual Progress Report
for the period
October 1994 through September 1995**

PRINCIPAL INVESTIGATOR
Dr. W. Steve Shepard

DECEMBER 1995

**Diagnostic Instrumentation and Analysis Laboratory
Post Office Drawer MM
Mississippi State University
Mississippi State, Mississippi 39762-5932**

**Prepared for the US Department of Energy
Agreement No. DE-FG02-93CH-10575**

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product or process disclosed or represents that its use would not infringe privately-owned rights.

U.S. DEPARTMENT OF ENERGY
NOTICE OF ENERGY RD&D PROJECT

1. DOE CONTRACT OR GRANT NUMBER DE-FG02-93CH-10575
☐ New contract ☒ Continuation/Revision
2. A. NAME OF PERFORMING ORGANIZATION Mississippi State University
B. Department or Division Diagnostic Instrumentation and Analysis Laboratory
C. Street Address Post Office Drawer MM
City Mississippi State State MS Zip 39762
D. Type of Performing Organization (circle only one two-letter code)
CU-College, university, or trade school NP-Foundation or laboratory not operated for profit
EG-Electric or gas utility ST-Regional, state, or local government facility
FF-Federally funded RD&D centers TA-Trade or professional organization
or laboratory operated for US-Federal Agency
agency of US government XX-Other
IN-Private industry
3. PRINCIPAL OR SENIOR INVESTIGATOR
A. Last Shepard First W. MI S.
B. Phone: Commercial 601-325-2105 FTS _____
4. DOE SPONSORING OFFICE OR DIVISION Environmental Management
5. TITLE OF PROJECT
Application of Modern Diagnostic Methods to Environmental Improvement
6. DESCRIPTIVE SUMMARY (limit to 200 words)
See Abstract (pg. 1, FY 95 Annual Technical Progress Report)
7. RESPONDENT INFORMATION. List name and address of person filling out this form. Give telephone number and extension where person can be reached. Record the date this form was completed or updated. This information will not be published.
Last Wade First Lillian MI _____
Address Post Office Drawer MM
City Mississippi State State MS Zip 39762
Phone 601-325-2105 Date _____

Table of Contents

Abstract	1
1 Plasma Torch Operation	1-1
2 Process Control	2-1
3 Emission Spectra	3-1
4 Laser Doppler Velocimetry	4-1
5 Coherent Anti-Stokes Raman Spectroscopy	5-1
6 Pyrometer Systems	6-1
7 FTIR Spectroscopy	7-1
8 Laser Scattering	8-1
9 Multicolor Imaging	9-1
10 Laser Optogalvanic Spectroscopy	10-1
11 Extinction-based Cross Correlation	11-1
12 Gas Analysis	12-1
13 Laser-induced Breakdown Spectroscopy	13-1
14 Laser Ultrasonics Viscosity Measurement	14-1
15 Torch Operations/Correlations	15-1
16 Modeling - Plasma Torch	16-1
17 Field Operations	17-1
18 Special Projects	18-1
19 Industrial Affiliates/Marketing	19-1
20 Continuous Emission Monitors	20-1

List of Figures

1-1	Sectional view of 250-kW plasma vitrifier.	1-6
1-2	Crucible 1 with refractory samples mounted.	1-7
1-3	Crucible 1 samples, close-up view.	1-8
2-1	Control implementation strategy.	2-7
2-2	Advisor-controller information flow.	2-8
2-3	Communication protocol systems	2-9
2-4	Image series for nitrogen (falsely colored to indicate temperature), grouped in order of decreasing torch pressure (left-to-right), and in- creasing current (top-to-bottom).	2-10
2-5	Alternative views showing rapid torch movement.	2-12
2-6	Numerical indicators of current and pressure.	2-12
2-7	Current and pressure estimations derived from image data.	2-13
3-1	Soil vitrification emission spectra recorded by the SPDA Emission Spec- troscopy system on January 23, 1995.	3-13
3-2	Mixed waste surrogate vitrification spectra recorded by the CCD Emis- sion Spectroscopy system at three different times: March 8, 1995 at ap- proximately 1:03 and 1:13 pm and March 9, 1995.	3-14
3-3	Mixed waste surrogate vitrification emission spectra recorded by the SPDA Emission Spectroscopy system on March 6 and 7, 1995.	3-15
3-4	Comparison as a function of time of the background-corrected SPDA emission intensities of Cs and O with surface temperature (in K), torch height (in cm), and torch current (in amps) for the March 6 test. ..	3-16
3-5	Three dimensional time display of the CCD-recorded emission spectra during the initial melt on March 6, 1995.	3-17

3-6	Variations in atomic line intensities with time over about a period of one minute on March 8, 1995 at 1:00 p.m.	3-18
4-1	A map of the velocity field between the tip of the PT-50 plasma torch and the graphite billet cathode.	4-6
4-2	Mean velocity recorded during the test on March 6, 1995.	4-7
4-3	Particle number density for the same time period as Figure 4-2. ...	4-8
5-1	CARS torch measurement experimental setup.	5-5
5-2	Single shot CARS torch spectrum taken at 1 in. below the electrode and 10 mm away from the arc center.	5-6
5-3	Variation of inferred temperatures obtained from a set of CARS data.	5-7
5-4	Temperature distribution 1 in. below the electrode at various torch operation currents.	5-8
5-5	Temperature distribution under various torch operation currents. .	5-9
6-1	Plasma torch interference-free regions in FTIR emission spectra (clean torch).	6-4
6-2	Plasma torch interference-free regions in FTIR emission spectra (WSRC mix #2 being processed).	6-5
6-3	Automated multiple target measurements by multiwavelength pyrometer (MWP) using the developed multifiber switcher.	6-6
6-4	Temperature measurements on WSRC surrogates in DIAL's PT-150	6-7
7-1	Block diagram of DIAL's plasma torch furnace and the FTIR measurement locations.	7-9
7-2	FTIR centerburst intensities measured during a plasma torch test run for evaluation of the PHP (TREAT) port assembly design.	7-10
7-3	On-line HCl calibration spectra.	7-11
7-4	The associated Beer-Lambert plot from the on-line calibration experiments.....	7-12

7-5	Typical extractive absorption trace collected during injection of the surrogate feed into the plasma torch furnace.	7-13
7-6	Comparison of the spectrum in Figure 7-5 with an on-line absorption spectrum.....	7-14
7-7	NO, NO ₂ , and total NO _x concentrations measured during a plasma torch test run.	7-15
10-1	Schematic of the DIAL LOGS apparatus.	10-9
10-2	Schematic of field implementation configuration for DIAL LOGS system.	10-10
10-3	Schematic of discharge regions of dc glow discharge and of variation of electric field.	10-11
10-4	LOGS calibration curve for uranium detected in air/acetylene flame. The error bars correspond to ± 1 standard deviation.	10-12
10-5	Schematic of DIAL LOGS prototype hollow cathode discharge cell.	10-13
10-6	Schematic of rf LOGS apparatus.	10-14
11-1	Schematic of test bed.	11-5
11-2	Variable beam spacing cross correlation system schematic.	11-6
11-3	CCS velocity measurement with a beam spacing of 0.19 in.	11-7
11-4	CCS velocity measurement with a beam spacing of 0.29 in.	11-8
13-1	Fitting of the computer simulated spectrum with the LIBS spectrum of glass from Envitco melter.	13-15
13-2	Schematic diagram of the LIBS experimental setup used for glass measurement at different temperatures.	13-16
13-3	Variation of inferred concentration ratio of Ni/Fe with molten glass temperature.	13-17

13-4	Calibration curve for Sn in 760 torr N ₂ using metal hydride generator	13-18
13-5	Calibration curve for Sn in 760 torr air using metal hydride generator	13-19
13-6	Cr calibration curve in air using a nebulizer.	13-20
13-7	Typical off-gas LIBS spectrum at DIAL/MSU from SR-surrogate feed at the central wavelength of (a) 360 nm and (b) 412 nm.	13-21
13-8	Variation of metal concentrations with time in DIAL/MSU off-gas.	13-22
13-9	Schematic of LIBS system and the SAIC's STAR Center alarm/interface system.	13-23
13-10	A LIBS spectrum recorded at STAR Center on June 8, 1995.	13-24
13-11	Variation of metal concentrations with time in SAIC's STAR Center off-gas on 6/8/95, 19:40-20:59.	13-25
13-12	LIBS spectrum of U in the spectral region of 407 - 426 nm.	13-26
13-13	LIBS spectra of Pu recorded in the spectral region of 444 - 463 nm.	13-27
13-14	LIBS spectra of Np recorded in the spectral region of 444 - 463 nm.	13-28
14-1	Experimental apparatus used to measure shear wave reflection coefficient for the determination of liquid viscosity.	14-6
16-1	The top is an experimental spectrum, measured by Dr. David Monts on DIAL's PT-50 plasma torch.	16-3
16-2	Typical FTIR extinction data covering a broad wavelength region.	16-7
16-3	(a) Particle size distributions computed by inversion program from synthetic data generated with the input distribution (solid line). (b) Comparison of the synthetic extinction data to the back calculated extinctions using the result distributions of (a).	16-8
16-4	(a) Particle size distributions from the analysis of combustion off gas extinction data. (b) Comparison of experimental data to reconstructed data	

	from computed distributions of (a).....	16-9
17-1	WETO facility, Butte, Montana.	17-9
17-2	DIAL's Air Stream-based Mobile Instrument Laboratory on location at the WETO facility, Butte, Montana.	17-10
20-1	Block diagram of the HCl continuous emission monitor.	20-6
20-2	Detector stability test for the HCl monitor.	20-7
20-3	Response from the HCl monitor during a plasma torch test run. ...	20-8
20-4	Gas stream temperature at the furnace exit.	20-9
20-5	HCl monitor responses for three different briquette injections. ...	20-10
20-6	Comparison of the system response for briquette injection with a nitrogen plasma and an air plasma.	20-11
20-7	As in Figure 20-6, but for different briquette compositions.	20-12
20-8	Initial calibration curve from the HCl monitor using the mass flow controllers.	20-13

List of Tables

1-1	Feed material constituents for WSRC test.....	1-2
2-1	Illustrative rule base of ESA prototype.	2-3
7-1	Comparison of FTIR and gas analysis results.....	7-6
10-1	Current LOGS and air ICP theoretical limits of detection (LOD). ...	10-4
12-1	Briquette mixture used for WSRC tests.....	12-2
13-1	Emission lines used to determine elemental concentrations by LIBS.	13-4
13-2	Mole ratio of elements and their weight percentages in the vitrified glass obtained by LIBS and MSCL, and their relative deviations.	13-6
13-3	LIBS detection limits of 10 RCRA elements.	13-8
14-1	Measurement of viscosity using piezoelectric transducers at 25°C. All values are in poise.	14-2
14-2	Measurement of viscosity using piezoelectric transducers at 60°C using temperature compensation scheme.	14-3
14-3	Measurement of viscosity at room temperature with laser generated shear waves and using magnitude technique.	14-3
15-1	Observed emission lines recorded during vitrification of Savannah River soil with dolomitic lime.	15-2

Abstract

The Diagnostic Instrumentation and Analysis Laboratory (DIAL), an interdisciplinary research department in the College of Engineering at Mississippi State University (MSU), is under contract with the U. S. Department of Energy (DOE) to develop and apply advanced diagnostic instrumentation and analysis techniques to aid in solving DOE's nuclear waste problem. The program is a comprehensive effort which includes five focus areas:

Advanced diagnostic systems; development/application;

Torch operation and test facilities;

Process development;

On-site field measurement and analysis;

Technology transfer/commercialization.

As part of this program, diagnostic methods will be developed and evaluated for characterization, monitoring and process control. Also, the measured parameters, will be employed to improve, optimize and control the operation of the plasma torch and the overall plasma treatment process.

Moreover, on-site field measurements at various DOE facilities are carried out to aid in the rapid demonstration and implementation of modern fieldable diagnostic methods. Such efforts also provide a basis for technology transfer.

1 Plasma Torch Operation

John Etheridge

Introduction

DIAL operated a 100-kW plasma torch for the development of plasma diagnostics during 1994. This system is relatively easy to operate and continues to serve as a basis for plasma diagnostic measurements. This system is capable of vacuum operation and has several optical ports. However, the need to analyze various parameters such as temperature and off-gas constituents and the need to develop a control strategy for a plasma torch vitrifier requires access to the off-gas from an actual vitrification process. Since we needed to keep the plasma diagnostics system clean, we constructed a plasma vitrifier which uses a 250-kW plasma torch. An off-gas scrubber system was also needed to clean up the effluent from this system. The scrubber system has been designed and is presently under construction.

Both of these plasma torch systems are available for cooperative research with other DOE sponsored laboratories. DIAL will also contract testing and evaluation services for DOE labs using these systems.

Work Accomplished

A plasma torch vitrifier was constructed in order to provide a test bed for the development of diagnostic instrumentation, to serve as a test bed for process control system design, and to provide a facility for vitrification experiments. Figure 1-1 is a cut-away view of the vitrifier. The system uses a 250-kW plasma torch mounted on a 3-axis gimbal. The material to be vitrified is placed in a graphite crucible inside the furnace. Optical access to the process is provided by four optical ports on the top of the vessel. (One of these ports is used for a video camera. All tests are video taped.) Electrical actuators control the position of the torch. The off-gas system has two pairs of optical ports near the exit from the furnace. The off-gas is routed through a combustion test stand which has a number of additional optical ports.

The plasma torch system is well instrumented by the manufacturer and several additional data channels have been added for both monitoring and control. Data collection is provided by a PC which is also the basis for a process control system that is being developed at DIAL. This system is used regularly for development and testing of diagnostic instrumentation and

vitrification experiments. The system is operated an average of one day per week.

DIAL performed a series of refractory lifetime tests for Westinghouse Savannah River Company (WSRC) using the 250-kW vitrifier. In preparation for the refractory tests, several system shakedown tests were done using soil from the Savannah River Site. The specifications for these tests were provided by WSRC. During the first tests, a small amount of lime was mixed with the soil, and the mixture was vitrified. The resulting glass was shipped to WSRC for analysis. During the second tests, the lime was placed in the crucible with the soil, but the two were not mixed. After vitrification, a sample was sent to WSRC for analysis. The second test was done to see if lime spread on top of the ground would mix with the soil during *in situ* vitrification and produce an acceptable glass product.

The refractory tests were done to test the relative lifetime of 32 refractory samples which were chosen by WSRC. These samples were mounted in a crucibles made from G10 graphite. Two tests were done with two sets of refractory samples in two identical crucibles. A feed material, which was also specified by WSRC, was formed into briquettes for ease of injection into the system. This material was chosen purposely to attack refractory and shorten the necessary testing time. The list of constituents for the feed material is given in Table 1-1.

Table 1-1. Feed material constituents for WSRC test.

FEED MATERIAL	PERCENT
PECAN SHELL FLOUR	13.8
PVC GRANULES	13.8
GLASS BEADS (Soda Lime Glass)	13.8
PERLITE (Harborlite)	13.8
IRON POWDER	13.8
ALUMINA	10.0
ALUMINUM POWDER	2.0
SILICA SAND	5.5
PORTLAND CEMENT	5.5
ACTIVATED CARBON	6.2

Table 1-1. Feed material constituents for WSRC test.

CESIUM CHLORIDE	0.3
CADMIUM CHLORIDE	0.3
LEAD CHLORIDE	0.3
CHROMIC CHLORIDE	0.3
CERIUM CHLORIDE	0.3
NICKEL CHLORIDE	0.3
TOTAL	100.0
BINDER	PERCENT
HAMACO 267 STARCH	7.5
WATER	20.0

The first test was intended as a test of the ability of the samples to withstand thermal shock. The crucible was charged with about five pounds of the briquettes prior to being placed into the furnace. Once the precharged briquettes had formed a molten puddle, additional briquettes were injected into the crucible until the molten puddle covered about half of each refractory sample. This was done in order to evaluate refractory performances both above and below the melt line. The initial test lasted about four hours. At the end of the test, the plasma torch was extinguished, and the furnace top was removed. On the following day the torch was restarted, and the feed material was remelted and held for another four hours after which the torch was extinguished, and the top of the furnace removed immediately. This concluded the shock test.

The second test was started in the same manner as the first test. But, the melt was held for about six hours, and the plasma torch power was slowly ramped down at the end of the test. The top remained on the vessel, and the melt was allowed to slowly cool overnight.

The crucibles with the remaining samples were shipped to WSRC where they were sectioned and analyzed. Several reports and papers describing the results of these tests were written. Figures 1-2 and 1-3 show the samples in one of the crucibles before and after the test, respectively.

Project Status

The two plasma torch systems at DIAL are operational and capable of support for diagnostic instrumentation development and control system

development. The 250-kW system is capable of vitrification and other thermal experiments. Both systems are very reliable.

Operation of the systems is provided by three technicians all of which are capable operators. A recent reorganization has provided the plasma torch operation group with a portion of the time of five engineers. These engineers are used as test engineers for tests with the plasma torch systems. They are responsible for seeing that each test is done in a manner that will provide the experimenter with the proper data and for preparing a report for each test. This has improved our overall testing program.

The off-gas system has been completely designed. It should be on-line in February of 1996. This system will be used for testing of off-gas cleanup components as well as for cleaning up our gas stream.

Project Significance

DIAL is one of the very few DOE sponsored projects with plasma torch systems and experience in plasma torch operation. We offer these system to other DOE sponsored facilities for testing and evaluation and for process development. Our plasma torch systems are also used as a test bed for the development of diagnostic instrumentation that is targeted for monitoring vitrification processes, including off-gas monitoring.

This project is therefore significant for the overall DOE vitrification program, because it provides needed support in several areas of interest.

FY 96 Plans

During FY 96, the 250-kW vitrification system will be modified to eliminate the need for a graphite crucible inside the furnace. At the same time the vessel will be modified to allow tilt tapping. This will give better optical access to the melt and provide a pour stream for testing and development of additional diagnostics.

The off-gas system will be brought on-line and will be used as another test bed for testing of off-gas monitoring instrumentation. Testing of off-gas system components will also be done using this system.

An open frame plasma torch will be constructed from the internal parts of the 250-kW plasma torch that we use. This torch will give optical access to the arc attachment in the rear electrode and will be used for testing of instrumentation and for analysis of electrode wear characteristics. It could also be useful for testing different electrode designs or for determining optimum operating parameters for extended electrode lifetime.

Operation of all plasma torch systems in support of diagnostic instrumentation will continue through FY 96.

References

1. Cicero, C.A., et al. 1995. *Vitrification of Savannah River Site contaminated soils*. Paper read at I & EC Special Symposium, American Chemical Society. Atlanta, GA.
2. Bauman, L.E., et al. 1995. *Emission spectroscopy studies of volatile species produced by plasma arc vitrification of mixed waste*. Paper read at International Symposium on Environmental Technologies: Plasma Systems and Applications. Atlanta, Ga.
3. Monts, D.L., et al. 1995. *Identification and characterization of volatile species produced by plasma arc vitrification of mixed waste surrogates*. Paper read at I & EC Special Symposium, American Chemical Society. Atlanta, GA.
4. Marra, J.C., et al. 1995. *Corrosion assessment of refractory materials for waste vitrification*. Proceedings of the Corrosion of Materials By Molten Glass, The 19th Annual Meeting of the American Chemical Society. Cincinnati, OH.
5. Kielpinski, A.L., et al. 1995. *Testing of refractory materials for plasma vitrification of low-level mixed wastes*. WM 95 Symposium. Tucson, AZ.
6. Etheridge, J.A., et al. 1995. *Refractory lifetime testing for Westinghouse Savannah River Company*. Mississippi State University: Diagnostic Instrumentation and Analysis Laboratory. DIAL 10575 TR 95-3.

Figure 1-1. Sectional view of 250-kW plasma vitrifier.

Figure 1-2. Crucible 1 with refractory samples mounted.

Figure 1-3. Crucible 1 samples, close-up view.

2 Process Control

J. B. Nail and Thomas Philip

Introduction

DIAL's plasma torch and process controls structure consists of a flexible supervisory control, linked to an artificial intelligence (AI) advisor, which in turn will link to diagnostic instruments. An over all configuration for the control system is shown in Figure 2-1.

The subtask objectives are 1) to implement a control system, interfaced to an AI advisor, 2) to prototype an expert system advisor for the control and test it, 3) to investigate applicability of fuzzy logic for advisor, 4) to select control parameters, and 5) to conduct an initial control study using plasma torch image data. The control parameter selection is needed also to build the knowledge base for the expert system advisor. Investigating multimedia for the expert system user interface also has been a minor objective.

The AI advisor (ESA) is configured to assist the progression which involves sensor fusion, heuristics, and training. This is one of the major reasons for structuring an AI system in advisory fashion. The supervisory control is expected to sustain robust operation. The AI advisory is expected to provide advice to enhance safety, efficiency, and economy. AI development will continue to dominate effort for some time to come. Much of this will be individually tailored for specific diagnostic systems as they progress from a laboratory to a process environment.

Work Accomplished

Visual Basic, VB-EZ and Formula One-VBX provide the software base for control development. Visual Basic allows custom programming with tabular and graphic display, VB-EZ performs data acquisition under Visual Basic, and Formula One-VBX allows on-line configuration and data archival in an Excel spreadsheet format. Visual Basic also supports serial communications, which provide links to the AI advisor, and to an Allen-Bradley programmable controller. System flexibility is enhanced by using an on-line spreadsheet structure to configure the system, and to archive data. Flexibility is extended by running this package under Visual Basic.

The hardware consists of a Pentium for supervisory control, another for the AI advisor, data translation cards for data acquisition, and an Allen-Bradley programmable controller for control outputs. Thermocouple signals are

measured as low-level differential inputs; all other signals are transmitted to the computer in 4-20 mA standard, then converted to single-ended signals at the Data Translation card. The SLC-503 Allen Bradley controller obtains commands from a data table, which the Pentium writes via serial communication. From there, various actuators are controlled by the SLC unit. A positive control command is required to increase a setpoint, and the opposite command is required to decrease the value. Each part of the process is open-loop stable, so if no command is received from the computer for some time, the system remains at the last commanded setpoint.

One of the major concerns is the integrity of the control system - robustness. Most of the supervisory components are common to the process industries. One exception is custom circuitry used to "duplicate" plasma torch controller 4 - 20 mA signals. These were implemented to avoid modification of the torch controller (except for replacement of inoperable devices to achieve transferred operation). As much as possible, standard process components were used for measurement and actuation.

The AI advisor prototype is developed using an object expert system shell. The system information flow is shown in Figure 2-2. The supervisory controller sends parameter information to the advisor through an RS 232 communication line. The advisor uses this information to infer appropriate advice in the form of actions for the controller, using a knowledge base

The protocol used for communication between ESA and the controller is given in Figure 2-3. Parameters from the Torch and also from the diagnostic instruments will be known to both the sub-systems. A similar protocol is used for communication to each diagnostic system. This is viewed as a worst-case (or low-end) communication strategy that should work to all instruments. A more network-oriented approach will be a continuing effort. The prototype advisor uses knowledge about parameter ranges and sends simulated advice to the controller. The controller displays the advice on its monitor, instead of applying any action. Table 2-1 gives an example rule base used for inference by the advisor. In the actual system these actions will be derived from diagnostic instrumentation, which the supervisory controller will apply to the torch system (within limits set by the operator). The rule firing sequence of the AI Advisor is controlled by timers, demons and WHEN CHANGED METHODS. Demons and WHEN CHANGED METHODS consist of actions to be done when an associated parameter changes.

Table 2-1. Illustrative rule base of ESA prototype.

Parameter	Condition	Action
gas flow rate	> 0 & < 50	action3,00
gas inlet flow	< 5 > 50	action4,01
power temp in	< 20 > 800	action6,01
power temp out	> 20 & < 500	action7,00
torch angle1	< 30 > 240	action14,01
torch angle2	> 30 & < 240	action15,00
torch angle2	< 30 > 240	action15,01
torch standoff	> 2 & < 10	action18,00
torch standoff	< 2 > 10	action18,01
torch voltage	> 20 & < 100	action19,00

A fuzzy logic shell was studied for applicability to the torch control system. An example control problem was studied, identifying fuzzy functions and linguistic variables. The technique is applicable to this environment provided appropriate linguistic variables are identified and their relationships are established. Due to stability concerns, this is not pursued further.

In regard to identifying parameters, a series of meetings were scheduled with each PI in charge of diagnostic instrument development. These were extremely helpful in identifying the goals common to the diagnostic instrument, and the vitrification process for which implementation was envisioned. In all cases, insight was gained from both perspectives. This will be continued as essential to bring the instrument into a process-match condition.

One of the goals in this effort was to identify the process variables most applicable to specific diagnostic instruments, and physical considerations appropriate to development. In addition, a plan of implementation was also developed, with links to LIBS, FTIR, Pyrometer, and PTM to receive first priority. LIBS will yield information on melt constituents, FTIR monitors off-gas constituents, the Pyrometer provides the melt processing temperature, and PTM is a monitor for the plasma torch. A "generic" process diagram for vitrification was developed to identify target points for each diagnostic device. This overview will serve as a guide for implementation, and as a baseline for revision of plans as needed.

An initial control study was performed on images from the 100 kW plasma torch. These images were obtained from a single-color CCD camera

system, with pixel intensity represented by an 8-bit integer. The uniqueness of each image was especially evident after false-coloring was applied to depict intensity range. A series of images were obtained as torch parameters such as current, torch gas pressure, gas type, and standoff (distance from ground electrode) were varied. The specific goal of the study was to estimate the value of current and pressure, given image data only. The standoff and gas type were restricted to bound this initial effort. Nitrogen was chosen for the gas type, for two reasons. First, it is certainly under consideration as a torch gas appropriate for vitrification. Second, the image set for nitrogen contained an anomaly that would certainly challenge a parameter estimation scheme, and thus provide a good test of capability.

Figure 2-4 is the image series for nitrogen (falsely colored to indicate temperature), grouped in order of decreasing torch pressure (left-to-right), and increasing current (top-to-bottom). Note that the regularity of progression is disturbed by the image in the upper-right.

Initially, a neural network approach to this problem was envisioned, but after consideration of the task, a simpler approach based on least-squares minimization was attempted. With either approach, a group of indicators were required - at least as many indicators as variables to be estimated. In this case, two were to be estimated, so two indicators were developed.

Visualization is enhanced by alternate views of the data. Two useful views are mesh plots and contour plots, shown in Figure 2-5. Mesh plots are especially helpful in developing indicators with current and pressure dependence. Contour plots emphasize the degradation due to interlacing, and once this is removed, the regions of rapid variation and nonlaminar plasma.

Indicators for use in optical diagnostics require a certain quality of adaptability, so that changes in focus, field-of-view, and light intensity can be accommodated. A ratio of two values, or an adaptive feature are possible examples. For a plasma torch, the image is quite regular near the torch exit, with intensity across the exit resembling a Gaussian distribution. Thus, one of the indicators was the ratio of mean intensity to standard deviation (at a station near the torch). Despite the more random nature of intensity at a distance from the torch, indicators from both ends of the plasma were required for adequate parameter estimation. The intensity rises like a mountain range on the horizon at both the torch and melt, indicating a significant transfer of energy at these extremes. In between, of course, the ridge diminishes. One useful indicator was formed by ratioing the volume of the peak at the torch end to that at the melt end of the plasma. The definition of volume depends on the "floor" from which computation is accomplished, and the floor was chosen for adaptive qualities. In particular, a percentage (typically 70%) of the average of the

ridge peaks in the interior was used as the computation floor. Figure 2-6 provides visual insight to these parameter definitions.

The adaptive features of these two indicators provided a coarse estimate of current and pressure, as indicated in Figure 2-7. Note that the data set was specifically chosen for level of difficulty, and these results are considered quite respectable under those circumstances. Improvements in frame-grabber hardware and image-processing software are planned for follow-on work. In addition, goals for the estimation of parameters useful for control (and not otherwise available) are planned.

A literature survey was done to collect information on multimedia interfaces. Features of interfaces like netscape were reviewed. It is helpful to direct operators to specific problems and solutions in a very realistic way.

Project Status

The Supervisory Control is operational, including signal monitoring and archiving, response to concurrent user commands, setpoint decisions and output to the SLC controller, and selected actuation devices. Provisions for up to 80 inputs and 20 outputs allow for significant expansion beyond present needs.

The AI advisor prototype is complete and tested with simulated inputs. Full testing is dependent on signals acquired from diagnostic instruments under development.

Communication between the AI advisor and supervisory control has been established and tested. Diagnostic instruments will be added at device maturity. The major effort will be tailoring the AI advisor for the particular instrument and the process, repeated for each instrument under development.

Project Significance

The visible parts of a control system are the components, especially the monitoring components. It is very important that the real goal is defined and faithfully pursued. The goal is not bells and whistles, but operational capability. The real goal is determination of process operational parameters that contribute positively to safe, economical, and efficient vitrification. These are the lasting quantities that can be transferred to other vitrification operations. The system in place should be adequate for many tasks and reconfigurable to additional needs.

The control structure in place is expected to serve well for moving diagnostic instruments into the process control environment. AI techniques should allow significant enhancement and tailoring of instrument output. Application

through a supervisory control structure should be an appropriate interface for any system destined for a vitrification process. The complete structure allows for experimental and validation effort to drive the diagnostic development.

FY 96 Plans

The effort under this subtask for FY 96 will be focused on four major areas as discussed in the following paragraph. Controlling the plasma torch parameters is essential for an efficient waste remediation process, helping to ensure the quality of off-gas and also the vitrified product. This process involves sensor fusion and heuristic approaches. Therefore, the first major effort is continued development of process control elements applicable to vitrification. This will involve experimentation, AI support development, and checkout in a simulated control environment.

Communication between computers is necessary, and control-critical components require linking in a protected fashion. A second area of emphasis will be development of an operational base with elements of network flexibility, but with the robust characteristics necessary for process control.

A third focus is the torch-melt interface, for which a series of experiments are planned to address questions of heat transfer, particle entrainment in the off-gas, and processing efficiency.

The fourth effort will apply AI to simple sensing components, in an attempt to characterize a feedstream for control purposes. This is a feasibility study designed to serve as a classifier for feed forward application in a realistic vitrification system.

Figure 2-1. Control implementation strategy.

Figure 2-2. Advisor-controller information flow.

CONTROLLER - AI ADVISOR COMMUNICATION

0. NOTATIONS USED

+ : followed by
= : consists of
[]m : contents within the brackets repeated a maximum of "m" times

E.g. file = [r1 +r2]25 means that file consists of 25 sets of r1 and r2

1. CONTROLLER TO ADVISOR

The two types of information sent to the AI advisor (ESA) from the controller are process parameters and control actions in the format:

Controller_info. = header + parameters + actions + terminator

header = 02 / one byte in length

parameters = [identifier + value]80 / 80 pairs

identifier = [character]12 / of type string of 12 characters
value = [character]? / of type floating point

actions = [identifier + value]20

identifier = [character]12 / of type string of 12 characters
value = [character]? / of type integer

2.0 ADVISOR TO CONTROLLER

The two types of information sent are diagnostic values and advice, in the format:

ESA_info. = header + diagnostics + advice + terminator

header = / one byte in length

diagnostics = [identifier + value]80

identifier = [character]12 / of type string of 12 characters
value = [character]? / of type floating point

advice = [identifier + values]20 / 20 advice

identifier = [character]12 / of type string of 12 characters
value = [character]? / of type integer

Figure 2-3. Communication protocol systems

Figure 2-4. Image series for nitrogen (falsely colored to indicate temperature), grouped in order of decreasing torch pressure (left-to-right), and increasing current (top-to-bottom).

MESH PLOT

CONTOUR PLOT

Figure 2-5. Alternative views showing rapid torch movement.

Axial View of Plasma Intensity Near the Torch

		Pressure		
		22	42	63
Current	175	1.475	1.066	1.433
	196	1.638	1.207	1.678

Standard Deviation/Mean

Side View of Maximum Plasma Intensity Level

		Pressure		
		22	42	63
Current	175	1.553	1.665	3.136
	196	0.379	2.277	5.921

Torch Intensity/Melt Intensity

Figure 2-6. Numerical indicators of current and pressure.

Figure 2-7. Current and pressure estimations derived from image data.

3 Emission Spectra

Leslie E. Bauman and David L. Monts

Introduction

Plasma optical emissions contain a prodigious amount of data about the plasma composition and physical state that could possibly be used for control and optimization of plasma processes. Plans for the use of emission spectroscopy systems included a mapping of plasma torch emissions and evaluation and development of techniques for temperature and electron number density determinations in the various plasmas.

Work Accomplished

Application of emission spectroscopy systems to a study of the volatile species present above the melt in a plasma vitrification process was the primary accomplishment of this year. The results of these experiments have been reported previously and are summarized here.^{1,2}

During a field campaign at the U.S. Department of Energy's Western Environmental Technology Office in Butte, Montana,^{3,4} an emission spectroscopy system observed atomic emission from gas-phase alkali elements outside the primary plasma arc centrifugal vitrification chamber whenever the plasma arc was moved close to the throat in order to clear the throat in preparation for a melt pour. In addition, emission from gas-phase alkali elements were observed while monitoring the pour of a joule-heated glass melter (operating under nonstandard conditions) located at the DOE/Industry Center for Vitrification Research at Clemson University's Environmental Systems Engineering Department.^{5,6} Given the presence of significant amounts of Cs-137 in radioactive waste streams, important operational implications are suggested by these measurements. During the spring of 1995, an extensive investigation using emission spectroscopy was undertaken to identify and characterize volatile species present inside the primary chamber of a plasma arc system during vitrification of Savannah River surrogates. Two different surrogate materials were studied: Savannah River soil and a Savannah River mixed waste surrogate.

Testing Configurations

The vitrification system used for this series of tests is based on a Plasma Energy Corporation PT-150 plasma torch with air as the plasma medium. The

plasma torch was operated in the nontransferred mode for the Savannah River soil studies and in the transferred mode for the Savannah River mixed waste surrogate studies. Clay graphite crucibles were used for the Savannah River soil tests, and graphite crucibles were used for the Savannah River mixed waste surrogate tests. The tops of the crucibles were cut off so that the contents of the crucibles could be monitored. Mixed waste surrogate briquettes were fed via a dual ball valve interlock system. Four optical ports are arrayed in the plasma chamber lid, enabling observation down into the bottom of the crucible: one was used for a television camera to provide real-time images of the melt inside the crucible; one port was used to feed the mixed waste surrogate briquettes into the plasma hearth; and the remaining two optical ports were used during these tests by emission spectroscopy systems and a two-color pyrometry (TCP) system.

Near-ultraviolet, visible and near-infrared radiation from inside the PT-150 was monitored by simple pickup lenses and was transferred via fiber optic cables to two different DIAL emission spectroscopy systems. The Silicon Photodiode Array (SPDA) emission spectroscopy system consists of a 0.156-m spectrograph, a 1024-channel photodiode array detector, and a dedicated computer. The spectrograph employed a low-resolution diffraction grating to cover the entire wavelength range from 558.2 nm to 1087.2 nm for the Savannah River soil studies and from 474.5 nm to 994.5 nm for the Savannah River mixed waste surrogate studies; the resolution is approximately 0.5 nm/pixel.

Radiation from inside the plasma hearth was also monitored by a CCD Emission Spectroscopy system. The CCD Emission Spectroscopy system consists primarily of a UV-sensitive CCD detector, a 0.5-m monochromator with a triple grating turret, a UV fiber optic cable, a UV pickup lens for collecting emission, and a computer for control, data acquisition, and data analysis. The pickup optics were back-aligned with a white light source to view about a 2.5-cm (1 in.) diameter area in the center of the crucible—considerably larger than the arc attachment point which was expected to occasionally be in the field of view. Spectra were primarily recorded in sets of 500 to 10,000 using the 1200-groove/mm grating with a shutter exposure time of 10 msec. With these settings, the bandwidth of the monochromator was about 45 nm in the UV and slightly more than 30 nm in the infrared. Selected spectral regions from 200 nm to 1100 nm were recorded; most of the data collected was in the UV.

These two emission spectroscopy systems provided complementary data; the CCD system was able to provide spectra with sufficient resolution in selected portions of the near-UV to near-IR to identify the atomic or molecular emitter, while the SPDA system could monitor the global emission changes over almost the entire visible and near-IR wavelengths. Emission spectra recorded by the CCD system permit the time-dependent intensities of a large

number of species to be followed over the course of several minutes, while the spectra recorded by the SPDA system enable time histories spanning an entire day's operation.

Results: Vitrification of Savannah River Soil

The study of volatile emissions was conducted in conjunction with a study to demonstrate the feasibility of both *ex situ* and *in situ* vitrification of contaminated soil with a plasma torch. Dolomitic lime powder was added as a vitrifying agent. The results of these soil vitrification studies have been reported elsewhere.^{7,8}

On January 23 and 24, 1995, the DIAL Silicon Photodiode Array (SPDA) emission spectroscopy system was used to monitor emissions inside the primary chamber of DIAL's PT-150 Vitrification System during vitrification experiments performed on Savannah River soil/lime mixtures. The soil/lime sample was put into the crucible prior to the beginning of each test and no additional sample was added during the test. For each test, 5.4 kg (12 lbs) of Savannah River soil and 0.65 kg (23 oz) of powdered lime were used. On January 23, the lime was uniformly mixed with the Savannah River soil in order to mimic *ex situ* vitrification; on January 24, all the lime was positioned in one pie-shaped sector of the crucible and covered with a 4-cm (1.5-in.) thick layer of soil in order to mimic *in situ* vitrification. For all the Savannah River soil vitrification tests, the plasma torch was operated a few inches above the melt for 10 - 15 minutes to allow the sample to soften, and then the torch was lowered to a distance of approximately 5 cm (2 in.) above the surface of the melt. The duration of each test was about 45 - 60 minutes of torch operation. For the January 23 test, the position of the plasma torch was fixed with no lateral movement; for the January 24 test, the torch moved only laterally.

Representative emission spectra are presented in Figure 3-1. The emission spectra consist of transitions from a small number of gas-phase atomic species and from calcium-containing molecular species superimposed on a blackbody continuum. A casual inspection of the figure shows markedly different emission spectra. A catalog of the observed atomic and molecular transitions identified was prepared. The Cu, N and O are probably associated with operation of the plasma torch and not with vitrification of the soil. Figure 3-2(a) is essentially blackbody emission with weak emission from Na, CaOH, Li, K, O and N. The valley near 945 nm is associated with absorption by the fiber optic cable used to transfer the signal from the plasma torch to the SPDA data acquisition system. In Figure 3-1(b), the blackbody emission is still very prominent, but is less intense than in Figure 3-1(a); however, the intensity of the Na, CaOH, Li and K transitions are relatively much more intense than in Figure 3-1(a). Emission from Ca^+ ion is present, but weak in Figure 3-1(b). The sensitive

lines of Ca do not lie in the spectral region monitored, and, hence, were not observed. Neutral calcium atoms are expected whenever Ca^+ ions are present in the primary plasma chamber. Since the SPDA system only monitors a small portion of the primary chamber and since we did not image, but used a simple pickup lens system, we are unable to ascertain which and how much of the changes in the emission spectra are indicative of changes occurring generally in the primary chamber and which are specific to changes occurring only in vicinity of the limited field-of-view (due to changes in the position of the plasma torch, etc.). In Figure 3-1(c), the blackbody intensity has decreased; the intensities of the alkali metals and of Ca^+ are comparable to that in Figure 3-1(b); but the intensity of the CaOH transitions has greatly increased. Note that the scale in Figure 3-1(d) [and Figure 3-1(e)] is different from that used for Figures 3-1(a) to 3-1(c). In Figure 3-1(d), the intensities of the alkali metals, of Ca^+ , and of the blackbody emission are comparable to those in Figure 3-1(c), but the intensity of CaOH greatly increased and the vibrational-electronic sequence bands of the $A^1\Sigma^+ \rightarrow X^1\Sigma^+$ system of CaO are clearly present. The increase in intensity at the short wavelength end of the spectrum is due to another CaOH vibrational-electronic band that is just outside the wavelength region monitored. In some of the emission spectra recorded on January 23, the CaOH peak exceeded the maximum resolvable SPDA intensity (using the shortest possible exposure time--5.14 msec). Thus, the emission intensity, and by extension the amount of gas-phase CaOH, was at times relatively large. Figure 3-1(e) presents a spectrum in which the CaOH and CaO bands are so intense that at this resolution, the alkali transitions are completely obscured as is one of the Ca^+ transitions.

In general, although there was some variation in intensity from one emission spectrum to the next consecutive emission spectrum, the overall pattern tended to persist for long periods of time. Figures 3-1(b) and 3-1(d) are the patterns that dominated these tests. Change, when it did occur, could be very rapid. Figures 3-1(a) to 3-1(d) illustrate the rapidity with which change can occur--these four spectra are consecutive spectra taken over a span of 20 seconds. Thus, the production of emitting species is not necessarily continuous, but can occur in bursts. Therefore, time resolution is an important requirement for monitoring emitting species in the primary chamber.

The fact that the atomic and molecular emissions are relatively narrow implies that the emitting species are in the gas-phase. There is a finite probability that because of gas flow through the chamber, the gaseous species may exit the primary chamber in the gas-phase rather than in the melt. The prevalence of alkali metal species in these emission spectra suggests that significant amounts of alkali can potentially exit the primary chamber in the gas phase.

rather than in the melt. This is a concern because of the presence of significant amounts of the alkali Cs-137 in the actual waste streams to be processed.

Additional insight may be gained by considering how the pattern of the emission spectra changed with time. The temporal patterns for Li and Na are qualitatively similar to that of K; this is as expected since all of these are alkali metals and consequently have similar chemical and physical properties. The temporal pattern of CaO is comparable to that of CaOH, but the intensity of CaO is often significantly less than that of CaOH. On January 23 when the lime was uniformly mixed with the soil in order to simulate *ex situ* vitrification, emission from Ca^+ was observed intermittently through out the test, and the intensity was never very large. On January 24 when the lime was segregated into one section of the crucible in order to simulate *in situ* vitrification, no Ca^+ emission was initially observed, although it was consistently observed in the latter portions of the test. These observations suggest that for *in situ* soil vitrification, the presence/absence of Ca/ Ca^+ emission when lime is used as the vitrifying agent can be used as an indicator of the presence/absence of vitrifying agent in the vicinity of the plasma torch; the presence of vitrifying agent is important because if it is not well mixed with the soil a satisfactory glass is not formed.

The plasma torch was started on Ar and then switched to air. On January 23, the first recorded emission spectrum shows the typical Ar plasma emission lines. The second spectrum recorded consists of a blackbody curve with emission from Na, CaOH, K, N, and O evident. Thus, these emitting species are present from the very beginning of the test. Although the emission patterns were similar, the sequence of emission spectra was very different on January 24 than that observed on January 23. The difference is related to the fact that on January 23, an effort was made to uniformly distribute the lime throughout the soil (the flashes of very intense CaOH intensity implies that these efforts were not completely successful), while on January 24, the lime was confined to one pie-shaped region of the crucible and covered with a layer of soil. (The soil/lime configuration used on January 24th was found not to produce a satisfactory vitrification product since the lime did not efficiently mix with the soil when heated.)

Results: Vitrification Of A Savannah River Mixed Waste Surrogate

A more extensive series of tests were performed on a mixed waste surrogate on March 6 to 9, 1995 in conjunction with a test to determine the durability of 31 different refractory materials when exposed to molten vitrification slag under plasma hearth operating conditions.⁹

On March 6, the experiment began with 0.9 kg (2 lbs) of surrogate inside the crucible and an additional 13.1 kg (28.95 lbs.) of Savannah River surrogate was fed into the DIAL vitrification system during the course of the day. The plasma arc was quickly turned off on March 6, thermally shocking the refractory samples. On March 7, the plasma torch was quickly turned on, the slag was remelted and maintained in a liquid state for several hours by the plasma arc, and then the plasma torch was quickly turned off. The same sample was used on March 7 as on March 6; no additional surrogate was added to the crucible. On March 8, experiments were performed on a new crucible with new refractory samples; during this day, 13.05 kg (28.8 lbs) of surrogate were added to the crucible that initially contained 0.9 kg (2 lbs) of surrogate. Again the plasma arc was quickly turned off on March 8. On March 9, an experiment was performed using the March 6 crucible/sample. On March 6 and 7, the SPDA and TCP system simultaneously shared one optical port, and the CCD Emission Spectroscopy system utilized a second optical port. Although both ports were purged with nitrogen, the port used by the CCD system quickly became covered with dust particles, although the problem was much less severe for the port used by TCP and SPDA. On March 8 and 9, SPDA, TCP, and the CCD systems shared the same port. It should be emphasized that during these Savannah River mixed waste surrogate/refractory tests the plasma torch was operated without rotating or stirring the vitrification crucible, and the torch movement was deliberately not automated to move systematically across the surface of the melt. This was done so that the heating of the different refractory samples would be consistent through out these tests.

Results show that the plasma torch melted surrogate waste exhibits an emission spectra rich in gas phase atomic and diatomic species superimposed on a blackbody continuum. In general, the atomic emission tended to be stronger than the molecular emission. Emission lines were positively identified for Al, C, Ca, Ca⁺, Cd, CN, Cu, Cr, Cs, Fe, K, Li, N, Na, O, Rb and Si. Tentatively identified were also Ni lines. Intermittent spectral features have been tentatively identified as N₂. A catalog was prepared of the definitely assigned spectral lines, although it cannot be considered an inclusive list since not all of the spectral regions were recorded with the CCD system. Spectral assignments were made primarily based upon the spectra recorded with the CCD emission spectroscopy system because of its higher resolution. Figure 3-2 illustrates example spectra recorded with the CCD system. Below 400 nm, assigned spectral lines included aluminum, ionized calcium, CN, copper, lead and silicon. No attempt was made to assign the multitude of iron and possibly nickel and titanium lines in the near-UV. Higher spectral resolution would be needed for unambiguous assignments in this congested spectral region.

The primary alkali doublets are all strong, broad and self-reversed, indicating relatively large alkali atom densities in the gas above the melt. In the visible region, the sodium D-line is particularly broad and deeply self-reversed; the full-width-at-half-maximum is about 2 nm. Other strong lines in the visible include CN, calcium, chromium, copper and iron. The emission spectra showed moderate levels of fluctuations so the most definite assignments are made from a single time-resolved spectrum that allows for a check of the self-consistency of the intensities versus line strengths. Spectra exhibiting single lines of an element were problematic for definite assignment because of the multitude of possible lines. In the near-infrared region the emission spectra consists of strong lines that can be unambiguously assigned to atomic lines of carbon, nitrogen, and oxygen and the alkali atom lines due to lithium, sodium, potassium, rubidium, cesium, singly ionized calcium and copper.

One ingredient in the mix from which no emissions were observed was cerium, a surrogate for transuranic elements. The prominent emissions for Ce are relatively weak and occur in complicated spectral regions so it may be that Ce is present in the gas phase but there is no evidence for that from the emission spectra.

Figure 3-3 illustrates the emission patterns in the visible and near-infrared regions monitored by the SPDA system. Figure 3-3(a) was one of the very first SPDA emission spectra recorded on March 6. Atomic transitions from cesium, lithium, nitrogen, oxygen, and potassium are readily apparent superimposed on a blackbody continuum. The atomic sodium D-line is overlapped by an as yet unidentified molecular transition. Figure 3-3(b) was recorded after most (but not all) of the surrogate had been added to the crucible; the pattern is very similar to that of Figure 3-3(a), but the intensities are significantly higher. In Figure 3-3(c), the blackbody continuum is relatively more intense and the molecular transitions are significantly less prominent.

On March 7, no additional sample was added, but instead the sample of March 6 was reheated by the plasma torch. Figure 3-3(d) documents a brief event on March 7 that occurred about 23 minutes into the test; during this event which lasted for about a minute, sodium and the molecular species dominated the emission. The species responsible for these prominent molecular electronic-vibrational transitions have not yet been identified; the observed transitions are not those of the most likely candidate species—the diatomic oxides of Al, Ce, Cr, Cu, Fe, Ni, Pb or Si. The fact that sodium and lithium are significantly volatilized relative to potassium and cesium implies that the melt was not homogeneous. Subsequent examination of cross sections of the vitrified sample reveal that the melt in the unstirred crucible cooled into easily distinguishable phases. It is likely that a phase separation occurred during

cooling on March 6 and that the event on March 7 occurred when the plasma torch melted an inhomogeneous region of the vitrified glass. Vitrification of mixed wastes will not in general involve reheating the vitrified product obtained; however, because the feedstream is not homogeneous, sudden bursts of emission can be expected.

Because a large number of emission spectra were recorded over the course of these tests, it was possible to extract information about the time dependence of the intensities of different emitting species and attempt to relate these intensity changes to operation of the plasma arc. An understanding of the interplay between emission intensity and operating conditions may lead to process control improvements based on these observations. The wavelength-dependent contribution of the blackbody continuum was determined for each SPDA emission spectrum and subtracted out to yield intensities associated with a single emitting species. Figure 3-4 show an example time history of Cs 852.1-nm transition and of the O 777-nm triplet which was recorded on March 6, 1995. The time histories of the alkali metals are qualitatively similar, except Na; the different alkali metals may not have been uniformly distributed throughout the surrogate batch.

How did the emission intensity of different species change with time as surrogate material was fed into the plasma hearth? At the beginning of the experiment on March 6, 1995, the CCD Emission Spectroscopy system was centered at 396 nm, and emission spectra were recorded as rapidly as possible to view the onset of emission. Figure 3-5 illustrates the results. Generally the intensities of lines from different species increased proportionally with time, and no sudden appearance or disappearance of particular atomic lines was seen.

For the CCD system, the largest variations in relative intensities were observed in the 400 to 450-nm region, with large changes in the relative intensities of calcium, iron, and chromium. Figure 3-6 presents one data set recorded in this spectral region on March 8 at 13:00 over a period of about one minute. During this time period, two batches of four briquettes each were added to the melt, roughly one batch every 30 seconds. Spikes in Fe and Ca emission line intensities were observed that seemed to be correlated with slight dips in the Cr line intensities. Overall Fe and Ca lines more than doubled in intensity while Cr, CN, and background emissions were fairly constant. The near constant blackbody background intensity during this time suggests that the melt temperature in the field of view was nearly constant. Moreover, the constancy of the blackbody background for this time period implies that the blackbody contribution (if any) from the plasma arc was constant over this time period.

The constant background in Figure 3-6 argues against a shift in the arc attachment being the source of the sharp increase in Ca and Fe line intensities. The most likely explanation is that the sharp spike of Fe and Ca line intensities is from the volatile emission released by the bubbling action. The SPDA system observed that when the plasma arc was turned off, that emission from atomic and diatomic species could no longer be observed, leaving only a weaker blackbody emission. If these species were being volatilized simply by evaporation from the hot glass surface, then emission should have continued after the torch was shut off, since the glass and the crucible continued to be hot for quite some time (tens of minutes) afterward. Thus this observation also supports the idea that boiling in the arc attachment area is associated with volatilization of species.

Norton has reported that the video monitor indicated that when the surrogate briquettes landed in the molten glass, they floated.¹⁰ After a few seconds, the briquettes appeared to "sweat"—beads of what appear to be a white liquid forms on the surface; this white liquid may be the PVC in the briquettes melting. Also luminous jets appeared to shoot from the surface of the briquette; this may be due to PVC and/or other organic substances in the surrogate vaporizing and decomposing, forming flammable gases that escape in the form of jets and then burn. [According to Norton (1995), this type of behavior is fairly common when many organic solids (such as coal, wood, plastics, etc.) burn: the heat from the fire causes the particle to heat up; and the heat causes the organic materials to pyrolyze and form flammable gases, which then burn in the gas phase.] Where the torch directly impinged on the glass surface, the glass glowed brightly; bubbling and vigorous circulation was also observed in this area. The circulation of the molten glass caused by the rising bubbles seemed to keep the surface clear in this area. The boiling appears to be associated with the passage of current; the boiling action immediately stopped when the current was cut off. Lindner (1995) has speculated that the boiling may be caused by the carrier gas flowing out of the plasma torch and agitating the molten surface. According to Norton, the plasma arc appeared to attach to the glass surface over a broad area; a single, very bright cathode spot was not observed as when graphite is the cathode. [When the pieces of refractory being tested broke off and floated on the surface of the glass, the refractory floaters were preferred arc attachment locations if they drifted into the attachment region. In this case, very bright cathode spots could be observed on the floating refractory, together with rapid erosion of the solid refractory.] The glass surface outside the arc attachment area appeared black on the video monitor as if some dark scum were covering the surface of the glass. Occasionally the dark scum seemed to have the appearance of a granular solid. Perhaps this dark scum acted as a "cold top", "sealing" off the glass that is not directly

heated and only permitting species to volatilize in the region of the arc attachment.

Besides simply monitoring lines for relative amounts of volatile species, the emission spectra may also be used as a temperature monitor. This could be multi-wavelength pyrometer-type measurement using the clear background regions of the spectrum to measure the melt temperature. Or, using line intensity ratios a measure could be made of the volatile gas temperature. In the visible and near-IR wavelengths, the atomic nitrogen lines span enough of a range in the upper state energy for a reasonable measure of excitation temperature. The measured temperature (7320 ± 2210 K) indicates that the nitrogen atoms are quite 'hot'. Here the estimate of the temperature uncertainty is based upon a linear least squares fit. The statistical uncertainty is of the same order as the inherent accuracy of such measurement; the measurement is based upon the Einstein A factors which have an uncertainty of $\pm 25\%$ for these lines. The spectra also indicate that calcium lines may provide a good monitor of temperature through a Saha-Boltzmann calculation since both neutral and singly ionized lines are strong and consistently present in the 390 to 450-nm wavelength region.

Conclusions

These volatilization studies support the use of emission spectroscopy for monitoring the gas phase emissions above a plasma torch melt process. With further development work, the resulting information might be used to optimize process control in order to minimize downstream treatment for producing acceptable off-gases. Emission spectroscopy is relatively inexpensive, robust and requires little optical access, a simple fiber port will suffice, and so should be considered for a real-time monitor of the torch arc itself or the gas phase species above the melt. Such a monitor would require relatively simple analysis with appropriate choice of spectral lines. A list was prepared of recommended lines for real-time monitoring of the presence of melt volatile species based upon line strength, lack of overlapping lines, unambiguous assignment, etc.

Project Status

The emission spectroscopy tasks were discontinued in March 1995, and effort has been redirected.

Project Significance

Emission spectroscopy is a classical technique for plasma study and the measurement of plasma properties is part of that should remain in the DIAL's arsenal for experimental measurements.

FY 96 Plans

An emission spectroscopy system is available as a field ready instrument for measurements as desired. Moreover, this technique is now being used to monitor the torch wear and to provide warning of the torch electrode failure.

References

1. Bauman, L.E., et al. 1995. Emission spectroscopy studies of volatile species produced by plasma arc vitrification of a mixed waste surrogate. Proceedings of the *International Symposium on Environmental Technologies: Plasma Systems and Applications*, October 8-11, 1995, Atlanta, GA. pp. 505-515.
2. Monts, D.L., et al. 1995. Identification and characterization of volatile species produced by plasma arc vitrification of mixed waste surrogates. Extended Abstracts of the *Emerging Technologies in Hazardous Waste Management VII Conference*, September 17-20, 1995, Atlanta, GA, pp. 5-8.
3. Cook, R.L., et al. 1994. *Initial report for plasma arc centrifugal treatment system*. Western Environmental Technology Office, MSE, Butte, Montana, October 17-21, 1994. DIAL Trip Report 94-3.
4. Jang, P.R., et al. 1995. Pyrometry studies of a mixed waste vitrification plasma arc centrifugal treatment system. Proceedings of the *Third Biennial Mixed Waste Symposium*, August 7-11, Baltimore, MD, pp. 8.2.1-8.2.9.
5. Cook, R.L., et al. 1994. *Initial report on stir melter glass melter*. Environmental Systems Engineering, Clemson University, July 25-29, 1994. DIAL Trip Report 94-1.
6. Jang, P.R., et al. 1995. Diagnostic studies of a mixed waste vitrification glass melter. Proceedings of the *1995 International Incineration Conference*, May 8-12, 1995, Bellevue, WA, pp. 521-526.
7. Cicero, C.A., et al. 1995. Vitrification of Savannah River contaminated soils. Extended Abstracts of the *Emerging Technologies in Hazardous Waste Management VII Conference*, September 17-20, 1995, Atlanta, GA, pp. 616-618.
8. Kielpinski, A.L., et al. 1995. Development of plasma vitrification technology for contaminated soil at the Savannah River site. Proceedings of *Waste Management '95 Symposium*, February 26-March 2, 1995, Tucson, AZ, paper 37-5.
9. Etheridge, J.A., et al. 1995. *Final report for refractory lifetime testing for*

Westinghouse Savannah River Company. March 6-9, 1995. DIAL Trip Report 95-3.

10. Norton, O.P. 1995. Private communication.

Figure 3-1. Soil vitrification emission spectra recorded by the SPDA Emission Spectroscopy system on January 23, 1995.

Figure 3-2. Mixed waste surrogate vitrification spectra recorded by the CCD Emission Spectroscopy system at three different times: March 8, 1995 at approximately 1:03 and 1:13 pm and March 9, 1995.

Figure 3-3. Mixed waste surrogate vitrification emission spectra recorded by the SPDA Emission Spectroscopy system on March 6 and 7, 1995.

Figure 3-4. Comparison as a function of time of the background-corrected SPDA emission intensities of Cs and O with surface temperature (in K), torch height (in cm), and torch current (in amps) for the March 6 test.

Figure 3-5. Three dimensional time display of the CCD-recorded emission spectra during the initial melt on March 6, 1995. The 1024 pixels cover a wavelength range of 376 to 417 nm. Every one hundredth spectrum (frame) from the two thousand spectra recorded over about four minutes is plotted.

Figure 3-6. Variations in atomic line intensities with time over about a period of one minute on March 8, 1995 at 1:00 p.m.

4 Laser Doppler Velocimetry

W. P. Okhuysen and O. P. Norton

Introduction

LDV stands for laser Doppler velocimetry, which is a nonintrusive, laser-based method for measuring flow velocity. For a number of years, DIAL has maintained the capability of routinely making LDV measurements, both in our own test facilities and at other facilities.

The FY 95 milestones for this subtask were planned with the intention of developing an LDV system for continuous, on-line process flow measurements. Due to the perceived lack of a market for such an instrument, this development effort was canceled at the direction of Al Tardiff, our DOE program manager.

During this past fiscal year, we have made a number of measurements with our existing LDV system. These measurements include a velocity survey of a plasma torch in the DIAL laboratory and velocity measurements in a torch off-gas system during a series of tests performed for Westinghouse Savannah River Company (WSRC). Typical results from these tests are given in the next section.

Work Accomplished

The work accomplished during FY 95 primarily consists of three sets of measurements.

WETO Facility, Operated by MSE, Inc., Butte, Montana

LDV measurements were made in the off-gas pipe leading from the PACT-6 system to the secondary combustor and the downstream gas cleanup system during the test series designated as 95-75HOUR-1 which lasted from October 17 - 20, 1994. Although these tests actually occurred in FY 95, we were able to include a summary of the results from this test in the annual report for the previous year.¹ Thus, these measurements will not be discussed further in this year's annual report. Further details of these measurements can be found in the trip report.²

Velocity Survey of a Plasma Torch

Among other test facilities, DIAL operates a model PT-50 plasma torch manufactured by Plasma Energy Corporation (PEC). Our original research

plan called for using our advanced diagnostic capabilities to improve our fundamental understanding of the physics of the torch. Therefore, we undertook to map the velocity field of the plasma as it flows from the end of the torch and impinges on a graphite billet. This billet serves as the cathode for the flow of current; the torch was operated in the transferred arc mode during these tests.

The results of some preliminary measurements were reported last year.¹ During these preliminary measurements, the gas delivery pressure to the torch varied while the velocity measurements were being made. The gas delivery pressure is cycled automatically while the torch is operated to move the arc attachment point and increase electrode life. For the current measurements, this pressure cycling was interrupted, and thus the torch operating conditions were held constant while the measurements were being made. We chose two different values of the gas supply pressure (53 psi and 22 psi) and two different values for the torch current (125 A and 175 A), which established a 2 x 2 test matrix. For each of these four possible combinations of gas pressure and current, we mapped the plasma velocity between the torch tip and the graphite cathode. For all of these measurements, the torch gas was nitrogen and the torch tip was five inches from the graphite cathode. Alumina (aluminum oxide) particles were injected into the plasma in order to provide the necessary light scattering particles for LDV.

Figure 4-1 shows the velocity field as we mapped it for one test condition (a nitrogen supply pressure of 53 psi and a current of 175 A). The circles indicate the axial component of the velocity (the component parallel to the torch axis, toward the graphite cathode) and the triangles indicate the swirl, or theta, velocity component. With the distance from torch tip to graphite fixed at five inches, we measured velocity profiles (variation of velocity across the diameter of the jet) one, two, three and four inches from the torch tip. When placed in sequence, as in Figure 4-1, these profiles show clearly the flow patterns between the torch tip and the graphite cathode.

A more complete description of these measurements can be found in the extended abstract of a paper presented at the ACS I&EC Division meeting in Atlanta.³ In addition, we plan to present a paper on these measurements at the upcoming AIAA Plasmadynamics and Lasers meeting in New Orleans.⁴

Off-gas Measurements During Refractory Testing for WSRC

The Diagnostic Instrumentation and Analysis Laboratory (DIAL) performed a series of tests at the behest of Westinghouse Savannah River Company (WSRC). In these tests, surrogate waste materials were vitrified in a PT-150 plasma torch system owned and operated by DIAL. The primary purpose

of these tests was to test ceramic refractory samples supplied by WSRC in the plasma torch environment.

The test program began in December 1994 with a shakedown run to test the plasma torch and the associated instrumentation. These shakedown tests continued throughout January and February 1995. The actual tests were performed on March 6 - 9, 1995.

The PT-150 plasma torch was contained within a vessel constructed by DIAL. The off-gases from the torch and the surrogate wastes were collected and piped to DIAL's combustion test stand, and from there flowed to the exhaust stack. In between the plasma torch containment vessel and the combustion test stand, the off-gases flowed first through a section of eight-inch pipe, equipped with optical access ports for the FTIR and LIBS instruments. Then, the off-gases entered a three-inch pipe, turned upward and across into the room where the combustion test stand is located. At the LDV measurement location, the pipe diameter was reduced to two inches in order to increase the flow velocity. This section of two-inch pipe also served as the access location for EPA Method 5 particulate measurements.

Typical results from these measurements are shown in Figures 4-2 and 4-3. Figure 4-2 shows the mean velocity, recorded at approximately the center-line of the pipe, as a function of time for the entire test of March 6, 1995. Several features of the flow are apparent from this figure. First, the velocity builds up slowly during the first two hours of torch operation. This is apparently the time required for the system (primarily the refractory lining of the torch containment vessel) to reach an equilibrium temperature. Second, the oscillations visible in the figure show the cycling in the gas supply pressure to the torch. Plasma torches manufactured by PEC, such as this one, use a periodic variation of the gas supply pressure to move the arc attachment location within the hollow rear electrode and thus evenly distribute the wear. Finally, several irregularities visible in the figure are clearly correlated with events noted in the operator's logbook. The velocity spike labeled "A" in Figure 4-2 exactly corresponds with a logbook entry that a window was removed for cleaning upstream of the LDV measurement location. An induced draft fan keeps the system under negative pressure, so removing a window causes an influx of room air and increases the gas velocity downstream.

Since the LDV system registers the passage of individual particles, it is possible to estimate particle number density from the information supplied by the LDV instrument. Figure 4-3 shows these estimates for the test on March 6, 1995. Further details, as well as velocity and particle data for the other days of testing, can be found in a special report issued by DIAL for these tests.⁵ This

report also discusses how the LDV off-gas velocity measurements were used to perform a mass balance on the system and estimate the air infiltration rate.

Project Status

Further development of the LDV system is on hold. The current system is field-ready, and is available for use, both at DIAL and on field trips.

Project Significance

LDV is a laser-based, nonintrusive method for measuring flow velocity. It can be used under very hostile conditions, such as in combustion systems and in plasma arcs where other, intrusive velocity measurement devices could not survive.

Although the information provided by this system is not perceived to be useful during routine system operation, such data may be useful earlier in the development process, as a means of studying the flow patterns within a system. In particular, the particle count information can be used to identify the operating conditions that produce excessive particles in the off-gas system.

FY 96 Plans

Further development work on this project has been canceled. Laser Doppler velocimetry will not exist as a separate subtask in FY 96. Instead, our current capability to make LDV measurements will be maintained and reported under FY 96 *Task 9 On-site Field Measurements and Analysis*. We are ready to make LDV measurements as required, both in DIAL's laboratories and "on the road".

One trip that is already being scheduled is a trip to make measurements on the Transportable Vitrification System (TVS) being developed by WSRC. WSRC has asked DIAL to perform a series of measurements on the TVS during shakedown testing with surrogates, and LDV measurements are among the measurements specifically requested by WSRC. This trip is tentatively scheduled during December 1995.

In addition, we are actively marketing our LDV measurement capabilities as a service we can provide to industry. Discussions are ongoing with several potential customers. This is a technology transfer activity, and is discussed further in the *Industrial Affiliates/Marketing* chapter of this report.

References

1. Shepard, W.S., et al. December 1994. *Application of modern diagnostic methods to environmental improvement*. Mississippi State University:

Diagnostic Instrumentation and Analysis Laboratory. DIAL 10575 FY 94 Annual.

2. Cook, R.L., et al. October 1994. *Plasma arc centrifugal treatment system, Western Environmental Technology Office, MSE, Butte, Montana*. DIAL Trip Report 94-3.
3. Norton, O.P. and Okhuysen, W.P. September 1995. *Laser Doppler velocity measurements in a transferred arc plasma torch*. Paper read at the ACS, I&EC Division Special Symposium on Emerging Technologies in Hazardous Waste Management, Atlanta, GA.
4. Norton, O.P. and Okhuysen, W.P. *Mapping of velocity fields in the exit plume of a plasma torch*. Paper submitted for presentation at the 27th AIAA Plasmadynamics and Lasers Conference, June 18-20, 1996, New Orleans, LA.
5. Etheridge, J.A., et al. March 1995. *Refractory lifetime testing for Westinghouse Savannah River Company*. DIAL 10575 TR 95-3.

Figure 4-1. A map of the velocity field between the tip of the PT-50 plasma torch and the graphite billet cathode. These measurements were made at the high pressure, high current condition of the test matrix. The nitrogen supply pressure to the torch was approximately 53 psi and the current was approximately 175 A. The circles indicate the axial (Z) velocity component and the triangles the swirl (θ) velocity component. The torch tip was positioned 5 inches from the graphite, and the different velocity profiles were made at different distances from the torch tip: A. 4 inches below the torch tip and 1 inch above the graphite; B. 3 inches below the torch tip and 2 inches above the graphite; C. 2 inches below the torch tip and 3 inches above the graphite; D. 1 inch below the torch tip and 4 inches above the graphite.

Figure 4-2. Mean velocity recorded during the test on March 6, 1995.

The dashed lines show the time interval during which the torch was energized. The periodic oscillations in the velocity reflect the variation in the gas flow rate to the torch. The gas supply pressure (and thus the flow rate) is deliberately cycled in order to move the arc attachment point in the hollow rear electrode and thus prolong electrode life. The gradual increase in velocity over the first 2 hours reflects the time required for the torch vessel and off-gas piping to come up to temperature.

The velocity spike labeled "A" coincides with the removal for cleaning of a window upstream of our measurement location. An induced draft fan keeps the torch vessel and the off-gas piping system under a slight vacuum, so when a colleague upstream of us needs to clean a window, the resulting inrush of air causes the velocity we measure to increase. For similar reasons, any leaks in the vessel or off-gas piping will cause the velocity to increase. The drop in velocity labeled "B" coincides with a log entry that a leak had been discovered and plugged where some thermocouple wires entered the vessel. The velocity spike labeled "C" cannot presently be explained.

Figure 4-3. Particle number density for the same time period as Figure 4-2. The spike labeled "A" cannot presently be explained.

5 Coherent Anti-Stokes Raman Spectroscopy

F. Y. Yueh and J. P. Singh

Introduction

Coherent anti-Stokes Raman spectroscopy (CARS) is a laser-based optical technique. It has been successfully applied to many practical combustion environments.¹⁻⁵ The CARS technique involves the use of two narrow band laser beams at pump frequency ω_1 and a broadband dye laser beam at Stokes frequency ω_2 . The three beams are phase-matched, and focussed to the test medium by a lens where the laser-like CARS signal is generated. The CARS signal occurs at the anti-Stoke frequency $\omega_3 = 2\omega_1 - \omega_2$ and is generated by a nonlinear process involving the third-order electric susceptibility $\chi^{(3)}$ of the medium. Since the $\chi^{(3)}$ depends on temperature and density of the test species, the CARS spectral shape is sensitive to those two parameters. Therefore, temperature and species concentration information can be extracted from a CARS spectrum by fitting the spectral shape. In a plasma field, CARS can provide temperature profiles across the plasma arc at various distances from the torch collimator. CARS measurements can provide both vibrational and rotational temperatures that will give an indication of the existence of thermal equilibrium in the plasma.⁶

Work Performed

CARS measurements were performed in DIAL's PT-50 plasma torch. The CARS laser beams were aligned on the south side of the torch chamber. The experimental setup for the measurements is shown in Figure 5-1. The details of the mobile CARS system is described elsewhere.⁷ To obtain better spatial resolution, a 30-cm focal length quartz lens was mounted inside the plasma torch chamber to focus the laser beams to the test point. All the measurements were performed with the arc length of 3.8 inches. The torch was operated on nitrogen. The single shot N_2 CARS spectra were recorded at different locations. The attempts to record the spectrum from the center of the arc were unsuccessful due to the insufficient laser power and also the phase-matching problem in the high density plasma. Most of the measurements were performed ~1 cm away from the arc center by shifting the arc eastward.

Study of the dependence of temperature on torch conditions continued after the laser cooler and OMA detector were repaired. The single-shot CARS temperature measurements were made under various torch operating conditions. The measurements were repeated at different arc locations. To extract accurate temperatures from the CARS torch data, an accurate theoretical model was necessary. A nonlinear least squares fitting program and a quick-fit technique were developed to analyze multiplex CARS spectra.^{6,8,9} To reduced the analysis time, a library of CARS spectra is generally pregenerated for later analysis.

The spectral shape fitting method and quick-fit method have both been used to analyze the CARS data recorded from an N₂ plasma. Noise can also greatly affect the reliability of CARS temperature fit. Due to the poor signal-to-noise (S/N) ratio, the smoothing technique was applied in most of the collected spectra in the quickfit analysis. The smoothing might modify the band-shape and peak height and cause some error in inferred temperature. A spectrum selection program was used to select the reasonable S/N data to be analyzed. The inferred temperatures from the spectral shape fitting method and the quick fitting methods were compared. Figure 5-2 shows a single shot CARS torch data. The inferred temperatures from the spectral shape fitting and a quick fit method are 2340 and 2320 K, respectively. The difference in the inferred temperatures was less than 5% for the data which have reasonably good S/N ratio. Since the quick fit techniques are more sensitive to the noise, the average inferred temperatures from various quickfit methods are generally lower than the spectral shape fitting.

N₂ CARS torch data were taken in the plasma torch at various torch operating currents. The data were collected from the different distances from the electrode. Figure 5-3 shows the results of inferred temperatures from a set of single shot CARS data. The variation of the temperatures is due to the fluctuation of the gas medium. Since the CARS measurement point was close to the edge of the arc to get the reasonable S/N ratio data, the inferred temperature is actually a spatial average of the temperature in the measurement volume. To obtain a representative result from the data in various currents, the inferred temperature distribution for each current was calculated. Figure 5-4 shows the data recorded at one inch below the electrode. The average inferred temperatures are lower than expected. This might be because the high temperature data have poor S/N ratio and are automatically excluded from the analysis. When the current increased from 125 to 150 A, the averaged temperature drop a little. But, the standard deviation (SD) of the inferred temperature is also reduced. It indicates a more confined plasma at that location and the measurement volume is a little outside the arc. When the current increased to 185 A, the average temperature increased and the SD of the inferred temperature

is further reduced. The results show the plasma is hotter and more confined under a higher torch operation current at this measurement point. Figure 5-5 shows the CARS data recorded at 2.25 and 2.75 inches away from the electrode. The measurements were made closer to the graphite work pieces. In these locations, the arc closest to the work piece diverges and the gas temperature is strongly affected by the arc attachment location. The inferred temperatures at these two measurement heights all show bimodal distribution. The average temperatures are close to the lower temperature. When the current increased, the separation of the two temperatures are more closer. The average temperature at the measuring height of 2.25 inches is closer to the colder temperature, while the average temperature at the measuring height of 2.75 inches is closer to the higher temperature.

Conclusions

CARS torch measurements were performed at different arc locations. The measurements were all performed away from the arc center due to the poor signal. The CARS system needs to be further improved to record the spectrum at the arc center. The quick-fit technique and spectral shape fitting were both used in the analysis. The quick-fit method has proved to be an effective way to analyze the single-shot CARS torch data. Since the temperatures within the probed volume in these measurements are consider too close to LTE, the single temperature model was used in the analysis. The results from measurements under different torch operating currents show the plasma is more confined at the higher current. The temperatures near the work pieces show a bimodal distribution.

Project Status

CARS is a field deployable instrumentation system for measurement of local temperature and temperature profile. No further development will take place in the near future.

Project Significance

CARS has been used to measure temperature at different locations of the arc which is an important parameter to evaluate the performance of a plasma torch.

FY 96 Plans

CARS temperature measurements will be made in the plasma torches, as requested.

References

1. Stenhouse, I.A., et al. 1979. *Appl. Opt.* 20:1178.
2. Klick, D.; Marko, K.A.; and Rimai, L. 1981. *Appl. Opt.* 20:1178.
3. Singh, J.P. and Yueh, F.Y. 1995. *Advances in multiphase flow*. A. Serizawa, T. Fukano and J. Batailla, eds. Elsevier, pp. 711.
4. Alden, M. and Wallin, S. 1985. *Appl. Opt.* 24:3434.
5. Beiting, E.J. *Appl. Opt.* 1986. 25:1684.
6. Yueh, F.Y. and Singh, J.P. 1994. 25th AIAA Plasmadynamics and Lasers Conference, AIAA 94-2429.
7. Singh, J.P., et al. 1992. *Appl. Spectrosc.* 46:1649.
8. Yueh, F.Y. and Beiting, E.J. 1986. *Comp. Phys. Commun.* 42:65.
9. Yueh, F.Y. and Beiting, E.J. 1988. *Appl. Opt.* 2:3233.

Figure 5-1. CARS torch measurement experimental setup.

Figure 2-2. Advisor-controller information flow.

Figure 5-2. Single shot CARS torch spectrum taken at 1 in. below the electrode and 10 mm away from the arc center.

Figure 5-3. Variation of inferred temperatures obtained from a set of CARS data.

Figure 5-4. Temperature distribution 1 in. below the electrode at various torch operation currents.

Figure 5-5. Temperature distribution under various torch operation currents. Measurement points are A) 2.25 in. and B) 2.75 in. below the electrode.

6 Pyrometer Systems

Ping-Rey Jang and David Monts

Introduction

The current pyrometer systems cannot make accurate emissivity-independent material temperature measurements in a plasma torch vitrification system because of spectral interference from the torch arc emission.¹ The main goal of this subtask is to identify the interference-free regions and develop a pyrometer system which can be utilized to measure the waste material temperature while the waste is being processed by the plasma torch.

Work Accomplished

From a previous plasma arc emission spectral study¹, we learned that a strong arc emission exists both in the UV and visible regions. The FTIR emission spectra show that there are some interference-free regions which are suitable for development of a low-cost pyrometer system. DIAL's FTIR systems were used recently to further investigate the spectral interference-free regions. Numerous torch experiments were carried out on DIAL's PT-50 and PT-150 torches. The FTIR's emission spectra (Figure 6-1) identifies several interference-free regions in a clean plasma torch (N₂, air) environment. The experiments shown in Figure 6-2 used the very general surrogate waste provided by WSRC. The interference-free regions are identified for this simulated waste stream. In addition to these experimental results, an atomic transition spectral interference library was compiled using the surrogate recipes provided by WSRC and ANL-West. Based on these experimental and theoretical results, a custom-made detector and appropriate optical filters were purchased for a two-color infrared pyrometer (TCIRP) system.

In order to increase the accuracy of temperature measurements with the TCIRP, the spectral response of the system must be taken into account in interpreting the detector output signals.² In particular, the detector output signal depends on the integral of the greybody function over the spectral response function. By utilizing DIAL's FTIR system, the spectral response for each purchased optical filter was measured. The results were then embedded into the developed on-line calculation software modules.

Since only one detector was purchased, a computer-controlled optical filter wheel was designed and fabricated, and the computer-control software

module was developed and merged with the TCIRP system software to obtain two different spectral response regions.

The development of a multi-fiber switcher (MFS) was completed and utilized by the Multi-Wavelength Pyrometer (MWP) system. This enables the MWP system to measure multiple target temperatures in near simultaneous mode. Figure 6-3 shows automated multiple target measurements with three distinct target spectra.

In addition to the system development task, DIAL's Two-Color Pyrometer (TCP) system was used to support refractory lifetime testing for WSRC.³ The melt temperatures were measured while the surrogate waste was being processed by the PT-150 torch. Figure 6-4 shows a typical measurement result from this test. Strong interference existed for the 1- μm TCP detector, and hence only the signal from the 2.17- μm detector was processed. The TCIRP system should eliminate this type of problem.

Project Status

In order to make accurate two-color pyrometry measurements, a temperature calibration source is required to measure the detector's blackbody response function.⁴ This last stage of the TCIRP system development was delayed due to the malfunction of DIAL's high temperature calibration source. This effort will be continued as soon as the calibration source is available.

Project Significance

Because of the strong spectral interference in the plasma torch vitrification system, current pyrometer systems cannot make accurate material temperature measurements. The significance of this project is to measure the waste material temperature while the waste is being processed by the plasma torch.

FY 96 Plans

The development of a pyrometer insertion tube for core temperature measurements in a joule-heated melter is scheduled for FY 96. Work will focus on constructing and deploying an insertion tube which will allow pyrometry measurements of the core area of the molten glass bath in a joule-heated melter. Several field measurements are also scheduled in FY 96. The pyrometer systems will be utilized to support temperature measurements at various facilities.

Reference

1. Shepard, W. S., et al. December 1994. *Application of modern diagnostic methods to environmental improvement*. Mississippi State University: Diagnostic Instrumentation and Analysis Laboratory. DIAL 10575 FY 94 Annual.
2. Jang, P.R.; Benton, R.D.; and Cook, R.L. June 1994. *Some observations on the spectral response in pyrometry*. AIAA 24th Plasmadynamics & Lasers Conference. AIAA 94-2445.
3. Etheridge, J.A., et al. March 1995. *Refractory lifetime testing for Westinghouse Savannah River Company*. DIAL 10575 TR 95-3.
4. Benton, R.D. and Jang, P.R. August 1993. Development of a multi-point pyrometer system (MPPS) for measuring surface temperature and emissivity. *Proceedings of the 28th Intersociety Energy Conversion Engineering Conference, IECEC*, pp. 2.111-2.113.

Figure 6-1. Plasma torch interference-free regions in FTIR emission spectra (clean torch).

Figure 6-2. Plasma torch interference-free regions in FTIR emission spectra (WSRC mix #2 being processed).

Figure 6-3. Automated multiple target measurements by multiwavelength pyrometer (MWP) using the developed multifiber switcher.

Figure 6-4. Temperature measurements on WSRC surrogates in DIAL's PT-150

7 FTIR Spectroscopy

J. S. Lindner

Introduction

Analysis of gas streams arising from plasma torch and joule-heated melter remediations of DOE's mixed-waste streams is critical for the evaluation of the effectiveness of the treatment process and for assessing environmental impact. Quantification of the inorganic and organic gasses such as NO_2 , NO , CO , CH_3 , SO_2 , NH_3 , etc., resulting from vitrifying the complex waste can be accomplished using Fourier transform infrared (FTIR) spectroscopy. A number of different experimental configurations are possible with this technique, and the fact that multiple components can be quantified simultaneously suggests a number of different applications.

Initial studies in the laboratories have been concerned with screening experiments on a plasma torch operating with air and nitrogen as the plasma forming gas.¹ The evaluation of two different types of joule-heated melters operated at Clemson University's Environmental Engineering laboratories for Westinghouse Savannah River Company (WSRC) and studies in the centrifugal plasma torch facility at MSE in Butte, Montana have been performed.²⁻⁴ The work reported here describes efforts directed at supporting the upcoming Plasma Hearth Process (PHP) bench-scale series of tests operated by Science Applications International Corporation (SAIC) at the Argonne National Laboratory West (ANL-West) TREAT facility. These experiments are scheduled for the spring of 1996 and represent surrogate, spiked and actual mixed-waste remediations using a 150-kW plasma torch. Considerations for the application of FTIR spectroscopy to a radioactive environment have included the evaluation of optical port assemblies, which maintain the barriers between the primary and secondary facility boundaries, and the means for calibrating the FTIR spectrometer for on-line, nonintrusive measurements across the gas stream of the air pollution control system. Specifications for other components necessary for extractive measurements have been finalized.

In preparation for these and other plasma torch measurements, a number of experiments were conducted on DIAL's 150-kW plasma torch facility. The surrogate waste stream consisted of the WSRC briquette material used for the refractory tests. FTIR extractive, on-line absorption and on-line emission experiments were performed. The extractive and on-line spectra indicated the presence of nitrosyl chloride, NOCl , which is formed by the reaction of NO

with HCl. The chemistry for NOCl formation also indicates that Cl_2 will also be produced. This result is of concern for potential corrosion of the downstream components.

Total NO_x ($\text{NO}_2 + \text{NO}$) concentrations from downstream extraction measurements were approximately 1.5 - 1.9% with the plasma torch operated on air and 0.5 - 1.1% when the torch was operated with nitrogen. With air as the plasma gas and no surrogate waste added, the NO_2 concentrations were typically between 1.1 and 1.3% while the NO concentrations ranged from 0.35 - 0.6%. Samples collected during briquette injection exhibited a different NO/ NO_2 partitioning with NO concentrations typically greater than 0.9% and NO_2 concentrations around 0.7 - 0.9%. This result indicates that the conversion of NO to NO_2 is reduced during injection of the feed, and this shift is due to feed reactions with the oxygen present.

Large organic molecules such as benzene and toluene were not observed in any of the torch experiments. Concentrations of CO and methane were below the limits of detection (ca. 100 ppb) of the FTIR calibrations. These results indicate that the waste is being destroyed at high efficiency using the torch operating conditions which have, to date, been investigated.

Work Accomplished

Preparations for PHP Testing at TREAT

A diagram of DIAL's plasma torch facility and the location of the optical penetrations and the sampling location are shown in Figure 7-1. A prototype port assembly to be used in the radioactive bench scale tests at the TREAT facility was designed in conjunction with K. Carney of ANL-West. The unit consists of an extension tube followed by a shutter, followed by a pressure sensor and then the window. A purge ring is located between the window and the pressure sensor and is used to direct nitrogen purge gas at a flow of 1 cfm towards the channel. A breach of the window causes a change in the sensor level which trips a relay and closes the shutter. In this way, any leak of the gas stream from the facility is stopped as soon as it is detected.

The port assembly was mounted on the exit duct from the plasma torch furnace, and a second port was provided on the opposite side of the channel. FTIR measurements were conducted in an absorption configuration. Values of the centerburst intensities were recorded over the duration of a run and are plotted against time in Figure 7-2. The results indicate that the windows remained clear over the duration of the experiment. Additional measurements on the penetration integrity were conducted at ANL-West and are cited here for completeness.⁵ The window assembly was pressure tested to 60 psi and

exhibited a leak rate of less than 5×10^{-5} scm³/sec. Maintaining the assembly at a temperature of 473 K for 17 hours did not result in any appreciable change in leak rate. The assemblies have been approved for use in the radioactive bench scale PHP tests.

FTIR experiments at the PHP facility will be conducted in an on-line, nonintrusive configuration and by extracting a portion of the gas stream and routing the sample to a long path, multiple-pass (White) cell. The nonintrusive measurements will be conducted between the evaporative cooler and the HEPA filter bank, and at this location the port assemblies described above will be used. The HEPA filters are expected to contain all of the radioactive elements which pass from the plasma torch furnace to the downstream. As a result, the extractive location is not expected to become radioactive. The temperatures of the gas stream here are similar to those which can be used during laboratory calibration. Consequently, the calibrations for the extractive measurement are straightforward.

Calibration at the upstream facility location is complicated by the higher gas stream temperatures. One option which has been investigated concerns *in situ* calibration of the FTIR. Experiments were conducted whereby known quantities of HCl and a diluent (nitrogen) were added to the gas stream using calibrated mass flow controllers. The original experiments were conducted with the torch off (room temperature) in order to establish the viability of the approach. This same method has, however, been used for calibration of the HCl emission monitor at temperatures of around 500 C (see *Continuous Emission Monitors* section). FTIR spectra were collected in an absorption configuration. Figure 7-3 contains an original spectrum (top trace), a pure spectrum of HCl from laboratory measurements (second trace from top), the difference spectrum (third trace from top), and the water and baseline corrected spectrum obtained by subtracting the water and baseline trace from the original spectrum. In this "reverse" subtraction method, all components are eliminated from the spectrum except the HCl. Integrated absorbance areas were then determined for all of the samples tested (different test runs) and are plotted according to the Beer-Lambert law in Figure 7-4. Although there is some scatter in the plot the results appear to be linear. Additional experiments are needed for other molecules and at torch operating conditions; however, based on the linearity of the plot and the results observed with this method described in *Continuous Emission Monitors* section, the calibration appears to be viable.

Other Plasma Torch Facility Experiments

Additional FTIR experiments were performed on DIAL's plasma torch facility. The surrogate waste was the same feed used in the WSRC refractory

testing experiments⁶ and consisted of inert material such as concrete, glass beads, sand, perlite, and iron powder, along with metal chlorides, poly(vinyl-chloride-PVC), and pecan shell flour. The materials for the feed were milled and then pressed into briquettes using starch and a binder. Total combustibles account for 36.4% of the weight with a total chlorine content (PVC + metal chlorides) of 7.14%. Initial extraction measurements with the addition of briquettes yielded spectra similar to that shown in Figure 7-5. Molecules such as NO, NO₂, HONO and CO₂ were expected based on our previous studies.¹ The band structure centered at a frequency of 1799 cm⁻¹ has been assigned to nitrosyl chloride (NOCl).⁷

The presence of the NOCl was initially surprising. The literature was consulted, and it was found that NOCl can be prepared by reaction of NO with HCl according to Jacobson:⁸

The equilibrium constants were calculated from data in the JANAF thermochemical tables⁹ and are 6.24E + 4 at 1000 K and 3.15E + 50 at 298 K. Of some concern with the formation of the NOCl is the accompanying generation of molecular chlorine.

Additional examination of reactions which could occur in scrubbers indicated that removal of the NOCl would not be an issue:⁸

However, removal of the chlorine in an acid gas scrubber may result in hypochlorite and chlorate,¹⁰

Undesirable reactions may also take place in a secondary combustor prior to scrubbing,⁸

Plasma torch facility air pollution control system designs need to take into account the corrosive nature of the gas stream produced from waste with high PVC or chlorine contents (typical of many DOE waste streams) and the fact that a reactive gas stream is generated.

HCl gas can react with stainless steel tubing such as that used in the sample extraction system for the FTIR experiments. The formation of the nitrosyl chloride was found, however, to be generated within or slightly downstream of the plasma torch furnace. In Figure 7-6 an absorption spectrum collected on-line is compared with the extraction spectrum. The presence of NOCl in the cross-duct measurement confirms the formation of the NOCl in the gas stream emanating from plasma torch processing of the surrogate waste.

Additional studies were initiated to quantify the NO and NO₂ emissions from the torch. For these experiments the extractive experimental configuration was employed, and the torch was operated with air and nitrogen plasmas. Briquette injections were performed during air operation. A revised data analysis program was used. The package consists of an interferogram collection module, a baseline correction routine, reverse spectral subtractions, chemometric routines, nonlinear fitting to calibrations, and a data transfer subroutine. The program performs all of these tasks, and following transfer of the data (if desired) to a host or control computer, the program will begin anew. The duration of these operations is approximately two minutes on an 80486 microprocessor operating at 33 MHz. A new computer has been obtained and the execution speed should be radically improved at a speed of 133 MHz.

NO, NO₂ and total NO_x concentrations measured during one of the plasma torch tests are plotted against time in Figure 7-7. The plasma torch predominately generates NO in the torch/furnace region. This NO is converted to NO₂ via

With air as the plasma generating gas, there is 21.9% of oxygen available for this reaction. At the downstream location there is considerably more NO₂ than NO. On injection of about 1/2 lb of the briquettes there is a different partitioning of the NO and NO₂ (Figure 7-7). The total NO_x concentration remains essentially constant, however, the NO concentration is increased and the NO₂ concentration reduced. This result is thought to be due to the reaction of some of the oxygen with the organics in the feed. The CO₂ concentration increased from 1.5 to 9.9% during feed injection.

The NO_x concentrations measured when the torch was operated on nitrogen are considerably less than those for air operation, and this was expected based on the lower oxygen levels. Additional measurements on nitrogen with the addition of the feed and with a nitrogen plasma and air injected into the furnace are needed.

Results from the FTIR measurements and conventional gas analyzers are collected in Table 7-1.¹⁰ The CO₂ concentrations are seen to be in good agreement and the lack of CO detected with the gas analyzer confirms the result from the FTIR. Some discrepancy is observed in comparing the NO_x concentrations. Differences in the values from the two instruments are thought to be due to reactions in the gas stream between the sampling locations and potential air leakage between the upstream (FTIR) sampling port and the downstream (analyzer) extraction penetration. Additional studies are needed for assessment of the extent of air leakage into the flow train.

Table 7-1. Comparison of FTIR and gas analysis results.

TIME	CO ₂ FTIR	CO ₂ GAS	NO FTIR	NO ₂ FTIR	NO _x FTIR	NO _x GAS	COMMENTS
11:48	16422	13400	4653	11691	16340	11300	Air
12:13	14858	14700	6021	11788	17800	11360	
12:36	14076	12400	3871	12863	16700	11480	
12:56	98923	98600	11300	7781	19000	11170	Feed Injection
13:32	54740	54100	9344	8563	17900	11250	Feed Injection
14:18	9384	5100	3936	7325	11300	9060	Nitrogen
14:41	5083	4300	4262	3906	8170	6730	

Project Status

All of the milestones for FY 95 have been completed with the exception of studies using the FTIR in control applications and a report on torch emissions. As noted above, some analysis results of the off-gas from the torch have been obtained, and all that is needed for the report are some added measurements with the nitrogen plasma and experiments on both air and nitrogen at different torch power levels and feed injection rates. The use of the FTIR in controls has been delayed into FY 96. At this time it is expected that the downstream for the facility will be completed in early 1996, and initial control experiments will involve the acid gas scrubber.

Project Significance

The work described above and planned for FY 96 is expected to provide valuable data regarding the destruction and/or conversion of mixed-wastes

using a plasma torch. The required methods, hardware and data processing tasks have been established, and remaining work concerns the extension of the FTIR calibrations to higher concentrations and additional molecules. Results from measurements on the DIAL plasma torch system have revealed interesting information regarding emissions and correlations with torch operating gases. Emissions from the torch, along with surrogate compositions, can be used for establishing the reaction taking place within and downstream of the torch primary furnace.

FY 96 Plans

The studies described above have built a sturdy base for the PHP tests at the ANL-West TREAT facility. These experiments are scheduled to begin in the spring of 1996 and will consist of a series of test runs on a surrogate waste stream followed by a series of tests on radioactive spiked waste and then test runs with actual DOE mixed-waste streams. Results from these experiments are expected to aid in the establishment of an emissions inventory and the means needed for accurately performing both nonintrusive (on-line) and extractive FTIR measurements. The results should be of value in process scaling and waste conversion analysis. The methods developed in this work will be transferred to ANL-West and for this a recursion process is planned.

Work on the use of the FTIR for controls will be performed along with studies on the recovery of particle size distributions from multi-wavelength extinction data. The presence of entrained particles will give rise to an attenuation of the transmission spectrum. In most applications the scattering contribution is ignored. Preliminary work has indicated that the distribution can be recovered from FTIR extinction data. The ability to quantify particle distributions, along with species concentrations and temperatures, adds to the potential applications for the FTIR in process monitoring.

References

1. Shepard, W.S., et al. 1993. *Application of modern diagnostic methods to environmental improvement*. Mississippi State University: Diagnostic Instrumentation and Analysis Laboratory. DIAL 10575 FY 93 Annual.
2. Shepard, W.S., et al. 1994. *Application of modern diagnostic methods to environmental improvement*. Mississippi State University: Diagnostic Instrumentation and Analysis Laboratory. DIAL 10575 FY 94 Annual.
3. Cook, R.L., et al. 1994. *Environmental Systems Engineering*, Clemson University. DIAL Trip Reports 94-1 and 94-2.
4. Cook, R.L., et al. 1994. *Plasma Arc Centrifugal Treatment System*, Western Environmental Technology Office, MSE, Butte, Montana. DIAL Trip Report

94-3.

5. Carney, K. ANL-West. Personal communication.
6. Etheridge, J.A., et al. 1995. *Refractory lifetime testing for Westinghouse Savannah River Company*. DIAL 10575 TR 95-3.
7. Burns, W.G. and Bernstein, H.J. 1950. *J. Chem. Phys.* 18:1669.
8. Jacobson, C.A. 1946. *Encyclopedia of chemical reactions*. Vols 3 and 4. Reinhold.
9. Dow Chemical Co. 1971. *JANAF thermochemical tables*. National Bureau of Standards, U. S. Department of Commerce, Washington D.C.
10. Horowitz, N.C. 1981. *Chem. Eng.* April 6:105.

Figure 7-1. Block diagram of DIAL's plasma torch furnace and the FTIR measurement locations.

Figure 7-2. FTIR centerburst intensities measured during a plasma torch test run for evaluation of the PHP (TREAT) port assembly design.

Figure 7-3. On-line HCl calibration spectra. Shown from top to bottom are: the original spectrum; a spectrum of HCl from the laboratory; the difference spectrum, which contains all spectral contributions except the HCl; and the final spectrum obtained by subtracting the difference spectrum from the original trace.

Figure 7-4. The associated Beer-Lambert plot from the on-line calibration experiments. Different symbols correspond to different test runs.

Figure 7-5. Typical extractive absorption trace collected during injection of the surrogate feed into the plasma torch furnace. The torch was operated on air and the gas cell path length was set at 75 meters.

Figure 7-6. Comparison of the spectrum in Figure 7-5 with an on-line absorption spectrum. The presence of NOCl in the on-line measurement confirms formation of this species within the torch furnace.

Figure 7-7. NO, NO₂, and total NO_x concentrations measured during a plasma torch test run. The first three data points were taken with the torch operated on air, the next two are for the injection of briquettes with the air plasma, and the final two data points are for the torch operated on nitrogen with no added feed.

8 Laser Scattering

F.Y. Yueh and J.P. Singh

Introduction

The possibility of developing a laser scattering (LS) system for plasma diagnostics has been explored. Three laser scattering techniques have been evaluated. There are Rayleigh scattering (RS) for gas temperature measurement^{1,2,3}, Thomson Scattering (TS) for electron density and electron temperature measurement^{4,5}, and stimulated Raman scattering (SRS) for electron density measurement.^{6,7} In the LS technique, an intense pump laser beam interacts with a high density plasma in the plasma torch, and the scattered light from the test medium is frequency and intensity analyzed to obtain electron density, gas temperature and electron temperature.

Work Performed

The laser scattering techniques were tested in the laboratory. The main units of the present LS instrument are a pump laser, a spectrograph, a diode array detector, a PMT detection system with spectral filter, and a data acquisition/analysis computer. To maximize the signals, the SRS signal was collected in the backward direction while the TS and RS signals were collected in the direction perpendicular to the direction of laser beam. The LS signal is very sensitive to the background noise from the plasma or from the detector. Various techniques to reduce stray light, plasma background and electronic noise were studied. The LS detection system was enclosed in a black cover to reduced the ambient light into the detection system. An oscilloscope was used to monitor the effects of various alignments on the signal-to-background ratio. LS signals were recorded in a sample cell filled with various gases and under various gas pressures. Laser scattering signals from various gases were recorded and compared. The data shows that the stray light is too high to obtain a reasonable signal-to-background ratio. An attempt to calibrate the LS system for gas temperature and electron density measurements with Ar and He-filled cell was not successful due to the problem of stray light.

To optimize the experimental setup for plasma torch measurements, the design of the present LS system must be modified to include the cooling of the PMT. The gain of the current detector is very sensitive to the ambient temperature. A PMT detector with an independent Peltier device to control temperature within 0.1 C will stabilize the detector gain and reduce the background

noise. More irises are also required to eliminate stray light into the detection system. For safety reasons, the initial experiments will use the laser wavelength of 532 nm. Since the background plasma light is lower in the near IR range than in the visible range, a laser frequency in the near IR should yield a better signal-to-noise ratio.

Various problems with the equipment postponed most of the planned tests. The researchers and equipment for the LS project were also tied up with the LIBS project. Due to lack of manpower and equipment, the major milestones for the LS project are not complete.

The laser scattering technique can be a useful tool for plasma diagnostics. The current LS system must be modified to further reduce the stray light. More experimental work is required for applying LS to a practical environment.

Project Status

Much effort is still required to make a usable LS system for plasma torch diagnostics. No further development will take place in the near future.

Project Significance

A laser scattering system can provide temperature and electron density information for a plasma torch. However, various problems related to background noise need to be solved before a practical system can be developed.

FY 96 Plans

There are no plans for the laser scattering system for FY 96.

References

1. Snyder, S.C.; Reynolds, L.D. and Shaw, C.B., Jr. 1991. *J. Quant. Spectrosc. Radiat. Transfer.* 46:119-124.
2. Stepowski, D. and Cahot, G. 1992. *Combust. and Flame.* 88:296-308.
3. Murphy, A.B. and Farmer, A.J.D. 1992. *J. Phys. D: Appl. Phys.* 25:634-643.
4. Orsitto, F., et al. 1995. *Appl. Opt.* 34:2712-2720.
5. Tracy, M.D., et al. 1992. *Phys. Fluids B.* 4:1576-1584.
6. Perry, M.D., et al. 1992. *Opt. Lett.* 17:523-525.
7. Radziemski, L.J. and Cremers, D.A. 1989. *Laser-induced plasma and application.* New York: Marcel Dekker, Inc.

9 Multicolor Imaging

R. K. Lengel

Introduction

In 1995, the plans for the multicolor imaging system were to take measurements as needed with the one color system, and to complete the three color system. Both of these tasks have been completed. The one color system has been used to take thermal images of the crucible during glass melting experiments, and to take plasma emission images to better understand the operating characteristics of a plasma torch. The parts for the three color system were acquired, assembled and tested. This system is now ready to be used for routine measurements.

Work Accomplished

The one color system, in which one CCD camera equipped with a narrow band interference filter is used to obtain images which are captured, stored and manipulated by a PC equipped with a digitizing board, was used for several different measurements this year. During preliminary tests of glass melting in the large PT-150 torch, thermal images of the crucible were taken with a long wavelength filter. These images showed that the crucible was of a uniform temperature throughout the viewing region. Images of the plasma from the PT-150 system have not been taken because of limited optical access. It is hoped that changes in this system will allow such images to be taken in the future.

The one color system was used for two different types of measurements of the PT-50 system. In the first of these experiments, done in support of the torch control project, high speed images of the plasma emission at 760 nm (the region of continuous emission) were taken. Using the electronic shutter on the CCD camera, images were captured with an exposure speed of 1/10,000 sec. With this short exposure, the plasma appears to be a narrow filament that is curved due to the gas vortex motion. The differences between the two overlaid, interlaced fields of the television frame, which are separated from each other by 1/60 sec, also give some indication of this gas rotation. These images show that it would be possible to monitor the gas rotation velocity optically, to give an indication of the correct operation of the vortex generator and thus improve the electrode lifetime.

The second use of the one color system was to take images of the plasma at the same time that spectral measurements were being taken. The UV-VIS spectra were taken at a number of points across the plasma near the exit of the torch body, and the imaging system was setup to capture the same area of interest. The spectral system provided good wavelength resolution but low temporal resolution, and the imaging system provided snapshots with less wavelength discrimination. The results from the two systems were in very good agreement. Basically, the images showed that for the continuous emission at 760 nm, the plasma is bell shaped when nitrogen or air is used as the working gas. In contrast, when argon is used, the plasma emission has more sharply rising sides and a flatter top. When a 520-nm filter is used in the imaging system, it is possible to see copper emission, an indication of rear electrode wear, when the torch is operated with air. This emission is concentrated at the edges of the plasma, giving distinct shoulders on the bell shaped curve. Also, the time resolution of the images show that the copper emission, and hence electrode erosion, is highest when the torch is first started, and when the pressure is increased.

The three color system consists of three CCD cameras with beam splitters and individual interference filters to produce a "color" image of the system under investigation. A television synchronization generator is required to make the cameras operate together, and a PC board capable of digitizing red, green, and blue (RGB) video signals is used to capture, store, and display the images. Also, a notebook computer, along with a docking station that will accommodate the digitizing board, is used with this system to make it more portable. Although only test images have been taken to date, it is planned to use this system to record images of the glass stream emerging from a joule melter at Clemson University. The intensity of any one of the colors will be used to determine the temperature profile of the stream, and the combination of the three colors will indicate any variation in the blackbody emissivity of the molten glass. In the future, this system will also be used to take images of the plasma torch emission, concentrating on copper spectral signals.

Project Status

With the completion and testing of the three color system, this project is essentially complete.

Project Significance

This project supplies information to two different customers. Field trips have been and will continue to be made to take images as requested. In the past these images have been used to ascertain the thermal profiles of the molten glass exiting from both joule and plasma torch heated systems. The other

significant measurements are those performed at DIAL. As indicated above, these measurements provide information about possible torch control strategies, and about electrode wear monitoring.

Future Plans

As stated above, this project is complete as far as instrument development is concerned. Minor improvements and modifications will be made as required. Both the one color and three color systems will continue to be used on a routine basis in house and for field measurements as required.

10 Laser Optogalvanic Spectroscopy

David L. Monts

Introduction

Laser optogalvanic spectroscopy (LOGS) serves as a process monitor of the concentration of metallic species in the off-gases of thermal treatment systems in order to ensure that the system is operating in compliance with environmental mandates. Species of interest among the off-gases include: gas-phase, elemental, toxic trace metals with appreciable vapor pressure such as As, Cd, Ni and Sb; selected radionuclides that are difficult to detect due to their long half-lives such as ^{99}Tc , ^{129}I , ^{235}U , ^{238}U , ^{239}Pu , etc.); and, selected radionuclides that are difficult to detect due to the fact that they emit weak (or no) γ -rays and the α or β particles that they do emit can be easily attenuated by other materials present (radionuclides such as ^3H , ^{90}Sr , ^{99}Tc , ^{129}I , ^{238}Pu and ^{239}Pu). Because LOGS uses electrical rather than optical detection, this technique alleviates the problem associated with monitoring small absorptions or weak emission in the presence of a strong optical background signal. Moreover, because the collection of charge can be significantly more efficient than the collection of photons, LOGS can have significantly lower limits of detection (typically one to two orders of magnitude) than techniques employing optical detection.

In a LOGS experiment (Figure 10-1), a pulsed tunable laser is tuned into resonance with a transition of a species (atomic or molecular) in an atomization source, temporarily increasing the excited state concentration of that species. Because the energy necessary for ionization is less for an excited electronic state than for the ground state, the rate of ionization temporarily increases due to laser-enhanced electron impact ionization:

and/or due to direct laser photoionization:

This process can be monitored as a transient (tens of microseconds) voltage change if a high voltage electrode (relative to ground) is inserted into the plasma. By scanning the wavelength of a tunable laser and recording the LOGS signal as a function of laser wavelength, the optogalvanic spectrum

(which is analogous to an absorption spectrum) can be obtained. Only the response of the plasma in the vicinity of the electrode is probed. For studies of practical thermal treatment systems, only optical access from one side of the gas stream is required since the electrode and laser beam can be introduced through the same optical port. If a short electrode is mounted on an insulated linear motion feedthrough, a segment-wise measurement of the species concentration across the gas stream can be obtained. For field implementation (Figure 10-2), a portion of the off-gases will be sampled via a slipstream that passes through the LOGS detection cell where particles will be atomized and the LOGS signal of the atoms detected before being returned to the off-gas system.

The objective of the LOGS project is to develop and implement a field-deployable LOGS system for detection of metallic species of concern present in the off-gases of mixed waste and high level radioactive waste thermal treatment vitrification facilities. The particular emphasis is on monitoring the concentration of species that are difficult to detect on-line and in real time with sufficient sensitivity by other methods.

Work Accomplished

Significant progress toward development of laser optogalvanic spectroscopy (LOGS) as a field-deployable system was made during FY 95. Efforts concentrated on evaluation of atomization sources for the field-deployable LOGS system. Almost all the reported quantitative determinations of species concentrations by LOGS have been performed in flame-based atomization sources. However, at some DOE facilities, deployment of a flame-based LOGS system may not be possible due to health physics safety considerations, while at other DOE facilities (such as Clemson University or Oak Ridge), a flame-based LOGS system could be deployed. Therefore, it is desirable (if feasible) to deploy an electric discharge-based atomization source for LOGS in order to avoid complications associated with combustible gases.

Because of the availability of a glow discharge system, our evaluation of electric discharge-based atomization sources began with a planar glow discharge system. Extensive efforts were made to optimize operation of the planar glow discharge system for LOGS. As the result of an exhaustive evaluation of the planar glow discharge system, it was concluded that although planar glow discharges are superb spectroscopic sources, they are not appropriate for field-deployment of LOGS. A schematic (not to scale) of the discharge regions of a dc glow discharge is presented in Figure 10-3. The Aston dark space, the cathode layer, and the cathode dark space are collectively referred to as the "cathode fall region". It is possible to observe LOGS signals when exciting in the cathode fall region. However, the cathode fall region is rather narrow (typ-

ically about 2 mm), and most of the variation of electric field across the discharge occurs in this narrow region. The consequence of this is that the LOGS detection sensitivity is a steep function of position within this region. The position of the laser beam must be controlled to within 0.01 mm in order to insure reproducibility of the LOGS detection sensitivity that is required for quantitative measurements. Moreover, the width of the cathode fall region is inversely proportional to pressure. Since planar glow discharges typically operate at a pressure of a few Torr, a small fluctuation in cell pressure can change the width of the cathode fall region and hence change the LOGS detection sensitivity. In addition, the laser beam power density is sufficiently large that if the laser beam strikes an electrode, then a LOGS signal is produced (due to ablation or photoelectric emission) that is significantly larger than the LOGS signal of the species of interest; thus, there is a limitation on how close the laser beam can be positioned to an electrode. Because these factors significantly degrade the precision with which LOGS concentration measurements can be made, it was concluded that excitation in the cathode fall region of a planar glow discharge atomization system is not appropriate for field-deployment for LOGS.

As Figure 10-3 shows, the electric field is essentially constant in the negative glow region of a dc glow discharge, thus avoiding the positional sensitivity that occurs in the cathode fall region. However, when LOGS excitation occurs in the negative glow region, most of the cations generated by LOGS are collisionally neutralized before they can reach the cathode and be detected. Thus, it is not possible to detect species of interest at the required levels of detection in a planar glow discharge.

Upon reaching the conclusion that a planar glow discharge is not feasible for field implementation for LOGS, we began an aggressive campaign to evaluate other atomization sources, including both flame-based and other electric discharge-based systems. Using an air/acetylene flame, we have characterized the LOGS response for As, Pb, Cd, Ni, Sb, Cr and U. The calibration curve for U is presented in Figure 10-4. An ultrasonic nebulizer is used to volatilize standard plasma emission spectroscopy solutions in order to produce metal particles for introduction into the flame; the ultrasonic nebulizer's desolvation column removes the solvent from the gas stream, leaving only dry metal particles. The ultrasonic nebulizer is employed because in off-gas systems of interest in the field, the metallic species will be entering the LOGS detection cell as particles rather than as free atoms and hence desolvated metal particles better approximate the real system than does a pneumatically nebulized solution.

The theoretical limits of detection (LOD) for flame-based LOGS obtained by applying the standard correction (taking into account the effi-

ciency of our ultrasonic nebulizer unit) are presented in Table 10-1. Our current theoretical limits of detection are comparable to those obtainable for air ICP¹ and those sought by EPA for CEM monitoring of RCRA metals in the off-gas, with the exception of As. The LOGS LOD for As is currently not as low as that obtainable by air ICP because the optimum transition to monitor for As is the resonance transition, whose peak wavelength differs by 0.01 nm from the peak of the Cd resonance transition. Our current laser bandwidth is wider than this separation so we cannot distinguish between As and Cd when monitoring that wavelength and hence must use a transition with a lower oscillator strength, resulting in a higher LOD. Means of reducing the LOGS LOD by an additional one to three orders of magnitude will be discussed in the FY 96 Plans section.

Table 10-1. Current LOGS and air ICP theoretical limits of detection (LOD).

Element	LOGS Transition (nm)	Max Laser Power (mW)	LOGS LOD ($\mu\text{g}/\text{m}^3$)	Air ICP LOD ($\mu\text{g}/\text{m}^3$)	EPA CEM Limits ($\mu\text{g}/\text{m}^3$)
As	278.1	6.5	300	47	5
Cd	326.1	1.5	9	13	5
Cr	357.9	1.5	9	1.3	5
Ni	341.5	3.5	3	1.9	5
Pb	283.3	7.5	20	4.7	50
Sb	287.8	2.5	12	270	5
U	386.1	1.2	36	44	---

In addition to flame-based atomization sources for LOGS, we are also pursuing evaluation of electric discharge-based atomization sources, in particular hollow cathode electric discharge. The advantages for LOGS of a hollow cathode discharge rather than a planar glow discharge are:

1. since the cathode fall region is narrower in a hollow cathode discharge than in a planar glow discharge, it is possible to excite species in the negative glow region that fills most of the hollow cathode and detect a LOGS signal;
2. the width of the cathode fall region is not inversely proportional to pressure as it is in planar glow discharges and hence the positional sensitivity for excitation is less in a hollow cathode; and

3. the significantly higher electron density within the hollow cathode facilitates the production of LOGS signal by laser-enhanced electron impact ionization [first equation].

The schematic of the DIAL prototype hollow cathode LOGS cell is presented in Figure 10-5. During FY 95, an "erector-set" type hollow cathode discharge system was constructed at DIAL in order to readily permit variation of the diameters, lengths and separation of the hollow cathode and hollow anode. Stable operating conditions have been determined for argon and for air.

A collaboration was formed with Professor Sean McGlynn and Dr. Devendra Kumar at Louisiana State University in order to evaluate the feasibility of quantitative LOGS determination of metal concentrations in an rf discharge (Figure 10-6). An rf discharge has the advantage that since the electrodes are external to the gas stream, they are not subject to corrosion or adhesion of particles that might adversely affect the operation of the electrodes in a hollow cathode discharge or in a flame-based system. This evaluation will be conducted at Louisiana State University at the beginning of FY 96.

A *Commerce Business Daily* solicitation for industrial partner(s) to commercialize LOGS was prepared. The mechanism for evaluating industrial applicants so that the optimum partner(s) can be chosen has been selected, and documentation has been prepared. Submission of the *CBD* solicitation has been postponed until a decision has been made on which atomization source will be employed for field implementation of LOGS.

Project Status

The DIAL flame-based LOGS system has been demonstrated in the laboratory. Because of the desire to avoid the complications associated with combustible gases, evaluation of various electric discharge atomization sources (planar glow discharge, hollow cathode discharge, and rf discharge) has been aggressively pursued and will be completed at the beginning of FY 96. Evaluation of a planar glow discharge atomization source revealed that it is not appropriate for field implementation. With the selection at the beginning of FY 96 of atomization source(s) for field deployment, the development and field deployment of LOGS is expected to proceed apace.

Project Significance

Laser optogalvanic spectroscopy (LOGS) provides the capability of detecting species of interest on-line and in real time at lower concentrations than is possible with techniques employing optical detection. Although LOGS is a general purpose technique that is applicable to a very wide variety of atomic and molecular species, we are concentrating our efforts on species that

are difficult to detect at the required concentration levels by other techniques. In particular, we are concentrating on environmentally regulated volatile, toxic trace metals (RCRA metals) and on selected radionuclides. Targets of opportunity for LOGS among the radionuclides include those that are difficult to detect because of their long half-lives (radionuclides such as ^{99}Tc , ^{129}I , ^{235}U , ^{238}U , ^{239}Pu , etc.); and also radionuclides that are difficult to detect due to the fact that they emit weak (or no γ -rays), and the α or β particles that they do emit can be easily attenuated by other materials present (radionuclides such as ^3H , ^{90}Sr , ^{99}Tc , ^{129}I , ^{238}Pu and ^{239}Pu). As discussed during the September 13, 1995 CMST-CP review of DIAL progress, detection of radionuclides is needed for concentrations of 10^{-11} molar or less. The current LOGS detection limits correspond to 10^{-10} molar. Implementation of straight forward improvements during FY 96 will permit limits of detection to be decreased by one to three orders of magnitude, providing the required detection sensitivity for radionuclides of interest. Thus, LOGS can meet DOE's needs not only for monitoring the concentration of the RCRA metals, but also for monitoring selected radionuclides of concern in the off-gases of thermal treatment vitrification systems

FY 96 Plans

The FY 96 milestones are grouped into four work elements. The first work element involves evaluation and selection of atomization source(s) for field implementation. This effort was aggressively pursued during FY 95, and will be completed during the beginning of FY 96. Both flame-based and electric discharge-based atomization sources are being evaluated. Our efforts will include optimization of the operating conditions and minimization of the limits of detection. For flame-based atomization sources, reduction of the limits of detection will be achieved by implementation of four different means. The first involves utilizing a different high voltage power supply in order to detect the LOGS signal using a higher collection voltage; the use of higher voltages has been demonstrated to increase the LOGS signal magnitude. Voltages of up to 3 kV have been reported in the literature; currently, we are limited to a maximum voltage of 1 kV. The second involves utilization of higher laser powers. Typically LOGS signals begin to saturate between 15 and 20 mW (for a 10-Hz laser). As shown in Table 10-1, the maximum tunable ultraviolet laser powers attainable with our current laser system were significantly below 10 mW for these wavelengths. When our new laser system is delivered, we will be able to substantially increase the ultraviolet laser power attainable and hence increase the LOGS signal intensity. Thirdly, we will optimize the settings of our gated integrator detection electronics to expand the range of output voltages, expanding the dynamic range of LOGS signals that can be monitored. Lastly,

we will replace our current 12-bit analog-to-digital (A/D) computer interface board with a 16-bit A/D board since the resolution of the A/D board limits the smallest LOGS signal that can be detected. From a combination of these factors, we expect to reduce the limits of detection by from one to (in the most favorable cases) three orders of magnitude. The last three means will also reduce the limits of detection achievable with electric discharge-based atomization sources.

Although quantitative determination of concentrations has been extensively investigated for flame-based atomization sources by a wide variety of researchers, there are only a very small number of reports of quantitative LOGS determination of concentration in electric discharges. Given the desirability of avoiding complications associated with combustible gases, an electric discharge atomization source is preferred if the limits of detection are comparable for both electric discharge-based and flame-based atomization sources. Selection of atomization source(s) for field deployment will be based on consideration of several factors:

1. Are the limits of detection of a given atomization source at or below the environmentally mandated detection levels?
2. Are the limits of detection significantly below those achievable using conventional on-line, real-time methods so that the expense and complexity of a laser-based diagnostic system are justified?
3. For atomization sources with LOGS electrodes immersed into the plasma, how does corrosion and adhesion of particles to the electrodes affect the reliability of the concentration determinations and the durability of the electrodes?

The second work element involves characterization of the LOGS signal: specifically testing the LOGS system on the DIAL test stand using surrogates; expansion of the LOGS repertoire to other species of interest; selection of which species will be monitored during the initial field deployment; and calibration of the LOGS signal intensity under standard operating conditions. The third work element is drafting and revising quality assurance/quality compliance (QA/QC) documentation for LOGS. The fourth work element is a preliminary field test at a DOE facility.

Reference

1. Baldwin, D.P.; Zamzow, D.S. and D'Silva, A.P. 1995. Detection limits for hazardous and radioactive elements in airborne aerosols using inductively coupled air plasma. *Journal of the Air & Waste Management Association*. 45:789-791.

Acronyms

CEM	continuous emission monitor
CMST-CP	Characterization, Monitoring, and Sensor Technology- Crosscutting Program
EPA	Environmental Protection Agency
ICP	inductively coupled plasma
LOD	limit of detection
LOGS	laser optogalvanic spectroscopy
Nd:YAG	neodymium:yttrium aluminum garnet
RCRA	Resource Conservation and Recovery Act
rf	radio frequency

Figure 10-1. Schematic of the DIAL LOGS apparatus.

Figure 10-2. Schematic of field implementation configuration for DIAL LOGS system.

DC Glow Discharge Schematic

Figure 10-3. Schematic of discharge regions of dc glow discharge and of variation of electric field.

Figure 10-4. LOGS calibration curve for uranium detected in air/acetylene flame. The error bars correspond to ± 1 standard deviation.

Figure 10-5. Schematic of DIAL LOGS prototype hollow cathode discharge cell.

Figure 10-6. Schematic of rf LOGS apparatus.

11 Extinction-based Cross Correlation

R. Arun Kumar

Introduction

The velocity of fluid flow in a duct or channel can be measured by introducing a marker into the fluid and then measuring the time required for this marker to be convected a known distance. In a well-known paper, G. I. Taylor discusses the theory and application of this marker technique.¹ Among other results, Taylor found that if the point of marker injection and the downstream detector were sufficiently far apart, the marker pulses would propagate at the average (across the channel cross section) velocity of the fluid.

The cross correlation technique is conceptually similar to the marker method, only instead of artificially introducing a marker, the technique takes advantage of naturally occurring property variations in the flow. This technique is commonly referred to as the cross correlation method of velocity measurement, after the computational algorithm that is usually used to identify the propagation delay time.

Clearly, many variations in the basic cross correlation technique are possible, depending on the variable that is chosen for measurement. The appropriate variable is often suggested by the nature of the flow stream. In combustion systems such as a burning flare or an MHD generator, the unsteady emission of light by the hot gas naturally suggests that measurements of emitted light intensity could be used for cross correlation velocity measurements.

We have previously reported on our work using emitted light signals from hot gas streams to make cross correlation velocity measurements.^{2,3} Although this method is ideal for combustion systems such as coal-fired MHD, it is not suitable for lower temperature applications where the gas is not luminous. The work performed this year is a continuation of the work performed in the last year. We have considered the problem of velocity measurement in lower temperature systems where the fluid is heavily laden with particles or droplets. In such a case, the natural occurrence of particles suggests that the particle or droplet concentration could be used as the measured quantity for the cross correlation technique. In the previous year we worked on a fixed beam spacing CCS, and this year have expanded the functionality/range of the technique by building a variable beam spacing system. This

should allow the system to be used over a wider range of velocities and process conditions.

Work Accomplished

Experimental Setup

A schematic of the test bed is shown in Figure 11-1. Air to the test bed is supplied from a 1.75-peak HP commercial wet/dry shop vacuum operating in blower mode. The blower sits under an optics table where the test bed is arranged. This provides vibration isolation from the measurement system. Air is delivered from the blower through a 1.5-in. flex hose to a 1.5-in. PVC pipe at the inlet of the test bed. The air is then Tee'd off into a bypass line and to the airstream measurement line. The airstream delivery line is 2 ft long from the Tee and has an exit diameter of 1 in. Flow control in the system is accomplished by the use of two gate valves, one on the main delivery line and another on the bypass line. The primary flow level is set by the valve on the main delivery line, and a finer adjustment is available by the valve on the bypass line. A water droplet sprayer is installed 2.5 in. from the exit of the measurement line. This sprayer is one that is generally used on lathes and other machine tools for cooling tool bits. It gets its atomizing air from the tank of an air compressor. Inlet air pressure to the water sprayer is maintained at 25 psig using a pressure regulator.

As mentioned earlier, this velocity measurement system is used to determine the cross correlation between two attenuated, parallel laser beams, one upstream of the other, which are passed through the flow. The attenuation of the laser beams in this system is caused by the water droplets injected into the air flow. Figure 11-2 shows a schematic of how the two parallel laser beams are generated. A 10-mW HeNe laser beam at 632.8 nm is used in our system.

In the variable beam spacing system (Figure 11-2), the laser beam is first split into two using a beam splitter. The spatially fixed beam goes through a beam expander and through a variable slit width assembly. The output beam from the slit is a narrow vertical beam which flows through the flow field of interest, gets attenuated before it passes through a 632.8-nm optical filter in the detector housing, before it is measured. The second beam is reflected, expanded and goes through a similar slit assembly. The narrow vertical beam is reflected off a mirror on a traverse and forms a beam parallel to the first one and gets attenuated through the flow field of interest. The beam spacing in this instrument can be varied by translating the two mirrors on this second beam.

The detectors are a ready-to-use, low-noise, amplified detector package with user-adjustable gain. An integrated silicon PIN photodiode and a hybrid transimpedance amplifier are provided in a single TO-5 package mounted in a

compact, aluminum housing. These detectors were acquired from Thor Labs Inc. The detectors have a bandwidth from DC-10 MHz and a sensitivity of 0.4 amps/watt at 632.8 nm.

Results

Figures 11-3 and 11-4 show measurements of velocity made at a distance of 1 in. from the exit of the air delivery tube. The water droplet injection was done 2.6 in. upstream of the exit. Figure 11-3 shows measured velocities and the normalized cross correlation coefficient for a beam spacing of 0.19 in. Figure 11-4 shows the velocity measurements at the same location but with an increased beam spacing of 0.29 in. The average measured velocities in the two plots are 34.37 m/s and 34.8 m/s, respectively. The normalized cross correlation coefficients in the two curves are also in the 0.6 - 0.9 range. A coefficient of 1 would indicate perfect correlation between the signals measured by the two detectors.

Conclusions

A variable beam spacing cross correlation system for the measurement of velocity has been developed. Measurements from the system are consistent with expectations, i.e., velocities measured by the system on the test bed are independent of the beam spacing used. This technique shows promise in application to measuring velocities in gas streams which can attenuate the laser beam being used.

Project Status

This project has been put on hold pending location of a customer.

Project Significance

In order to meet current environmental regulations, there exists a need for innovative gas velocity measurement techniques. These techniques should provide real time, cross-sectionally averaged, measurements of flow which can be used to determine compliance with regulations. We believe that the cross-correlation technique provides one such method for velocity measurement.

FY 96 Plans

This project will be resumed provided a customer for the instrument can be identified and brought in for support.

References

1. Taylor, G.I. 1954. The dispersion of matter in turbulent flow through a pipe. *Proceedings of the Royal Society, A*. Vol. 223, pp. 446-68. Reprinted in *The scientific papers of Sir Geoffrey Ingram Taylor*, Vol. II, edited by G. K. Batchelor, Cambridge, 1960.
2. Norton, O.P. and Arun Kumar, R. 1990. *Cross correlation velocity measurements in a simulated MHD environment*. 28th AIAA Aerospace Sciences Meeting. Reno, Nevada. AIAA 90-0350.
3. Norton, O.P.; Arun Kumar, R. and Srikantaiah, D.V. 1991. *A direct comparison of cross correlation velocity measurements with laser Doppler measurements*. 29th AIAA Aerospace Sciences Meeting. Reno, Nevada. AIAA 91-0213.

Figure 11-1. Schematic of test bed.

Figure 11-2. Variable beam spacing cross correlation system schematic.

Conditions:

Filename:	LAC	Beam Spacing:	0.19 inches	Standard Deviation:	2.77 m/s
Frequency:	450 KHz	Average Velocity:	34.437 m/s	c-coefficient average:	0.72

Figure 11-3. CCS velocity measurement with a beam spacing of 0.19 in.

Conditions:

Filename:	LAO	Beam Spacing:	0.29 inches	Standard Deviation:	2.54 m/s
Frequency:	400 KHz	Average Velocity:	34.8 m/s	c-coefficient average:	0.64

Figure 11-4. CCS velocity measurement with a beam spacing of 0.29 in.

12 Gas Analysis

Robert A. Green

Introduction

Gas analysis capabilities are a vital part of controlling and operating any thermal treatment facility. DIAL has the capability to monitor most of the routine gases encountered in thermal processors using conventional gas analyzers. These analyzers are used on a routine basis to monitor and record the gas composition of the effluent from DIAL test facilities.

The gas analysis system is a flexible system that is capable of being transported to other facilities. Analyzers can be easily used during tests to monitor changes in operating conditions of the test facilities at DIAL which include two plasma torches and a combustion test stand.

In addition to the conventional gas analysis, DIAL has the capability to perform several EPA methods including Method 5, Determination of Particulate Emissions. This capability was utilized in a series of tests conducted during FY 95 for Westinghouse Savannah River Company.

Work Accomplished

The primary purpose of this task was to operate the gas analysis system in support of the routine operation of DIAL's facilities. The gas analysis system was operated in support of numerous tests of the plasma torches. Data were collected, analyzed and reported for these tests. The gas data were then used for comparison to other diagnostic methods under development at DIAL and found to compare well.

A series of tests was conducted this year for the Westinghouse Savannah River Company using the PT-150 plasma torch at DIAL. Gas analysis and EPA Method 5 capabilities were specifically requested and supplied for this series of tests. The purpose of the tests was to evaluate the suitability of various refractories for use with glass melts expected to be encountered in the treatment of mixed wastes. A simulated waste mixture of various materials was prepared and pressed into briquettes which were then fed into the plasma torch operation. The composition of the briquette mixture is reported in Table 12-1.

Table 12-1. Briquette mixture used for WSRC tests.

Material	Concentration (%)
Pecan Shell Flour	13.8
PVC Granules	13.8
Glass Beads (Soda Lime Glass)	13.8
Perlite (Harborlite)	13.8
Iron Powder	13.8
Alumina	10.0
Aluminum Powder	2.0
Silica Sand	5.5
Portland Cement	5.5
Activated Carbon	6.2
Cesium Chloride	0.3
Lead Chloride	0.3
Chromic Chloride	0.3
Cerium Chloride	0.3
Nickel Chloride	0.3

Since the plasma torch is typically run using nitrogen as the plasma gas, the gas analysis is usually not very exciting. Unless feed material is added to the crucible and pyrolyzed, we see only nitrogen oxides (NO_x) and oxygen. Both the NO_x and oxygen are due to the air supplied as plasma gas or that which finds its way into the vessel. However, when briquettes are added to the crucible and pyrolyzed, the gas analyzers detect a decrease in NO_x and O_2 while indicating an increase in the level of CO_2 . If many briquettes are added rapidly, then levels of CO and unburned hydrocarbons are also observed.

Sampling of the off-gas when processing this feed material presents problems in itself. The particulate loading is a problem since the gas is extracted from a point upstream of any filtering device. Depending on the feed rate of the briquette material, the particulate filters used in the gas conditioning system became overloaded, requiring frequent changing. This difficulty was overcome by using two filters with a large surface area placed parallel to the flow loops. The large surface area provided greater sampling time before the filter needed changing. By having the two filters parallel, the sample flow

can be switched from one filter to the other allowing filters to be changed without interrupting the collection of gas data.

EPA Method 5 sampling was also conducted for the WSRC tests. The equipment had to be reconditioned and some new equipment had to be ordered. Once this was accomplished a training program was initiated to re-familiarize team members with the procedures involved in a Method 5 test. Several preliminary tests were conducted on the plasma torch in preparation for the WSRC test.

The major technical obstacle to overcome in the WSRC Method 5 testing was the low gas velocities in the off-gas system. The gas velocities were calculated to be only a few feet-per-second, resulting in a Pitot tube pressure differential of only a few thousandths of an inch of water--a value difficult to measure. The only option to increase the velocity was to decrease the cross sectional area of the off-gas system. This was done by installing a two-inch diameter spoolpiece called the diagnostic test section (DTS) into the off-gas system at a location convenient for making measurements. This increased the velocities to measurable values and had the added benefit of providing optical view ports that were used by the LDV system to measure gas velocities as well.

The Method 5 tests were conducted, and data on particulate loading were obtained. However, maintaining isokinetic sampling proved difficult due to the fluctuations in the off-gas flow rate. The resulting velocity changes were due to several factors including the necessity of varying the flow rate through the torch to keep the arc attachment point moving on the rear electrode. Another significant perturbation to the flow was the sudden increase in gas volume which resulted from the pyrolyzation of the feed material as it was added. Rapid changes in the off-gas flow rate required frequent manual adjustments to the Method 5 system. These adjustments could not be made fast enough to keep up with the flow rate changes.

Following the WSRC tests, the condensate collected in the Method 5 impingers was analyzed for chloride and some heavy metals. With one exception no heavy metals were found in the water, however significant amounts of chloride were found in each sample. The test during which briquette material was fed rapidly resulted in detectable levels of cadmium and lead being present in the impinger water. A complete account of the gas analysis and Method 5 sampling for WSRC can be found in the test report.¹

Another task undertaken was the development of updated software for the gas analysis system. The software in use by the system is based on older computer technology and works well for most of our purposes. The major drawback of the software is that it is inflexible, making it difficult to add new analyzers to the gas analysis system. Future plans to export real time data to

other systems such as the torch control system also called for a software update.

After a careful evaluation of the existing software, specifications were developed for the new software. These specifications were sent to several vendors with a request that the vendor provide additional information on their product based on our needs. This information was evaluated resulting in the selection of a new software development system. Further, the selection process was kept general and documented so that the procedure could be used in future selections. This selection procedure was documented in a technical report.² With minor modification, this procedure can be easily adapted as the basis for selection of other software packages.

A bonus of the EPA method work was the development of spreadsheets to handle the data recording and calculations involved in the methods. Initially, these spreadsheets were constructed with a focus on the WSRC tests and the facilities available at DIAL. Since that time, additional work has been spent on making these spreadsheets more general and of value to a larger audience. As these become better developed they will be made available for use by others.

DIAL also conducted an evaluation of the FireJet 1000 cutting torch this year. Part of this evaluation involved the determination of the particle size distribution found in the gas stream from the scabbling of concrete. After evaluating several of the standard particle sampling methods, an ambient air monitor were purchased for use with the FireJet 1000. Results from this test were promising and the difficulties encountered such as high particle loadings, high temperatures, and low velocities were overcome. Results from these tests are reported in the final report for the FireJet 1000 cutting torch evaluation.³

Continued use of the briquette material specified in Table 12-1 for tests resulted in a decreased lifetime of sensors on the combustibles and oxygen analyzers. Since previous testing revealed that the gas was typically highly acidic, the manufacturer was contacted, and it was determined that acid gases were indeed responsible for the shortened sensor lifetimes, and an acid gas scrubber was needed. Such a scrubber was designed and installed on the analyzers that require it. This will ensure acceptable sensor lifetimes and eliminate the reliability problems caused by the acid gases.

Project Status

This is an on-going project, and it is on schedule.

Project Significance

This project is significant in that it allows routine monitoring of the gases generated at DIAL's test facilities, thereby providing the customer with a complete picture of the process. The collection and archiving of this data adds to the engineering knowledge database of plasma torch processes.

FY 96 Plans

Plans for the gas analysis system include the continued operation of the system when the test facilities are operated. This will continue to provide data on the operation of facilities, archival data for trend analysis, and data to be used for comparison with, and in support of, other systems and instruments.

Expansion of the gas analysis system is also planned. Other gases have become of interest, and analyzers to detect them will be purchased. Of specific interest is HCl and Cl₂. An evaluation will be made of which gas is of greatest interest and if an appropriate analyzer is available which can be utilized.

Unburned hydrocarbons have been observed in previous tests, however no instrumentation exists at DIAL to specifically determine these hydrocarbons. Plans are to purchase a flame ionization analyzer that will give total carbon present in a gas stream. This instrument will be used to expand our EPA methods capabilities, specifically Method 25A, Determination of Total Gaseous Organic Concentration Using a Flame Ionization Analyzer.

Difficulties encountered in maintaining isokinetic sampling in the plasma torch off-gas system can be overcome by automating the sampling rate adjustments. A Method 5 apparatus is now available which provides this capability. We plan to purchase such an apparatus during FY 96. This will be a significant cost savings over developing such a system in-house.

To further improve the accuracy of the gas analysis data collected, a gas dilution system will be purchased and used to calibrate the instruments. This system will accurately dilute gas samples to various known concentrations allowing a calibration curve to be made for each analyzer. This curve can then be programmed into the new gas software to compensate for any small deviations in the linearity of the analyzer output.

References

1. Etheridge, John A., et al. 1995. *Refractory lifetime testing for Westinghouse Savannah River Company*. Mississippi State University: Diagnostic Instrument and Analysis Laboratory. DIAL 10575 TR 95-3.
2. Green, Robert A. and Philip, Thomas. 1995. *Evaluation procedure for the selection of a graphical programming language for gas analysis software devel-*

opment data. Mississippi State University: Diagnostic Instrument and Analysis Laboratory. DIAL 10575 TR 95-2.

3. Kumar, R. Arun. 1995. *FireJet 1000 test report.* Mississippi State University: Diagnostic Instrument and Analysis Laboratory. DIAL 10575 TR 95-2.

13 Laser-induced Breakdown Spectroscopy

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

Introduction

Laser-induced breakdown spectroscopy (LIBS) is a laser-based advanced diagnostic technique for measuring the concentration of various elements in the test medium. In the LIBS technique, a pulsed laser beam is focused at the test point to produce a spark. The spark in the focal region generates a high density plasma which produces and excites various atomic elements in the test volume. Atomic emission from the plasma is collected with a collimating lens and sent to the detection system. The intensity of the atomic emission lines observed in the LIBS spectrum are then used to infer the concentration of the atomic species.

Toxic metal emissions from various waste processing off-gas systems represent a significant health hazard. The real time measurement of selected toxic metals in stack emissions would be useful to control the quantities of these species emitted into the atmosphere. A real time toxic metal monitoring system is also needed to measure the metal concentrations in the off-gas system to monitor and control the processing system. LIBS is being evaluated as a near real time measurement technique for monitoring the concentration of metallic species in the off-gases from waste processing facilities.¹

Recently, a portable, mobile and versatile LIBS system has been developed at the Diagnostic Instrumentation and Analysis Laboratory (DIAL), Mississippi State University (MSU) to monitor toxic metal concentrations in the off-emission of a plasma hearth process system. It has been used to measure the concentration of toxic metals in the off-gas from a Savannah River (SR) surrogate vitrified with DIAL's plasma torch facility.² Off-gas measurements have also been made at the Western Energy Technology Office (WETO) torch facility/ Mountain State Energy (MSE), Montana.³ In addition, the performance of this system has been evaluated in the Advanced Analytical Instrumentation Demonstration (AAID) test at Science Applications International Corporation (SAIC)'s Star Center, Idaho Falls, ID.^{4,5}

Work Accomplished

Work was performed during 1995 to explore various LIBS applications to expand the LIBS scope. These applications are summarized as follows. LIBS can be used to monitor RCRA metal concentrations in the off-gas and in melt glass/slag of various waste treatment facility's off-emission and in melt glass/slag. LIBS has also been found to be applicable for measuring RCRA metals in dust, soil and water. Concentration measurements of both major and minor species in the melt glass can be performed to measure the composition of the glass. Concentration of radionuclides in off-emission and in melt glass can also be measured. These various species concentration measurements in real time or near real time can be used to develop a process monitor for various hazardous waste treatment facilities.¹

DIAL has three different LIBS setups. Two systems are to perform various studies in the laboratory, and the third one is to perform field measurements. The results of various studies and measurements with these systems are given in the following sections.

Quantitative Analysis of Vitrified Glass

Glass from the EnVitco melter was analyzed by recording the LIBS spectra with a 0.75-m Spex spectrograph equipped with 1800 lines/mm grating. A PARC OMA II system was used as a detection system. The details of the LIBS instrument are described elsewhere.⁶ The inferred concentration from LIBS is compared with a chemical analysis to evaluate the quantitative measurement capability of the LIBS technique.

A broad range of wavelengths, from 260 to 520 nm, was investigated in order to perform a comprehensive elemental analysis. Such a wide range investigation is necessary, because emission lines in some wavelength ranges are not suitable for quantitative analysis due to the lack of information on the transition probabilities of the emission lines or self-absorption. Moreover, a wide range recording is very helpful for the identification of the spectral lines, improving the reliability of the line assignments.

The resolution of the spectrum is quite good, but the information in one spectrum is less due to its narrow coverage of 8 nm. The emission intensities were calculated by the net peak heights, rather than by the net peak areas. The relative concentrations of the elements were obtained by the ratio of line intensities of different species within one spectrum. Generally, several lines were chosen for one species in the determinations of the relative concentrations. This procedure was performed by a computer fitting program with the use of the least square fit. Figure 13-1 shows a typical fitting spectrum in which the

neutral iron line, 371.99 nm, was not fitted by the program due to its self-absorption. The lower level energy of this line is zero.

Plenty of ion lines were observed in the experiment. The ionization degree of various species is quite different and very sensitive to the plasma temperature. The contributions of ions should be included in the determination of relative concentrations. Generally, upper level energies of most ion species require much more energy than that of neutral species, resulting in a lower number density of excited ions. Therefore, the emission lines from ions were difficult to observe, even though there were plenty of ions in the plasma. For the gate width of 30 μ s, plasma properties tend to be stable during the experiments. The ionization degree of an element in the plasma depends on the ionization potential of that element, the plasma temperature, and ratio of partition functions of that atom to the ion.

In our case, the electron density was about $1.3 \times 10^{15} \text{ cm}^{-3}$, which was obtained from the Fe(I) and Fe(II) lines in the spectrum centered at 279 nm.

Rearranging Saha's equation and substituting the value of the electron density we have

$$\log\left(\frac{\alpha}{1-\alpha}\right) = 0.684 + \frac{3}{2}\log(T) - \frac{5040}{T}V + \log\frac{Q_i(T)}{Q_a(T)}$$

By using this equation, the mole ratios of two elements are greatly improved. The calculation details are described elsewhere.⁶

The validity of the Boltzmann and Saha equations is based on the assumption that the plasma is in LTE. In an LTE plasma, the collision excitation and de-excitation processes must dominate with respect to the radiative processes, which require a minimum electron density. The lower limit for electron density for an atomic level in a particular ionic state to be in collision-dominated equilibrium with higher levels is determined by the criterion:⁷

$$n_e > 7 \times 10^{18} \frac{Z^6}{n^{17/2}} \left(\frac{kT}{E_H}\right)^{1/2} (\text{cm}^{-3})$$

where Z is ionic charge, n principal quantum number, T plasma temperature, and E_H ionization energy of hydrogen. In our case, the principal quantum number of the lowest energy level is 3, and the highest temperature is 7300 K, resulting in a lower limit for electron density of $1.3 \times 10^{14} \text{ cm}^{-3}$. The measured densities are greater than this value, indicating that LTE is likely to exist

throughout the excited states of species in the plasma.

Table 13-1 lists the central positions of the spectra and the emission lines used for the concentration determinations. The lines which were not used for the analysis due to their strong absorption, or the lack of transition information, or the overlap with other lines for which transition probabilities were unknown, are not listed in the table. Some elements were analyzed in several spectra, and the results were quite consistent. After making the ionization correction, the values measured by LIBS were in good agreement (approximately 10%) with the values of the Mississippi State Chemical Laboratory (MSCL) analysis, except Ni, Mn, Ti and Cr. The agreements indicated the importance of the ionization correction in the determination of relative concentration. Further work continued to find reasons for not applying the ionization correction for some of the elements.

Table 13-1. Emission lines used to determine elemental concentrations by LIBS.

Central Position (nm)	Element	Wavelength of Emission Line (nm)
264	Fe ⁺	260.71, 261.19, 261.38, 261.76, 262.17, 262.57, 262.83, 263.11, 263.13, 264.62, 266.47, 266.66
	Al	265.25, 266.04
	Si	263.13
279	Fe	275.63, 278.82
	Fe ⁺	275.57, 277.99
	Mg	277.98
300	Fe	297.31, 297.32, 298.14, 298.36, 299.44, 299.45, 299.95, 300.09, 300.05, 300.81, 301.76, 301.90, 302.40, 302.56, 302.58, 303.74
	Ni	298.17, 299.45, 300.25, 300.36, 301.20, 303.79
	Ca	299.50, 299.73, 299.96, 300.09, 300.92
326	Ti ⁺	323.45, 323.66, 323.90, 324.20, 324.86, 325.29, 325.43, 326.16
	Cu	324.75, 327.40
332	Na	330.24, 330.30

Table 13-1. Emission lines used to determine elemental concentrations by LIBS.

332	Fe	330.63, 330.60
	Ti	334.19, 335.46
	Ti ⁺	332.29, 332.95, 333.52, 334.03, 334.19
344	Ni	349.30, 350.09, 351.03, 351.51, 351.98, 352.45
	Fe	342.71, 346.59, 347.55, 347.67
352	Ni	349.30, 350.09, 351.03, 351.51, 351.98, 352.45
	Fe	349.06, 349.78, 351.38, 352.13, 352.60
359	Fe	356.54, 358.12, 358.53, 358.70, 360.89, 361.88
	Ni	356.64, 359.77, 361.94
	Cr	357.87, 359.35, 361.94
372	Fe	368.75, 370.92, 372.26, 372.76, 373.33, 373.49, 373.71, 374.34, 374.56, 374.59, 375.83, 374.95
	Ti	372.98, 374.11, 375.29, 376.13
	Ca ⁺	370.60, 373.69
387	Fe	383.42, 384.04, 384.11, 385.00, 385.64, 385.99, 387.80, 387.86, 388.63, 388.71, 388.85, 389.57, 389.97, 390.65, 390.68
	Si	390.55
404	Fe	404.58, 406.36, 407.17
	Mn	403.08, 403.31, 403.45, 403.57, 404.14, 404.88, 405.55, 405.89
	K	404.41, 404.72
429	Fe	427.18, 432.58
	Ca	428.94, 429.90, 431.87
519	Cr	520.45, 520.60, 520.84
	Mg	516.73, 517.27, 518.36
	Ti	517.37, 519.30, 521.04
	Ca	518.89

Most of the elements in the sample were detected in the experiment, which compose of a high percent composition in the sample. The absolute concentrations of elements can be derived by converting the mole ratios of elements to the relative weight percentages of their oxides, normalizing the results by total weight of the oxides, and then converting the weight percentages of the oxides to the weight percentages of the elements. Table 13-2 lists the absolute weight percentages of the elements in vitrified glass obtained by LIBS and MSCL. Relative deviations of the LIBS method to MSCL are within 6 to 13% for most of the elements.

Table 13-2. Mole ratio of elements and their weight percentages in the vitrified glass obtained by LIBS and MSCL, and their relative deviations.

Element	Mole Ratio Normalized by Fe (LIBS)	LIBS Weight Percentage (Wt %)	MSCL Weight Percentage (Wt % $\pm$ 0.05 - 0.1%)	Relative Deviation (%)
Si	39.84 ± 2.31	22.69 ± 1.32	24.23	-6.4
Ca	17.34 ± 1.32	14.09 ± 1.06	14.05	0.28
Fe	1	1.13	1.2	-5.8
Al	12.28 ± 0.79	6.72 ± 0.43	7.6	-11.6
Na	18.82 ± 1.03	8.77 ± 0.48	9.6	-8.6
Ni	0.109 ± 0.005	0.130 ± 0.006	0.16	-18.8
Mg	1.45 ± 0.20	0.71 ± 0.10	0.64	10.9
Mn	0.049 ± 0.001	0.055 ± 0.001	0.049	12.2
Ti	0.535 ± 0.005	0.052 ± 0.004	0.055	-5.5
Cr	0.051 ± 0.005	0.054 ± 0.005	0.059	-16.4
Cu	0.036 ± 0.004	0.046 ± 0.005	0.055	-16.4
K	4.14 ± 0.24	3.28 ± 0.19	3.0	9.3

Effect of Glass Temperature to the LIBS Measurement

The LIBS experimental setup was modified, as shown in Figure 13-2, to record the LIBS spectra at different glass temperatures. The glass from the EnVitco melter was kept in a crucible with an inner diameter of 5 cm and height of 7.5 cm and melted in a furnace whose temperature was raised to 1400°C. The crucible with melt glass was kept on a traverse system to record

the LIBS spectra. The temperature of the surface of the melt glass was monitored with a pyrometer. The concentration ratio of Ni/Fe was inferred at different temperatures from the spectra. Figure 13-3 shows the variation of Ni/Fe concentration at different temperatures. The concentration ratio of the melt glass inferred by LIBS is the same as glass at room temperature. Further work continues to compare the LIBS inferred concentration of various species with melt glass and glass at room temperature.

Calibration

LIBS spectra were calibrated with a metal hydride generator.^{8,9} Metal hydrides with N₂, He or Air as a buffer gas has been filled in a stainless steel sample cell. LIBS spectra were recorded at different metal hydride concentrations to plot a calibration curve. Figures 13-4 and 13-5 show the calibration curve for Sn in 760 torr N₂ and Air, respectively. The slope of the calibration curve in the air is ~ 7% higher than in the N₂. A calibration curve was also obtained in the He to compare the sensitivity in different atmospheres. Similar calibration curves were obtained for other toxic metals. The details of various results are described in Reference 8. In brief, He gives a lower plasma background than N₂, and also the intensity of atomic emission lines is higher in the former than later. The limit of detection (LOD) for Sn in the presence of He is ~2.5 times higher than in N₂. The LIBS signal varies with time in a steady flow measurement. The time period in which the signal is constant and maximum is 0 - 50 sec in N₂ and 100 - 400 sec in He. The signal during this time period was used for calibration. The various LIBS measurements are quite reproducible.

LIBS calibration was also performed for RCRA metal by using a nebulizer.⁴ Figure 13-6 shows the calibration curve for Cr in air. Similar calibration curves were obtained for other RCRA metals. The limit of detection (LOD) of the various elements was derived from calibration curves, as shown in Table 13-3. The precision and accuracy near the LOD was higher than the measurement at high concentration. The precision and accuracy presented in the table was averaged from the low and high concentration data points. The LOD is estimated using the following formula

$$LOD = (3\delta)/S$$

where δ (counts) is the noise obtained from the background signal, S is the slope of the calibration curve in counts/ppm.

Table 13-3. LIBS detection limits of 10 RCRA elements.

Element	Line (nm)	Det. Limit $\mu\text{g/scm}$	Precision %	Accuracy %
As	278.02	1,199.0 ^a	24.6	8.9
Be	313.04 (+)	1.2	13.2	6.1
Cd	326.11	239.8	18	3.4
Cr	425.44	12.0	10.4	14.7
Co	345.35	48.0	19.9	8.2
Hg	253.65	1,360.0	8.2	13.5
Mn	259.37 (+)	12.0	15.3	2.7
	257.61 (+)	7.0	17.8	4
Ni	341.48	61.7	3.4	8.9
Pb	405.78	136	8.5	13.4
Sb	259.81	239.8	20.0	8.6

^a LOD will reduce to 240 $\mu\text{g/scm}$ with 189.0-nm line.

Mobile LIBS System

A portable, mobile and versatile LIBS system was developed during 1995 at DIAL to monitor toxic metal concentrations in the off-emission of a plasma hearth and melter which are being used to process hazardous waste. It has been used to measure the concentration of toxic metals in the off-gas from a Savannah River (SR) surrogate vitrified with DIAL's plasma torch facility.² In addition, the performance of this system was evaluated in the Advanced Analytical Instrumentation Demonstration (AAID) test at Science Applications International Corporation's (SAIC) STAR Center, Idaho Falls, ID.^{4,5} This system was also used to investigate the possibility of detecting radionuclides at Argonne National Laboratory-West (ANL-W). The results of some of the measurements are described in the following section.

Plasma Torch Measurements

The heart of the DIAL plasma hearth facility is a 250-kW Plasma Energy Corporation, PT-150 plasma torch. The plasma torch was operated in the transferred mode with air as the plasma medium. The hearth was a small graphite container, 30 cm inner diameter and 23 cm height. The LIBS measure-

ments were performed at an optical port located 112 cm from the plasma torch chamber.

Tests at DIAL on the WSRC surrogate feed were performed in March 1995 to determine the lifetime of various refractory materials. The simulated feed in a briquette form was fed into the torch hearth for vitrification. Typical LIBS spectrum at a central wavelength of 360 nm and 412 nm are shown in Figure 13-7. The various identified lines are marked in the figure. The spectra were recorded with a 2400 l/mm grating.

The elements present in the off-gas just downstream of the graphite crucible were identified as Al, B, C, Ca, Ce, Cd, Cr, Cs, Fe, K, Mg, Mn, Na, Pb, Si, Ti, Y and Zr from the LIBS spectra recorded at various spectral regions during several SR surrogate test runs. It should be noted that various refractory materials were initially placed in the graphite crucible to study their durability under vitrification with the surrogate waste. Special attention was given to the spectral regions with Pb, Cr, Cd and Cs atomic transitions. The LIBS spectra were also collected continuously to study the variation of metal concentration with time. The typical data integration period for this test was 3.5 seconds. Generally, the metal concentration increased right after new feed was added to the plasma torch. Therefore, the metal concentration remained nearly constant for a few minutes, then started decreasing. However, this also depended on the arc attachment point in the melt glass which was quite random. The concentration ratios of various metals were also monitored with time. Figure 13-8 shows the concentration of Cr, Fe, Pb and Ti inferred from the LIBS data collected on March 6. The times when briquettes were added is marked with an X in the figures. For DIAL torch LIBS measurements, the data were evaluated with a calibration based on the Sn hydride generator.^{8,9} The individual element concentrations were calculated using experimental element intensity ratios and taking into account the response function of the detection system and the spectroscopic intensity parameters. The data analysis was based on the peak area of the analyte line.

Three Cd lines near the 361-nm spectral region were observed in most of the recorded spectra. However, it was difficult to obtain reliable concentrations from those lines due to the poor signal-to-noise ratio. Cs-137 is a radioactive element which is of concern in the treatment of DOE mixed waste. Concentration measurements of Cs -137 can be useful in process control. A Cs-137 line at 852.12 nm was observed during these test runs. The Cs concentrations were found to be rather constant during the various tests.

LIBS spectra were also recorded during the shutdown of the torch on March 8 to monitor the variation of the concentration of Pb and Fe during this shutdown process. The concentration of Pb and Fe dropped rapidly at the

moment the current was shut off. Since the glass and crucible were still hot for some time after the torch was shut off, this shows that much of the metal volatilization is due to the highly localized heating of the plasma arc. These observations are consistent with those obtained by using emission spectroscopy to monitor the emission of volatile species in the plasma torch chamber during these experiments.

SAIC's STAR Center Measurement

DIAL's LIBS system was used for near real time monitoring of toxic metal concentrations during a week-long test at SAIC's STAR Center. The STAR Center plasma system consists of the following components: plasma chamber; secondary combustion chamber; baghouse; HEPA filter; stack; and instrumentation and system control. The details of the STAR Center's facility are described in Reference 5. Two waste types were processed during the tests inorganic and organic sludge. The simulated wastes for the test were formulated in the STAR Center. The recipe of the simulated wastes can also be found in Reference 5. LIBS measurements were performed continuously at a port between the baghouse and the HEPA filter. To obtain a good signal-to-noise ratio, the typical sample integration time was 50 seconds in this test; this corresponds to averaging 500 laser pulses. The intensity of atomic emission lines observed in the LIBS spectrum was used to infer the concentration of the atomic species using calibration data obtained from a nebulizer. The EG&G OMA2000 software was used to collect the LIBS data. A user-written macro program was used to analyze and display the data in near real time. The detector controller was also interfaced with the facility computer to provide information on the metal concentration levels. Figure 13-9 shows the interface layout of the LIBS system with the SAIC's STAR Center alarm/interface system. The concentrations of three elements vs time and the currently acquired LIBS spectrum are displayed on the computer screen. Moreover, the concentration of five selected species can be displayed at the bottom of the computer monitor during the data acquisition. TTL signals are sent to the alarm/interface system, and a warning message is also shown on the bottom of the computer screen whenever the concentration of the probed species is above the alarm level during the LIBS measurements. This can allow the operator to modify operational parameters of the plasma system to prevent emissions that exceed the pre-established facility limits.

Five metals, Pb, Ni, Cr, Se, Hg and Ce (as a nonradioactive surrogate for Pu) were preselected by the facility for real time monitoring with LIBS. The spectral regions near 418 and 359 nm both cover five of the six desired metals and were selected to monitor the metal concentrations during this test. Calibration data of Ce, Cr, Pb and Ni were collected in the DIAL laboratory with a nebulizer. Pb 393.99-nm lines in the 359-nm spectral region showed strong

interference from Fe lines which came from the metal container used to contain the feed. This interference prevented accurate concentration measurements of Pb in this spectral region. The data recorded in the 418-nm spectral region showed that this spectral region provides less interferences than the 359-nm spectral region. Data were collected in this spectral region for the rest of the test. The metals monitored in this spectral region are Pb, Ce, Cr and Hg. Although there were some Se^+ lines in these spectral regions, they were well below the detection limit and therefore were not monitored in this test. Unfortunately, there was an interference between the CN emission band and the Ce line in the 418-nm region; this reduced the accuracy of the inferred Ce concentrations. Therefore, the inferred Ce concentrations have an uncertainty of ~100%. The concentration accuracies for Cr were estimated to be between 1 and 15% for concentrations above 100 $\mu\text{g}/\text{scm}$. The accuracies were estimated to be ~15 - 30% for concentrations below 100 $\mu\text{g}/\text{scm}$. Since the Hg 435.83-nm line is a relatively weak line, the calibration data of this line has not been obtained experimentally. Rather, the calibration factor for Hg used in the analysis was calculated based on the calibration of the Cr 425.435-nm line. The error in the Hg calibration was mainly from the uncertainties in the spectroscopic constants and the gas temperature and was estimated to be 200%. Figure 13-10 shows a LIBS spectrum recorded in the spectral region of 397 - 440 nm at 22:05 on June 8. The emission lines of the analyte elements are marked in the figure. The inferred metal concentrations of Pb, Ce and Hg from this spectrum are all above the alarm limits. The emissions from CN, Ca, Mn and Fe can also be seen clearly in the figure.

Figure 13-11 shows a typical variation of the metal concentration with time on June 8, 1995, 19:41 - 20:59. Most of the time, the metal emission was near or slightly above the LIBS detection limit. From time to time, metal emissions went up close to the alarm levels. It indicated there might have been some problems in the plasma torch operation or in the baghouse at that particular moment. The TTL signals were successfully sent to the alarm/interference system when the concentrations went above the alarm limit. Details of results of these measurements were described further in Reference 4.

ANL-W Measurement

A study was performed to investigate the possible use of LIBS for measurement of the radionuclides in a high-level waste site. LIBS spectra of Pu and Np samples were recorded in a glove box and U LIBS spectra were recorded in an ordinary laboratory at ANL-W. Figures 13-12 - 13-14 show some typical spectra of U, Pu and Np. The trace impurities from the samples were determined, and the spectral interferences were studied by recording the LIBS spectra in different spectral regions. The U spectra were also recorded at

various concentrations at DIAL to obtain the U calibration. The details of the LIBS study of radionuclides is described in Reference 10.

Conclusions

DIAL's LIBS system has been used to record LIBS spectra of various elements in the off-gas streams at two thermal treatment facilities. The emission lines were calibrated to infer the concentration of the elements. These measurements show that LIBS can be used to monitor the concentration of selected toxic metals in the off-gas. In particular, the tests at various waste treatment facilities indicated that LIBS real time toxic metal measurements can be used as a process control monitor during hazardous waste processing. LIBS measurements at various locations in the off-gas emission can also provide information on operation of particular system components, such as the baghouse, HEPA filter, etc. Interfacing of LIBS with a waste treatment facility main computer can be used to control the waste treatment process for safe operation of the facility and also to satisfy the EPA compliance requirements for selected toxic metal emissions. For example, for plasma torch processing the air flow or the feed to the plasma torch can be automatically adjusted whenever the LIBS toxic metal concentration increases beyond a certain preassigned threshold limit. Interfacing of the LIBS system with a plasma torch facility computer for plasma torch control is currently being tested at DIAL.¹¹

Project Status

One of the milestones, LIBS measurement with melt glass at Clemson University, was delayed because the field trip was postponed. A field trip is being planned during December 1995 to measure the composition, both major and minor species, of melt glass. All other milestones were completed.

Project Significance

The measurement of RCRA metals in the off-gas emission at various DOE sponsored test facilities shows that LIBS can be used as a process control monitor during the treatment of various wastes. The preliminary work on melt glass and radionuclides also supports the idea of using LIBS to monitor both off-emission and waste products which can be used to develop a process control even for treating nuclear waste.

FY 96 Plans

Initial work on the quantitative measurement of glass composition is very encouraging. Further work will continue to improve accuracy and detection limits. Work on quantitative measurement of melt glass composition and

quantitative concentration measurement of radionuclides in off-emission will continue in FY 96. Various field measurements will also be performed as requested by DOE facilities or private industries. The FY 96 plans are described in detail in the FY 96 TTP.

References

1. Singh, J.P., et al. 1996. Study of laser induced breakdown spectroscopy as a process control for hazardous waste remediation. *Appl. Opt.* To be published.
2. Etheridge, J.A., et al. 1995. Refractory lifetime testing for Westinghouse Savannah River Company. Mississippi State University: Diagnostic Instrumentation and Analysis Laboratory. DIAL 10575 TR 95-3.
3. Cook, R.L., et al. 1994. Plasma arc centrifugal treatment system, Western Environmental Technology Office, MSE, Butte, Montana. Mississippi State University: Diagnostic Instrumentation and Analysis Laboratory. DIAL 10575 Trip Report 94-3, pp. 38-53.
4. Cook, R.L., et al. 1995. Advanced analytical instrumentation demonstration - LIBS measurement, SAIC's STAR Center, Idaho Falls, Idaho. DIAL 10575 Trip Report 95-1.
5. Cornelison, C., et al. 1995. Final report for the advanced analytical instrumentation demonstration, SAIC/MSE. SAIC Report SAIC-95/1308.
6. Feng, Simin. 1995. *Quantitative elemental analysis of vitrified glass by laser induced breakdown spectroscopy and plasma characterization*. M.S. Thesis, Mississippi State University.
7. Hauer, A.A. and Balidis, H.A. 1989. *Laser-induced plasmas and applications*. L.J. Radziemski and D.A. Cremers, eds. New York: Marcel Dekker, ch. 3, p. 105.
8. Singh, J.P., et al. 1995. Investigation of the effects of atmospheric conditions on the quantification of metal hydrides using laser induced breakdown spectroscopy. *Appl. Spectrosc.* Submitted.
9. Zhang, H.; Singh, J.P. and Yueh, F.Y. 1996. Quantitative metal concentration measurement by laser induced breakdown spectroscopy. To be published.
11. Yueh, F.Y., et al. June 1996. *Interfacing of laser induced breakdown spectroscopy system with a plasma torch control computer for hazardous waste process control*. 27th AIAA Plasmadynamics and Lasers Conference, New Orleans.

10. Singh, J.P., et al. 1995. A preliminary study of the determination of uranium, plutonium and neptunium by laser induced breakdown spectroscopy. *Appl. Spectrosc.* To be published.

Figure 13-1. Fitting of the computer simulated spectrum with the LIBS spectrum of glass from Envitco melter.

Figure 13-2. Schematic diagram of the LIBS experimental setup used for glass measurement at different temperatures.

Figure 13-3. Variation of inferred concentration ratio of Ni/Fe with molten glass temperature.

Figure 13-4. Calibration curve for Sn in 760 torr N₂ using metal hydride generator.

Figure 13-5. Calibration curve for Sn in 760 torr air using metal hydride generator.

Figure 13-6. Cr calibration curve in air using a nebulizer.

Figure 13-7. Typical off-gas LIBS spectrum at DIAL/MSU from SR-surrogate feed at the central wavelength of (a) 360 nm and (b) 412 nm.

Figure 13-8. Variation of metal concentrations with time in DIAL/MSU off-gas. The Cr, Fe, Pb, Ti concentrations were monitored between 11:21:00 - 11:40:33 and 13:33:25 - 13:38:25.

Figure 13-9. Schematic of LIBS system and the SAIC's STAR Center alarm/interface system.

Figure 13-10. A LIBS spectrum recorded at STAR Center on June 8, 1995.

Figure 13-11. Variation of metal concentrations with time in SAIC's STAR Center off-gas on 6/8/95, 19:40-20:59.

Figure 13-12. LIBS spectrum of U in the spectral region of 407 - 426 nm.

Figure 13-13. LIBS spectra of Pu recorded in the spectral region of 444 -463 nm.

Figure 13-14. LIBS spectra of Np recorded in the spectral region of 444 - 463 nm.

14 Laser Ultrasonics Viscosity Measurement

Jagdish P. Singh, R. Daniel Costley and Krishnan Balasubramaniam

Introduction

Work on this project began in August 1995. The plans for the first year were to show the feasibility of measuring the viscosity of various liquids using conventional ultrasound and laser ultrasound. The technique being used exploits the relationship between the shear wave reflection coefficient from a solid-liquid interface and the viscosity of the liquid. Shear waves are ultrasonic type waves that propagate in solid materials such that the particle motion associated with the traveling wave is perpendicular to the propagation direction. Their speed of propagation is roughly half that of longitudinal waves. The technique being investigated involves launching shear waves into a solid material and reflecting them off of an interface between the solid and the liquid of interest. This result is compared with a reference signal, obtained by reflecting a shear wave off of a solid-air interface (or else with a liquid with negligible viscosity). The ratio of the amplitude of the reflected shear waves for these two cases is the reflection coefficient.

Work Accomplished

Theoretical studies performed this year have extended the work of other investigators.^{1,2} These results basically show that the shear wave reflection coefficient from a solid-fluid interface is a function of the viscosity and density of the fluid. The reflection coefficient is a complex number and either its phase or magnitude can be used to calculate the viscosity. The density and shear wave speed of the solid also enter in as factors. By choosing solids with desirable properties, the reflection coefficient can be made sensitive to different viscosity ranges. A window of 20 - 100 poise has been identified as a desirable range for waste glass processing. With this in mind, our goal should be to determine the actual viscosity in this range to within 10 poise and to be able to determine when it is not within this range.

In conjunction with the theoretical analysis, a series of experiments have been performed using conventional ultrasonics. In order to measure the reflection coefficient of shear waves, an ultrasonic shear wave transducer was mounted on one end of a solid block, or shoe. The other end of the shoe was immersed in the viscous liquid. The shoe was designed so that a repeatable reflected shear wave could be recorded and compared with a reference, or zero

viscosity, case. Care also had to be taken with mounting the transducer so that the coupling between the transducer and the shoe would not vary and thus cause unwanted variations between the reflected signals. The design has gone through several iterations and substantial improvements have been made. Progress is still being made in its design, particularly in finding suitable materials for making measurements at high temperatures.

A simple schematic of the experimental arrangement used is shown in Figure 14-1. For most of the experiments a 2.25 MHz shear wave transducer was used in pulse-echo mode. A standard ultrasonic pulser unit served to excite the transducer and receive and amplify the reflected signals, which were then recorded with a digital oscilloscope. These signals were transferred to a mini-computer. Using algorithms developed during the theoretical studies, these signals were processed to predict the viscosities of the various liquids tested.

A second set of experiments were performed at moderately elevated temperatures. The temperature was controlled using a temperature bath. It was found during this set of experiments that the temperature gradient in the solid shoe had to be accounted for. This was done by using water, instead of air, as the fluid with which to take the reference signal and heating it to the same temperature as the liquid being measured. The viscosities of various liquids, up to 250 poise, were measured in both sets of experiments. The results are displayed in Tables 14-1 and 14-2. As can be seen, in many of the trials we are meeting our goal of measuring within 10 poise.

Table 14-1. Measurement of viscosity using piezoelectric transducers at 25°C. All values are in poise.

Calibrated Viscosity	Viscosity measured with phase technique				Viscosity measured with magnitude technique			
	Trial 1	Trial 2	Trial 3	Trial 4	Trial 1	Trial 2	Trial 3	Trial 4
52	44	65	73		165	60	61	
104	115	103			132	77		
224	182	280	212	113	174	186	257	232

Table 14-2. Measurement of viscosity using piezoelectric transducers at 60°C using temperature compensation scheme. All values are in poise.

Calibrated Viscosity	Viscosity measured with phase technique	Viscosity measured with magnitude technique
23	22	28
85	81	56
123	175	119

This past year we were also able to perform experiments demonstrating the feasibility of laser ultrasonics to measure viscosity of liquids. The technique is basically the same as with conventional ultrasonics. The viscosity is still measured by determining the reflection coefficient of shear waves. The main difference is that the ultrasound is generated by a pulsed laser and detected using a laser interferometer so that the technique is completely non-contact as far as the transducer is concerned. However, for the feasibility study performed this past year, the feasibility of using laser ultrasound was demonstrated using piezoelectric transducers instead of an interferometer to detect the reflected shear waves. The results of these experiments are shown in Table 14-3. The results are very encouraging. The results of both approaches, the conventional ultrasonics with piezoelectric transducers and laser ultrasonics, are discussed in more detail elsewhere.^{2,3}

Table 14-3. Measurement of viscosity at room temperature with laser generated shear waves and using magnitude technique.

Density (kg/m ³)	Calibrated Viscosity (poise)	Measured Viscosity (poise)
875	52	46
881	104	117
887	224	276
891	416	412

Project Status

The feasibility of using the shear wave reflection technique to measure viscosity has been clearly demonstrated. In addition, the laser beam power density is sufficiently large that if the laser beam strikes an electrode, then a

LOGS signal is produced (due to ablation or photoelectric emission) that is significantly larger than the LOGS signal of the species of interest; thus, there is a limitation on how close the laser beam can be positioned to an electrode. The viscosity of various calibration liquids have been measured with both conventional ultrasound and laser ultrasound. As previously mentioned, the repeatability of the measurements and the sensitivity of the technique need to be improved. We believe this can be done by improving the coupling between the transducer and the solid shoe. This problem was avoided with the laser generated ultrasound because there is no transducer to couple.

For the laser ultrasonics case, improvements in the signal-to-noise ratio need to be made in the laser interferometer so that the reflected shear waves can be recorded. However, when using laser generated ultrasound with piezoelectric detection, the system performed at or above expectations.

Project Significance

Viscosity is an important parameter in the processing of waste glass for several reasons.^{4,5} The most obvious of these is that this parameter indicates whether the molten material will indeed pour, or if it will clog the outlet ports instead. Just as importantly, the viscosity of the melt also affects the quality of the final glass product, whether it will indeed become an amorphous solid or whether some crystallization will occur. Also, allowing the melt viscosity to reach too low a value could cause excessive corrosion in the melter.

In some types of processes, such as found in the glass or metals processing industries, the viscosity can be determined from the temperature of the melt because the materials which make up the melt, and their relative amounts, are well known. However, the constituents which make up waste streams are not well known. This makes the prediction of melt viscosity from temperature measurements difficult.

FY 96 Plans

The plans for this next year are to continue the development in both the conventional ultrasonic and laser ultrasonic approaches. The effort in conventional ultrasonics will be to improve the repeatability of the measurements and increase the sensitivity. We will also make a transition from the shoe to a buffer rod. The buffer rod will serve the same purpose as the shoe in that it will be the intermediate solid between the liquid and the transducer. However, it will have to be longer and made of a material that can withstand the high temperatures encountered in the melt. Thus, it will also have the function of insulating the transducer from the melt.

We will also continue the development of the laser ultrasonic approach to measure viscosity. The experiments performed last year with laser generation and piezoelectric detection will be repeated next year. However, for these experiments the piezoelectric transducers used for detection will be replaced by a laser interferometer. An interferometer for detecting ultrasound has already been assembled and is working. Improvements are being made to improve signal-to-noise ratio and to make it portable and field ready.

Once these measurements have been accomplished satisfactorily, these measurements will be repeated again at the higher temperatures that we expect to find in a waste processing facility. The plan at present is to modify a laboratory scale oven to allow optical access and to perform the measurements in the oven. It is also planned to develop a field ready system and identify a facility at which these measurements can be made.

References

1. Sheen, S.H.; Chien, H.T.; and Raptis, A.C. 1995. An in-line ultrasonic viscometer. In *Review of Progress in QNDE, Vol. 14*. D.O. Thompson and D.E. Chimenti, eds., pp. 1151-1158. New York: Plenum Press.
2. Shah, V., et al. 1996. Measurement of viscosity in liquids using reflection coefficient...phase difference method. To be published in *Review of Progress in QNDE, Vol. 15*. D.O. Thompson and D.E. Chimenti, eds. New York: Plenum Press.
3. Costley, R.D., et al. 1996. Shear wave wedge for laser ultrasonics. To be published in *Review of Progress in QNDE, Vol. 15*. D.O. Thompson and D.E. Chimenti, eds. New York: Plenum Press.
4. Arun Kumar, R. 1995. *Viscosity Measurements in Glass Melters*. Mississippi State University: Diagnostic Instrumentation and Analysis Laboratory. DIAL 10575 TR 95-1.
5. U.S. Environmental Protection Agency. May 1992. *Vitrification Technologies for Treatment of Hazardous and Radioactive Waste*. Report EPA/625/R-92/002, Center for Environmental Research Information, Cincinnati, OH 45268.

Figure 14-1. Experimental apparatus used to measure shear wave reflection coefficient for the determination of liquid viscosity.

15 Torch Operations/Correlations

Robert L. Cook

Introduction

In this section, we briefly review the correlations observed and the implications for application of an emission spectra monitor.

Work Accomplished

Emission spectra recorded during the vitrification of Savannah River soil consist of transitions from a small number of gas phase atomic species (Ca^+ , Cu, K, Li, N, Na, O) and from calcium-containing molecular species (associated with the dolomitic lime that was added as a vitrifying agent) superimposed on a blackbody continuum.

Emission spectra were observed from above the melt, from the primary chamber, and from the plasma itself. In contrast, emission spectra recorded during vitrification of a Savannah River mixed waste surrogate were rich in gas phase atomic and diatomic species also superimposed on a blackbody continuum. Emission has been positively identified for Al, C, Ca, Ca^+ , Cd, CN, Cr, Cs, Cu, Fe, K, Li, N, Na, O, Rb, and Si; emission from Ni and N_2 has been tentatively identified.

Besides simply monitoring lines for relative amounts of volatile species above a plasma torch melt process, the emission spectra can also be used as a temperature monitor. This could be multiwavelength pyrometer-type measurements using the clear background regions of the spectrum to measure the melt temperature. Or, using line intensity ratios, a measure could be made of the volatile gas temperature. In the visible and near-IR wavelengths, the atomic nitrogen lines span enough of a range in the upper state energy for a reasonable measure of plasma temperature. The measured temperature (7320 ± 2210 K) indicates that the nitrogen atoms are quite "hot". Here the estimate of the temperature uncertainty is based upon a linear least squares fit. The statistical uncertainty is of the same order as the inherent accuracy of such measurement; the measurement is based upon the Einstein A factors which have an uncertainty of $\pm 25\%$ for these lines.

The spectra reported here also indicate that calcium lines may provide a good monitor of temperature through a Saha-Boltzmann calculation, since

both neutral and singly ionized lines are strong and consistently present in the 390 to 450-nm wavelength region.

Information from emission spectroscopy could be used to optimize process control in order to minimize downstream treatment for producing acceptable off-gases. Emission spectroscopy is relatively inexpensive, robust and requires little optical access, a simple fiber port will suffice, and so should be considered for a real time monitor of the torch arc itself or the gas phase species above the melt. Such a monitor would require relatively simple analysis with appropriate choice of spectral lines. Table 15-1 gives recommended lines for real time monitoring of the presence of melt volatile species. These lines were chosen on the basis of line strength, lack of overlapping lines, unambiguous assignment, etc.

The emission project has been refocused to provide a real time monitor of the plasma torch performance and, in particular, to provide a monitor of electrode wear and to provide warning of a possible torch failure.

Table 15-1. Observed emission lines recorded during vitrification of Savannah River soil with dolomitic lime. The list includes only those assigned with some certainty. The wavelengths listed are generally those from the *MIT Wavelength Tables* for atomic species, and from *Pearse and Gaydon's Identification of Molecular Spectra* for molecular species.

Species	λ (nm)	Species	λ (nm)
Cu	510.55*	O	777.19/777.47
Cu	515.32*	Cu	793.13
Cu	521.82*	Cu	809.49
Na	588.99	CaO	816.7
Na	589.59	N	818.80
CaOH	603.8	N	821.43
CaOH	623.0	O	844.62/844.64/844.68
CaOH	641.5	Ca ⁺	849.90
Li	670.78	Ca ⁺	854.21
CaO	698.3	CaO	865.2
CaO	733.9	Ca ⁺	866.21

Table 15-1. Observed emission lines recorded during vitrification of Savannah River soil with dolomitic lime. The list includes only those assigned with some certainty. The wavelengths listed are generally those from the *MIT Wavelength Tables* for atomic species, and from *Pearse and Gaydon's Identification of Molecular Spectra* for molecular species.

Species	λ (nm)	Species	λ (nm)
K	766.49	N	868.03/868.34/868.62
CaO	768.78	N	870.33
K	769.90	CaO	922.9
CaO	771.22		

* Observed in second order

Project Status

Correlations and implications of diagnostic measurements will, in the future, be covered in the various diagnostic task discussions.

Project Significance

The measurement of various performance parameters and their correlation with the facility operation are important to the development of process monitors.

FY 96 Plans

This particular effort will be incorporated into the individual diagnostic tasks.

16 Modeling - Plasma Torch

O. P. Norton

Introduction

One focus area under this subtask was to develop a first principles numerical model of the plasma torch. A computational fluid dynamics (CFD) model for the gas flow issuing from the torch and impinging on a flat surface was augmented with a model for the current flow through the hot plasma. When this was combined with equilibrium chemistry calculations to compute the composition of the hot plasma, and with electrical conductivity calculations to predict the plasma's electrical properties, the resulting package had considerable capability for simulating the flow of plasma from the torch. Sample results, including predicted convective heat flux distributions on the flat surface (representing the glass melt in an actual vitrifier) were given in last year's annual report.¹

Work Accomplished

During FY 95, developmental effort on the plasma torch model was concentrated on quantifying the radiative heat transfer from the hot plasma. In many combustion systems, radiative heat transfer from the combustion gases is the dominant mode of heat transfer, and we suspected that the same might be true for the plasma torch, especially considering the high temperatures found in the plasma arc column.

To accomplish this, we used a code called NEQAIR2, developed at NASA's Ames Laboratory to predict radiative heat fluxes encountered during hypersonic flight. This program has considerable capability; the user specifies the composition of the plasma, and also the translation, rotational, vibrational, and electron temperatures. Given this information, the NEQAIR2 program computes the nonequilibrium radiative properties of the plasma.

Our use of NEQAIR2 is based on the equilibrium approximation. From the CFD model, we get the temperature distribution across the plasma arc. Using our equilibrium chemistry code, we generate the corresponding plasma composition profile across the plasma arc. Then, these numbers were input into NEQAIR2 to compute the spectrum which an observer would see when viewing the plasma arc along a line-of-sight across the diameter of the arc. (In keeping with the equilibrium assumption, the translational, vibrational, rotational, and electron temperatures were all equal.)

Figure 16-1 shows the results of this calculation compared to an experimental spectrum measured on DIAL's PT-50 plasma torch by Dr. David Monts. The agreement is quite good, especially considering that the experimental spectrum is not corrected for detector response.

Project Status

The CFD model of the plasma torch is working. We can model the flow of gas and current from where the plasma jet exits the end of the torch until it impinges on the flat cathode. We can predict the distribution of heat flux on the cathode. We can also predict the radiative properties of the plasma.

However, given the complex physics taking place in the plasma, further work could be done to improve our modeling of the plasma physics. Examples would include using a two-temperature model to allow the electrons to have a different temperature from the rest of the plasma, and the calculation of the magnetic field induced by the current flow and their effect on the flow of gas and current.

Project Significance

When using a plasma torch to vitrify waste materials, the "bottom line" is the delivery of heat flux to the melt. This is something that we can predict with this model. Clearly, the heat flux to the melt is the desired effect, but if this flux is concentrated in too small an area, excessive surface heating and volatilization can occur. Thus, the model we have developed would be applicable to studying this important problem.

Also, torch electrode (anode) life is an important problem. We believe that the wear process which occurs at the anode is a function of the intense heat flux produced at the arc attachment point. With further development, this model could be used to predict the properties of the arc attachment region inside the hollow anode and thus help us understand electrode wear.

FY 96 Plans

Further development work on this project has been canceled, due to lack of an identified customer for this technology.

References

1. Shepard, W.S., et al. 1994. *Application of modern diagnostic methods to environmental improvement*. Mississippi State University: Diagnostic Instrumentation and Analysis Laboratory. DIAL 10575 FY 94 Annual.

Figure 16-1. The top is an experimental spectrum, measured by Dr. David Monts on DIAL's PT-50 plasma torch. On the bottom is a spectrum computed by the program NEQAIR2. The two appear to coincide closely, especially when one considers that the experimental spectrum is not corrected for detector response. (The experimental spectrum is nearly missing the features past 1000 nm, due to a falloff of the detector response in this region.)

Modeling - Particle Size Distribution

John C. Luthe

Introduction

The main purpose of an FTIR instrument is to provide data on molecular species. However, in the typical infrared absorption spectrum observed on a waste treatment off-gas system, the molecular absorption bands do not cover the entire wavelength region. The otherwise unused background regions between the molecular bands include the extinction due to particles in the off-gas stream. The goal for these milestones of the modeling subtask, is to extract particle size distributions from the FTIR extinction data.

Work Accomplished

The concise statement of the problem is, given the measured optical depth as a function of wavelength, $\tau(\lambda)$, can anything be learned about the size distribution of the particles causing the optical extinction:

$$\tau(\lambda) = \int_0^{\infty} \pi r^2 Q(\lambda, r, m) n(r) dr$$

Where Q is the extinction efficiency, a function of the incident wavelength, particle size, and particle index of refraction, and n is the particle size distribution. The milestones for this subtask are the sequential steps to extracting the particle size distribution by solving the inverse problem.

The first step completed was the development of a program for the direct fit of the extinction data. With a nonlinear least squares fit it is possible to get reasonable estimations of the mean size and shape parameters for an assumed form particle distribution and particle index of refraction. While the shape of the fitted distribution is not a unique solution the fit does give a good estimate of the index of refraction. Any of the techniques for the integral inversion involve the computation of the integral kernel, in this case the Mie extinction cross section which is a function of the index of refraction.

The second step completed was the development of a program to perform the numerical inversion of the integral equation. The inversion is done with a modification of the constrained linear inversion method¹ as described by Ramachandran and Leith.²

The third and final step for the year was the correction and improvement of the inversion code. Since the inversion problem is ill-posed the solutions are non-unique and unstable with respect to errors and variations in the input data. These problems were overcome by optimizing either the input data subsets or the kernel integration limits to give the minimum deviation between the input data and the representations of the data reconstructed from the extracted distribution.

An example of typical FTIR data for a broad wavelength region of one to six microns is shown in Figure 16-2. The regions away from the molecular lines and bands are used for the analysis. Figure 16-3(a) shows the resulting particle size distributions from the inversion of synthetic data computed with the input distribution shown. The extracted distributions are the result of computations on subsets of the input data. Figure 16-3(b) shows the input synthetic data and the extinctions reconstructed from the corresponding result distributions in Figure 16-3(a). By minimizing the deviation of the reconstructed data from the input data, varying the input data selection, an optimal result distribution can be computed. Figures 16-4(a) and 16-4(b) are analogous to Figures 16-3(a) and 16-3(b) but using input FTIR data from combustion off-gas. The values for the input index of refraction was determined by a direct fit of the data. The various distributions are the results from different selections of the input experimental data.

Project Status

The programs to compute a particle size distribution from FTIR extinction data are working. Reasonable distributions can be extracted from typical combustion off-gas broad wavelength data. The validity of the results will be tested as part of the upcoming year's project.

Project Significance

The FTIR is a powerful diagnostic instrument for the monitoring of waste remediation off gas. In addition to the molecular absorption lines used for the standard chemical composition determinations, the inter-band extinction data will yield information about the entrained gas stream particles.

FY 96 Plans

The project plans for FY 96 will complete the development of this technique. Data from bench top and plasma torch off-gas system seeded with known sized particles will be analyzed to determine the uncertainties and confidence limits of this method. The software will be implemented in the FTIR

field system, to be used as part of the field measurement analysis. This entails porting the programs from a workstation environment to a PC.

References

- 1 Twomey, S. 1977. *Introduction to the mathematics of inversion in remote sensing and indirect measurements*. Amsterdam: Elsevier.
- 2 Ramachandran, G. and Leith, D. 1992. *Aerosol Science and Technology* 17:303-325.

Figure 16-2. Typical FTIR extinction data covering a broad wavelength region. This data is from air with particles. Only the regions away from the molecular absorption bands are used for the size distribution computations.

**Particle Size Distribution from Inversion of Extinction Data –
Examples of inversion of computed extinctions
Results for various subsets of data**

Figure 16-3. (a) Particle size distributions computed by inversion program from synthetic data generated with the input distribution (solid line). The various result distributions arise from analyzing different subsets of the input synthetic data.
(b) Comparison of the synthetic extinction data to the back calculated extinctions using the result distributions of (a).

**Teststand off-gas Experimental Data –
Inversion using optical parameters from direct fit
Results for various subsets of data**

Figure 16-4. (a) Particle size distributions from the analysis of combustion off gas extinction data. The various result distributions arise from analyzing different subsets of the input experimental data. (b) Comparison of experimental data to reconstructed data from computed distributions of (a). A choice for most reasonable distribution is that with least standard deviation of the reconstructed extinction.

17 Field Operations

Robert L. Cook

Introduction

The purpose of DIAL's *Field Operations* program is to aid in the rapid demonstration and implementation of modern fieldable diagnostic methods for characterization, monitoring and control purposes by coordinating and supporting field tests.

Work Accomplished

WETO Campaign

The major field campaign this field year was a trip to the WETO facility in Butte, Montana. A team of scientists and engineers from the Diagnostic Instrumentation and Analysis Laboratory (DIAL) at Mississippi State University visited the WETO facility in October of 1994. The purpose of this visit was to make measurements on the Plasma Arc Centrifugal Treatment (PACT-6) facility during a test series designated as 95-75HOUR-1, which began on October 17, 1994 and ended on the evening of October 20, 1994. The facility is illustrated in Figure 17-1. This diagnostic demonstration/evaluation represents the first attempt to apply a number of modern diagnostic methods to a large-scale plasma torch facility. Measurements were carried out at a number of locations along the treatment system. Interface discussions were held with representatives of MSE and the following measurement locations and specifications were identified:

- View ports to observe the melt discharge at the throat of the primary chamber;

- Opposed view ports (2-in.) to observe/sample hot gas stream before secondary combustion chamber;

- Opposed view ports (2-in.) after the scrubber/agglomerator/demister for particle diagnostics;

- Downstream sampling port for off-gas measurements.

To implement the test plan required the transportation of the following systems to Butte:

- Multi-Color Pyrometer Systems

- Multi-Purpose Imaging System

Laser-induced Breakdown Spectroscopy System
Fourier Transform Infrared Spectroscopy System
Laser Doppler Velocimeter System

These were transported with DIAL's Air Stream-based Mobile Instrument Laboratory shown outside the WETO facility in Figure 17-2.

Objectives

The primary objectives of these measurements were to (a) characterize the gas stream at the measurement locations, (b) demonstrate the capability of the measurement techniques, (c) provide useful facility data, (d) enable planning for future tests. It should be emphasized that the character of the gas stream at the measurement location is a very important element in the success of any diagnostic technique. Hence, one of the most important results of these tests was the initial characterization of the gas stream environment along the test train.

Measurement Methods/Equipment

The various measurement systems that were employed at WETO are described below.

TCP: Two-color Pyrometer (surface temperature, emissivity)

This system measures the surface temperature and emissivity of the surface. The technique is based on Planck's radiation law, and requires measurements of the radiation intensity from the surface at two wavelengths, assuming a graybody radiator. The system uses two single detectors operating at near one and two microns to measure the radiation from a hot surface. The single color pyrometers are configured to target a single spot by using a cold mirror.

MCP: Multi-wavelength Pyrometer (surface temperature, emissivity)

A silicon diode array detector mounted on a monochromator allows for the collection of radiation spectra over a wavelength range which depends on the grating used. This system is calibrated with a blackbody source and is then used to determine temperature and emissivity by fitting the radiation spectrum to Planck's radiation law assuming a graybody emitter. The radiation signal may be coupled to the monochromator through an optical fiber.

LDV: Laser Doppler Velocimeter (local velocity, velocity profile, turbulence level)

This system measures the gas velocity and turbulence level at a given point in the gas stream. The technique is based on measurement of the modu-

lation frequency of the scattered light from a particle traversing a measurement volume formed by intersection of two focused laser beams.

MPIS: Multi-purpose Imaging System (thermal images)

The imaging system, consisting of a wavelength-filtered CCD television camera, a frame grabber PC board, and a computer, is used to capture images of the molten glass stream as it exits from the melter. The shape of the melt stream, as determined from the store images, is used to infer properties of the molten glass. The intensity of the images, as recorded with 760 and 900-nm filters, is used to determine the temperature distribution of the stream.

FTIR: Fourier Transform Infrared Spectroscopy (chemical analysis)

FTIR spectroscopy is a proven analytic method for the identification and quantification of chemical species. The technique is based on the absorption or emission of infrared radiation as a molecule undergoes a transition from one vibration-rotation level to another. All molecules, except homonuclear diatomics (N_2 , O_2 , etc.), are amenable to analysis. Each molecule possesses a unique structure of vibrational-rotational levels, and consequently, the FTIR method is molecular specific.

LIBS: Laser-induced Breakdown Spectroscopy (heavy metal monitor)

LIBS can be employed to monitor, in real time, toxic heavy metals (THMs). It uses a high power, pulsed laser to generate a laser-induced breakdown in the test medium. The high density plasma produced in the test medium gives emission spectra of the heavy metals. Since it is an emission technique, it has the capability to provide simultaneous multispecies measurements. The spectral intensity of various heavy metal lines can be used to extract the relative concentrations of the heavy metals.

Demonstration Measurements

The following details the test measurements made and the instrumentation used:

- Melt discharge temperatures with TCP, MCP;
- Temperature images of the melt discharge with MPIS;
- Hot off-gas measurements at the exit of the treatment vessel with FTIR;
- Off-gas heavy metal detection with LIBS;
- Downstream off-gas HCl, and/or organics with FTIR (extractive);
- Velocity profile and turbulence level at exit of treatment vessel

with LDV.

Measurement Results and Conclusions

Fourier Transform Infrared Spectroscopy Measurements

Two DIAL Fourier Transform Infrared Spectrometers were used to characterize the gas stream, at three different locations, of the MSE WETO plasma torch facility. One of the units was configured for measuring the radiation emitted by the molecules in the elevated temperature gas stream between the torch furnace and secondary combustion unit. The second unit was operated in an absorption mode and was used to evaluate the gas stream composition before and after the ammonia NO_x reduction unit.

Emission spectra consisted of transitions due to CO_2 , NO and H_2O . Lines from CO were not observed. Determination of an average gas stream temperature from analysis of the rotational lines in the NO R-branch yielded a value of 1070 K. This result was independent of the operational mode of the plasma torch (feeding or pouring). Comparison of the experimental spectra with spectra synthesized using a computer model indicated good agreement for a gas temperature of between 1000 and 1200 K at an NO concentration of 7000 ppm.

Molecules identified in the downstream absorption spectra consisted of NO, NO_2 , CO_2 and minor quantities of HONO. Other organic molecules which could result from incomplete combustion were not observed. Measurements upstream and downstream of the ammonia catalytic unit allowed the determination of the reduction efficiencies for NO and NO_2 . The destruction of NO_2 ranged from 40 to 90% as the injected ammonia went from 1 to 4 lb/hr. The destruction of NO ranged from 70 to 95% for the same conditions. Comparison of the experimental spectra downstream of the catalytic unit with a laboratory spectrum of NH_3 revealed a limit of detection for the experimental measurements of about 1 ppm. NH_3 was not observed in the effluent from the SNCR indicating that slip at concentrations greater than 1 ppm was not occurring.

The results obtained indicate the potential power of FTIR spectroscopy as a diagnostic tool for evaluating many different process parameters concerning the torch and downstream emission modules.

Emission data indicates that the gas stream exiting the plasma torch is constant with regard to temperature and NO concentration. Changes in the CO_2 concentration appear to be strictly a function of the feed injected into the furnace. Similar comments apply to H_2O , CO or other products of incomplete

combustion were not observed in the emission spectra and were also not found in the downstream (gas sample extraction) measurements. Major process products observed downstream were CO₂, NO and NO₂. NO_x reduction efficiencies were greater than about 90% at an injected ammonia rate of 4 lb/hr to the NO_x catalytic reduction unit.

Further measurements when the furnace is operated on a feed with a larger organic content would be of interest in additional evaluation of some of the other downstream air pollution control devices inherent to the MSE WETO facility.

LIBS Measurements

Laser-induced breakdown spectroscopy (LIBS) is a laser-based advanced diagnostic technique for measuring the concentration of various elements in a test medium. In this technique, a pulsed laser beam is focused at the test point and produces a spark at the focal point due to the high electric field. The spark generates a high density plasma which excites various atomic elements present in the focal volume. The atomic emission from the plasma is collected with a collimating lens and sent to the detection system. The wavelength and the intensity of the atomic emission lines observed in the LIBS spectrum are, respectively, used to identify and infer the concentration of the atomic species.

LIBS spectra were recorded in various spectral regions during the three segment test runs. Special attention was given to the spectral regions with Fe, Cr, Ni and Ce atomic transitions. The elements present in the off-gas emission were identified from the recorded spectra. The strongest Cr lines were in the spectral regions of 431 and 359 nm. There were also some Fe lines nearby the Cr lines. Therefore, the relative concentration of Cr and Fe can be inferred from these two spectral regions using the intensity ratio.

The attempt to identify the Ce line from the LIBS data recorded near 418.66 nm was unsuccessful due to the strong interference from the emission of CN at the same spectral region. CN formation was readily observed from the spectra of the laser spark of air. The observed CN band in the 418-nm region is believed to be due to its formation in the high density plasma produced by the laser spark. Atomic emissions from N were found from the recorded LIBS spectra at the 743-nm spectral region. A strong C line at 247.86 nm was also identified from the observed LIBS spectra. This line was used to monitor the C concentration at different run conditions. The carbon concentration decreased by a factor of two from Segment 1 to Segment 2.

Ni lines were also found from some of the spectra recorded near 302 nm. The signal-to-noise ratio of the data recorded in this spectral region was

generally too poor to be analyzed. The Ni line intensity and relative concentration could only be obtained from the data taken from the Segment 1 test run on October 17.

The Na concentration in the different segment tests was monitored using the Na D lines. The intensities of Na D lines were only slightly increased from Segment 2 to Segment 3 (less than 20%). Since the Na concentration in the feed is about four times higher in Segment 3 than that in Segment 2, the measurement shows that most of the Na had gone to the slag.

In summary, the Cr concentration in the off-emission decreased from the Segment 1 test run to Segment 2 and also in the Segment 3 test run. Metal emission was nearly uniform during the Segment 2 and the Segment 3 measurements as compared to the Segment 1 measurement. There is a variation of about four times in the metal (Cr) emission during the Segment 1 test run from the first day (October 17) to the next day (October 18). The metal concentration also decreased during the pour, as expected. The increase of the Na_2CO_3 concentration in the feed did not increase the Na concentration in the off-emission by the same amount.

LDV Results

LDV stands for Laser Doppler Velocimetry, and is a nonintrusive method for measuring velocity. Here, two laser beams are focused at a common crossing point in the flow, and light from both beams is scattered into the detector by particles that pass through the focal volume (or crossing point).

A pair of horizontally opposed 2-in. diameter penetrations were provided by WETO in the 10-in. (nominal) diameter stainless steel pipe that carried the torch off-gases to the secondary combustor. This pipe had a 2-in. refractory lining, so the flow stream was 6 in. across. DIAL supplied window assemblies that bolted onto the 2-in. pipe flanges furnished by WETO. The window assemblies also provided a support rail that was used for mounting optics. A small purge flow of nitrogen next to the window inner surface was provided to keep the window clean. During these tests, a flow of approximately 30 scfh per side was sufficient to keep the windows fairly clean.

We successfully measured the gas velocity in the pipe leading from the plasma torch vessel to the secondary combustor in the PACT-6 facility at WETO. In general, the centerline gas velocity is about 10 - 12 m/s, although it does fluctuate higher and lower at times. We measured mean velocity profiles and the variation of the centerline mean velocity as a function of time during a pour cycle. The velocity profile was relatively constant across the center region of the pipe, and fell sharply at the wall. The LDV measurements also clearly

reflected variations in the feed rate to the torch vessel. These appear as significant changes in the LDV data rate.

Multicolor Imaging System Measurements

The DIAL multicolor imaging system, which consists of a CCD television camera, various lenses and filters, and an image digitizing system, was used to create thermal images of the molten glass stream of the PACT-6 system. Images from the 95-75HOUR-1 run were taken at both the exit of the throat and at the top of the receiving barrel. The expected results of this test were met in that images of good spatial resolution with intensities corresponding to absolute temperatures were obtained.

Various images were obtained showing the temperature and shape distributions seen during a typical pour looking up into the throat region of the PACT-6. The false colors of the images provided temperature bands ranging from 1090°C to about 1490°C. The spatial scale of the images were also obtained. Typically, the pour starts out as a thin (7 mm), cool ribbon, gets wider and hotter until a 100-mm sheet is formed, then reverses as the pour comes to an end. Although this sequence was fairly typical, there were pours in which the wider sheets never formed, showing only the narrower structures. It should also be noted that there was a considerable amount of temperature variation across the molten stream, particularly for the wide sheets.

The second set of images were taken later in the week from the window at the end of the slag removal door and show the stream in the 18.5-mm gap between the barrel and the chamber. Typically, at this location the stream was much narrower (about 10 mm), and was also cooler (910 - 1230°C). When seen in real time, these streams move across the screen as the PACT-6 rotates.

Pyrometer Measurements

During the WETO/MSE 95-75HOUR-1 field measurements, the slag temperature between the pour chamber's shroud and the top edge of the slag barrel holder was measured through the observation window on the door of slag collector section. Due to the swirling slag stream, the temperatures measured were fluctuating and discontinuous. Typical temperatures were in the range of 1210 to 1810 K. This, and other melt temperatures, were measured for the first time with DIAL's pyrometer systems. The pyrometer systems were also employed to measure point temperatures and emissivity of the melt discharge at the throat of the primary chamber. Due to swirling melt discharge, temperature fluctuations are expected. Typical temperatures were 1310 to 1890 K.

At the beginning of each pour, the plasma torch was moved near the exit (throat) of the primary combustion chamber in order to remove any

obstructions to the slag flow by melting any slag in or near the throat. When this was done, emission from gas phase atomic species appears in the emission spectra; atomic emission from sodium, potassium, nitrogen and oxygen was observed in the wavelength region monitored by the multiwavelength pyrometer system. When the plasma torch was not near the throat, no atomic emission was evident in the emission spectra. It should be noted that it might be possible for some of the volatilized atomic species to escape from the primary thermal treatment chamber during such events, and this needs to be considered in the operation of the torch system.

Project Status

Application of DIAL's fieldable instrumentation systems will continue, and it is expected that additional measurement capabilities will be added.

Project Significance

In addition to providing useful operational data, these measurements illustrate the usefulness of these systems as process monitors which can characterize the overall treatment process and the process components and subsystems.

FY 96 Plans

In FY 96, we expect to carry out other field campaigns. In particular, we will be making a series of measurements on the Transportable Vitrification System (TVS) developed by Westinghouse Savannah River Company.

*Figure 17-2. DIAL's Air Stream-based Mobile Instrument Laboratory
on location at the WETO facility, Butte, Montana.*

18 Special Projects

R. Arun Kumar

Introduction

During the past year two major projects were undertaken under this task. For a more detailed description of the work please refer to the reports that have been written and referenced.

Work Accomplished

Viscosity Measurements in Glass Melters

At the request of WSRC, a report was prepared that evaluates the application of commercial viscometers which have primarily been used under laboratory conditions to more practical glass melter applications.¹ The adverse conditions that prevail in a glass melter require significant adaptation before they can be used. In order to complete the study, we have looked into the available literature on glass viscosity measurement techniques, spoken to some manufacturers, and also researched literature into materials suitable for wetted parts.

A method that has been considered for the stir melter has been to relate the torque required by a motor to keep the stirrer rotating at some speed to the melt viscosity. We have utilized available empirical relationships and some of the glass melt property data provided by WSRC and developed an operating envelope under which this relationship of measured torque to melt viscosity is valid. This is important since increased rotational speeds cause turbulent flow over the vanes of the stirrer, rendering invalid the relationships used for viscosity calculation using this technique.

One method that we have suggested for measuring the melt viscosity utilizes a differential technique. In this method, a conventional viscometer head is used to measure the torque required to keep a specially fabricated spindle, immersed in the melt, rotating at some specific speed. One torque measurement is made at some unknown depth of insertion of the spindle. The spindle is then immersed by some known incremental depth into the melt and a second torque measurement is made. The viscosity of the melt can then be related to the difference in torque measured, the incremental depth of insertion and other known spindle dimensions and calibration factors. These cali-

bration factors for the system would need to be determined but can be done off-line.

FireJet 1000 Torch Test Evaluation

The FireJet 1000 torch is marketed as a cutting/ablating device with applications to metals, alloys and other materials including concrete. In this system, kerosene and oxygen are combusted and exit from a cutting head at supersonic conditions. DIAL was contracted to do a performance evaluation of this system. Specific tasks included the cutting of a 4-in. thick plate of carbon steel and 5-in. thick concrete specimens, as well as the scarifying of a 1/4-in. layer of concrete doped with cerium oxide from the concrete specimens. Comparison with industry standard techniques was done. Capital and operating costs for the system were also determined. Miscellaneous acoustic, particulate, flow and a number of other measurements were performed during the course of testing. Results from the tests can be found in a comprehensive report.²

The FireJet 1000 system comprises a mobile cart, which houses the fuel tank, pumps for kerosene and cooling water, as well as the associated flow control and operating and safety circuitry for the system. The cart is connected to a cutting wand by 50 ft of hose line. Kerosene and oxygen are injected into a combustion chamber in the wand where they are ignited and burn. Combustion gas flow is choked going through a throat, and the following expansion nozzle causes conditions to be supersonic at the exit of the cutting head. In our system, the cutting wand was mounted on a motorized x-y traverse system. Cutting and scarifying rates could thus be accurately controlled and measured with a computer.

Project Status

The assigned topics for this subtask were completed as required. The subtask will be reactivated as necessary to address any special problems referred to DIAL.

Project Significance

The topics of research and evaluation performed this year were found to be valuable to the customers.

FY 96 Plans

The subtask will be reactivated as necessary to address any special problems referred to DIAL.

References

1. Arun Kumar, R. 1995. *Viscosity measurement in glass melters*. Mississippi State University: Diagnostic Instrumentation and Analysis Laboratory. DIAL 10575 TR 95-1.
2. Shepard, W.S. and Arun Kumar, R. 1995. *FireJet 1000 test report*. Mississippi State University: Diagnostic Instrumentation and Analysis Laboratory. DIAL 10575 TR 95-4.

19 Industrial Affiliates/Marketing

Robert L. Kirkland

Introduction

The objective for FY 95 was to establish an Industrial Affiliates program to provide a basis for technology transfer of DIAL's accomplishments in environmental improvements under DOE's Environmental Management program. DIAL would recruit and maintain industrial affiliates who would provide a wide representation from the environmental, chemical, instrumentation, utilities, metal and industrial heating industries. In addition, we would identify and establish potential markets for the instrumentation systems and develop programs for present and future test facilities.

Work Accomplished

Industrial Affiliates Program

During FY 95, three corporations were enrolled as Industrial Affiliates--Plasma Energy Corporation, Westinghouse Savannah River Company, and Tennessee Valley Authority. Five verbal commitments were made for FY 96.

Marketing

DIAL is currently working with 43 different corporations in various stages of development and relationships. The areas of work range from research and development to testing and verification. The majority of the marketing effort has focused upon:

Laser-induced Breakdown Spectroscopy (LIBS)

DIAL is currently working with corporations to utilize LIBS for detection of species in molten baths, metals within the off-gas stream as well as in solid form. The ability to provide this information on a real time basis is very valuable to the customers. During FY 95, DIAL identified an application with a company which has expressed interest in purchasing LIBS if a system can be developed in a more competitive price range. Developing and packaging in a smaller, more economical configuration is DIAL's objective for FY 96.

Multiwavelength Emission Absorption Spectroscopy (MEAS)

With the MEAS system, DIAL is providing absolute, real time temperature measurements on development burners.

Laser Doppler Velocimetry (LDV)

LDV is used to determine the velocity of both gas streams, as well as the flames of the plasma torch and fossil fuel burners. Requests have been made by customers to use LDV for particle sizing and particle size distribution.

Fourier Transform Infrared Spectroscopy (FTIR)

The marketing effort for FTIR has focused upon real time combustion control and the detection of organics in the off-gas stream.

Implementation Plan

DIAL's objective was to establish and implement a plan whereby plasma torch manufacturers could utilize the developed technology and implement them into their own software and hardware. This plan was compiled from input from three plasma equipment manufacturers. This plan was integrated into *Task 7: Torch and Process Control System Development* for FY 96.

Test Facilities

DIAL performed two different tests for Westinghouse Savannah River Company (WSRC), vitrification of soil and surrogate low level radioactive wastes. In addition, DIAL performed tests on 31 refractory samples in support of the vitrification project at WSRC. During FY 95, DIAL contracted for plasma torch and process development projects. These contracts will be conducted during FY 96.

Project Significance

DIAL is continually expanding its efforts to provide direct instrumentation support to benefit government agencies as well as industries in the fields of environmental, industrial heating, chemical, advanced materials, glass, petroleum and utilities. This transfer of technology broadens the base of DIAL's capabilities and expands the areas of applications. The focus of DIAL's programs provides a natural basis for its formal Industrial Affiliates Program. DIAL is committed to helping industries become more competitive through cost reductions which can be realized with more effective consumption of raw materials, more efficient use of equipment, and lowered energy requirements. Effective testing and evaluation of processes leads to more reliable operation and the detection of problems which can result in reduced emissions. Industrial affiliates have access to DIAL's staff and research personnel and are kept updated on, and have early access to new technologies. When appropriate, implementation plans are provided which address a particular need of an industry through a research and development program.

The Industrial Affiliates Program provides direction for DIAL with regard to applications and continued support for research and development. It focuses on the technology needed by industries and provides an immediate route for transferring technology to industry.

By working in collaboration with industries to identify opportunities for diagnostic research and development, DIAL can assist DOE to accomplish this congressionally mandated aspect of federally funded research while contributing to the improved efficiency and competitiveness of U.S. industry.

FY 96 Plans

Industrial Affiliates Program

We will continue to recruit and maintain industrial affiliates in order to provide a basis for technology transfer of DIAL's efforts in environmental improvement under the DOE program. The goal for FY 96 is to recruit a minimum of five companies.

Marketing

The marketing plans for FY 96 include:

LIBS

DIAL has identified several corporations to manufacture and market the LIBS system. We are preparing to develop and package a smaller, more economical configuration as well as to install the system in three industrial applications during FY 96.

MEAS and LDV

DIAL will establish markets for these systems and install systems for several industrial customers. At present, there are three corporations interested in utilizing these technologies.

Real Time Combustion Controller

DIAL will prepare a package of information and initiate a strong marketing campaign to interested companies within the industrial heating field.

Test Facilities

During FY 96, DIAL plans to more fully utilize the facilities, i.e., plasma waste treatment furnace, combustion test stand, as part of the off-gas system. Currently, DIAL has approximately eight potential customers interested in testing at DIAL's facility.

Viscosity Measurement Techniques

The target is to establish this technique by utilizing laser-based ultrasonics. Customers have been established to utilize the technology as soon as it is available for vitrification processes.

Air ICP

Plans are to initiate a marketing campaign for the use of this technology for monitoring and/or treatment of organics in certain off-gas streams as soon as it is commercially available.

20 Continuous Emission Monitors

J. S. Lindner, P.R. Jang and L. Gresham

Introduction

Many DOE mixed waste streams contain large quantities of poly(vinyl chloride) (PVC). Plasma torch treatment of these feeds results in the formation of HCl which must be removed from the gas stream according to existing environmental regulations. Quantification of the HCl prior to the scrubber would allow for controlling this device which will lead to a more efficient operation. In most situations, such a measurement requires the extraction of a gas sample followed by analysis using either an FTIR or an instrument based on gas filter correlation. Extraction may not, however, be possible at certain plasma torch or melter facility locations. The ability to sample will depend on the gas stream temperature and any radiological considerations.

On-line *in situ* measurements are also possible using an FTIR, however the response time of the system will depend on the extent of signal averaging, and this will depend on the resolution of the interferometer and the concentration of the gas present. Although such measurements appear quite feasible (see *FTIR Spectroscopy* section), an attempt has been made in this work to develop an inexpensive nondispersive HCl emission monitor.

The instrument was developed based on technology employed in the Real Time Combustion Controller (RTCC) which was described previously and for which a patent application has been made.^{1,2} The HCl instrument offers rapid measurement capability and can be operated in an emission or absorption configuration.

Test runs using a surrogate mixed waste indicated that the residence times of the PVC in the torch furnace could be determined. This measurement capability may be valuable for future torch facility optimization studies. On-line calibration of the unit is possible following the method outlined in the FTIR section. Interference effects were observed from a combinational band of NO₂. During torch operation, the interference gives rise to a sinusoidal signal corresponding to the changing of the gas flow in the plasma torch. On injection of feed, the resulting HCl peak is overlaid on the signal due to NO₂. The NO₂ signal (see below) allows for the monitoring of systematic changes of the plasma torch.

Work Accomplished

A block diagram of the system is given in Figure 20-1. Infrared radiation, either from an SiC source on the opposite side of the gas stream or from the elevated temperature gas stream, is modulated by the chopper and routed to bandpass filtered infrared detectors. Selection of the bandpass filters for the on and off resonance lines was initially done by comparison to an FTIR spectrum for HCl. It was later found necessary to restrict these ranges due to a competing signal contribution from the NO_2 molecule. The detectors are two-stage thermoelectrically cooled PbSe elements. The signals are amplified and then passed to the system computer which processes the data for both channels and provides a continuous plot of signal against time. Typical signal responses measured in the laboratory with a blackbody source are given in Figure 20-2. Standard deviation errors for both detectors are less than 0.6%.

Following the establishment of the optical configuration and bench-scale testing the unit was located at the optical penetration directly downstream of the plasma torch furnace. The feed to the torch was the WSRC surrogate waste briquettes containing approximately 12.8% by weight PVC. Some briquettes were spiked with hexachlorobenzene for gas chromatography/mass spectroscopy experiments, and these results will be reported later.

The response of the monitor during torch operations on air and nitrogen plasmas is given in Figure 20-3. For this experiment, DIAL's large plasma torch was operated at a power of about 110 kW. The cycling in the trace corresponds to the cycling of the gas to the plasma torch used to move the arc attachment point along the torch rear electrode. The cycling waveform increased in signal intensity as the test run progressed. This trend is also evident in the gas stream temperature measured by a thermocouple located at the exit of the furnace, Figure 20-4. A comparison of Figures 20-3 and 20-4 indicates that the signal level from the NO_2 emission correlates with temperature changes.

The monitor responds to the injection of the PVC-laden briquettes. The signals reach a maximum followed by a gradual decay. Switching the plasma to nitrogen resulted in a decrease in the intensity of the background signal and is thought to be due to the lower NO_x concentrations arising from the nitrogen plasma (5,000 - 8,000 ppm) compared to 10,000 - 17,500 ppm for operation on air and to the decreased exit temperature.

Figure 20-5 compares the cycling-corrected and time-shifted HCl emission intensities during the injection of eight WSRC briquettes (lower trace) with the same number of briquettes, each spiked with 10 mg of hexachlorobenzene (middle trace), and with eight briquettes, each spiked with 25 mg of C_6Cl_6 . The total PVC content of the feed is 12.8% by weight. This and other

sources of chlorine (metal chlorides) correspond to a total chlorine content of approximately 7.14% by weight. Eight briquettes constitute a mass of about 227 g of which 16.2 g is chlorine. The 10-mg spiked briquettes correspond to a total chlorine weight of 16.28 g, while the higher spiking level (eight at 25 mg) contains 16.38 g of total chlorine. The integrated areas for each of the responses is similar; however, the shapes of the curves differ and this may be related to the nature of the spiked and unaltered briquettes.

All of the response curves exhibit a rapid increase corresponding to a rapid evolution of HCl from the briquette followed by the gradual decrease. The initial response peak appears to increase with an increase of chlorine in the feed. The effect may result from a more rapid destruction of the hexachlorobenzene. Further studies are needed on different feed compositions.

Interesting effects are observed when comparing the response for briquettes injected in a nitrogen plasma and in an air plasma. Figure 20-6 compares the instrument response, again corrected for cycling and superimposed in time, for eight regular briquettes with the torch gas as nitrogen (top trace) and air (lower trace). The integrated areas here are different, and this is thought to reflect the different data collection times relating to different furnace conditions (see Figure 20-3 peaks labeled 8 and 4). The HCl evolved during operation of the torch with nitrogen has a more pronounced peak and falls off more rapidly than conversion of the briquettes with the torch running on air.

Similar results were obtained in comparing the surrogate waste conversion with nitrogen and the 25-mg spiked briquettes with the air plasma. These traces are shown in Figure 20-7, and the specific injections are labelled 7 and 8 in Figure 20-3. In both Figure 20-6 and 20-7, the HCl response as the torch is operated on air appears to be more complicated than the response observed with the nitrogen plasma. Specifically, it seems that with air the decay cannot be represented by a simple form. There appears to be a change in the rate of decay which may indicate that not all of the HCl is being initially generated as the briquettes enter the plasma furnace. This may arise from different briquette destruction mechanisms. The briquettes can be destroyed by direct interaction with the plasma, by pyrolysis in the gas above the melt, or by pyrolysis within the melt. The relative importance of the three destruction mechanisms will depend on the gas, melt and plasma temperatures along with the concentration of oxygen in the reactor.

Residence times can be determined from data such as that in Figures 20-6 and 20-7. For the torch conditions encountered during this test, all of the HCl signals during briquette injection (except peak 1 in Figure 20-3) yielded residence times of between 4 and 5 minutes. The estimation of when the signal approaches the baseline is difficult from this initial data. Changes in residence

times are anticipated depending on the feed composition, the feed rate, the plasma gas (air, nitrogen, or nitrogen with added air to the furnace) and with torch power. Calibration of the system allows for directly relating the signal to the HCl concentration which can potentially be used for control of a downstream scrubber.

Calibration of the system followed that for on-line FTIR measurements. By limiting the chosen spectral range using a bandpass filter, however, the limits of detection (LOD's) will be greater than those from the entire rotational envelope in the dispersive FTIR measurement. The limit of detection will depend on the transition cross-section and the path length according to the Beer-Lambert law. Increasing the path length will result in lower measurable concentrations.

Figure 20-8 represents the emission intensity at different gas stream HCl concentrations. These concentrations were obtained by varying the gas input using the mass flow controllers. The lowest concentration attempted is around 660 ppm which is about five times the concentration measurable with on-line FTIR at the same path length (FTIR section). The high LOD's possible with the HCl monitor preclude the direct use of this device in stack monitoring. As observed from Figure 20-3, the signal levels from the mass flow controllers were somewhat higher than the signals from the briquettes, and there is not a sufficient number of low concentration data points on the calibration curve (Figure 20-8) for resolving the entire signal trace. Additional experiments will rectify this situation.

Establishment of the on-line calibration allows conversion of the HCl monitor signal to concentration units which can then be converted to mass. Integration of the mass response permits determination of the amount of HCl at any particular facility location. As noted above, the total mass of chlorine in eight briquettes is 16.2 grams. Analysis of peaks 6 and 7 (Figure 20-3) yielded 12.6 and 13.4 grams of HCl, respectively. These values appear quite reasonable, considering the partitioning of the HCl into NOCl and perhaps other chlorinated inorganics.

Project Status

All of the original milestones for this project have been completed with the exception of some additional programming required for implementing the calibration routine and the subsequent calling of this routine during normal operation. The instrument has been tested in a pilot-scale plasma torch facility and has been shown to exhibit application to typical DOE waste streams. The final milestone concerned the identification of additional continuous emission

monitors for other applications. A number of these have been identified and are being pursued as separate projects in FY 96.

Project Significance

The ability to determine the HCl concentration on-line and in real time along with an indirect monitor for the torch gas flow suggests further applications of this instrument. It is noted that for batch processing of mixed waste streams, the instrument will provide residence time data which may be difficult to obtain using other instrumentation. The use of the unit in an emission optical configuration is also an advantage.

FY 96 Plans

Work on the HCl CEM is not formally continuing through FY 96. It is expected that the instrument will be used for monitoring the HCl emissions from the DIAL plasma torch facility. Incorporation of the instrument in a control system should be straightforward and is in progress. Torch gas flow rates and facility temperatures are already catalogued by the control system and correction for flow variations (concentrations) will be possible on-line.

References

1. Shepard, W.S., et al. 1994. *Application of modern diagnostic methods to environmental improvement*. Mississippi State University: Diagnostic Instrumentation and Analysis Laboratory. DIAL 10575 FY 94 Annual.
2. Lindner, J.S., et al. 1994. Real Time Combustion Controller. U.S. Patent Application 08/283, 795.

Process HCl Monitor

Figure 20-1. Block diagram of the HCl continuous emission monitor.

Figure 20-2. Detector stability test for the HCl monitor.

Figure 20-3. Response from the HCl monitor during a plasma torch test run. For this test the monitor was located at the torch furnace exit and operated in an emission configuration.

Figure 20-4. Gas stream temperature at the furnace exit. The trend in thermocouple temperatures is also evident in Figure 20-3.

Figure 20-5. HCl monitor responses for three different briquette injections.

Figure 20-6. Comparison of the system response for briquette injection with a nitrogen plasma and an air plasma.

Figure 20-7. As in Figure 20-6, but for different briquette compositions.

Figure 20-8. Initial calibration curve from the HCl monitor using the mass flow controllers. For this test, the calibration was not extended sufficiently to the lower concentration regime.