DIAGNOSTIC INSTRUMENTATION AND ANALYSIS LABORATORY

APPLICATION OF MODERN DIAGNOSTIC METHODS TO ENVIRONMENTAL IMPROVEMENT

**FY 94 Annual Technical Progress Report
for the period
January through October 1994**

December 1994

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United States Department Of Energy
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FY 94 Annual

**APPLICATION OF MODERN DIAGNOSTIC METHODS
TO ENVIRONMENTAL IMPROVEMENT**

Annual Progress Report
for the period
January through October 1994

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ABSTRACT

The Diagnostic Instrumentation and Analysis Laboratory (DIAL), a 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 real world processes; measurements are made in hot, highly corrosive atmospheres in which conventional measurement devices are ineffective.

Task 1 of this agreement is concerned with the development and application of various diagnostic methods to characterize the plasma properties, the melt properties and the downstream emissions from a plasma torch facility designed to vitrify mixed waste. Correlation of the measured properties with the operating parameters of the torch will be sought to improve, optimize and control the overall operation of the plasma treatment process. As part of this program, diagnostic methods will be developed and evaluated for characterization, monitoring and control purposes of treatment processes in general.

Task 2 of this agreement is concerned with the development of a system to monitor and control the combustion stoichiometry in real time in order to minimize environmental impact and maximize process efficiency. Staged fuel injection is also being studied to minimize NO_x formation.

TECHNICAL PROGRESS

TASK 1. PLASMA TORCH PROJECT

Task 1. Subtask 1. Plasma Torch Operation

John Etheridge

DIAL's PT-50 plasma torch system is set up in the transferred arc mode and is used as a test bed for plasma diagnostics and plasma process control system development. The torch is mounted in a vacuum vessel which has six optical access ports. This system can be pumped down and back-filled with the plasma gas (argon, helium, nitrogen, etc.) so that even short duration tests can be run with very little atmospheric infiltration. The system has been very reliable through 127 tests totaling 110 hours during which very few operational problems were encountered.

The one system problem that took some effort to overcome involved the cooling water system for the plasma torch. The problem was first encountered when internal arcing occurred during start up of the plasma torch. A chemical analysis of the cooling water indicated the presence of 5 mg/l of fluorine and 18 mg/l of chlorine. After examination of the internal parts of the torch, Dr. Koelling of the MSU Chemical Engineering Department determined that the chlorine and fluorine reacting with iron in the system had caused rapid corrosion in areas such as surface cracks and under O-rings due to, in the case of chlorine, the formation of ferric chloride which reacts to produce HCl. We have replaced all carbon steel parts of the water system, except the housing of the water pump, with stainless steel. The torch cooling water was replaced with distilled water, then pumped through deionizers and activated charcoal filters to remove any residuals left in the system. This seems to have corrected the problem.

A second plasma torch vitrification system which uses a 250 kW plasma torch is being constructed. This plasma torch is capable of both transferred and nontransferred operation which gives added versatility to the system. The vitrification vessel was made from a hot walled vessel that was previously used for the separation of zinc from aluminum scrap. It has an inside diameter of approximately 30 inches and a depth of about 2 feet. A three-axis motorized gimble mount for the torch is under construction. The system is expected to be in use by November 1994.

Task 1. Subtask 2. Plasma Torch/Process Control

Bert Nail and Thomas Philip

A control system structure has been proposed that:

1. provides the stabilizing strength of conventional controls,
2. incorporates expert system characteristics in a safe manner,
3. allows vernier control from an expert system/neural advisor, and
4. provides override capability to the operator.

A key consideration is the interface to diagnostic systems, most of which are PC-based. Some of these systems may prove so useful that direct incorporation is desirable. To provide this compatibility, a Pentium-90 was chosen for the development platform.

Control system software

Experiments were performed with various commercial software packages that run under WINDOWS, primarily Visual Basic and various compatible utilities. Visual Basic, VB-EZ, and Formula One-VBX were found to provide a powerful base for software development. Data acquisition, tabular and graphic display, on-line configuration, and data archival are currently operational. Communications to the Allen-Bradley programmable controller, and to the neural advisor are the next items of effort.

Supervisory control hardware

The 250 kW plasma torch and controls are in place. The control system provided with this system will serve as a local control. As the supervisory control system is developed, the torch control will be treated as a component under supervision, just as furnace, secondary combustion, and off-gas treatment components. In order to employ the torch control system provided with the 250 kW system, incoming data must be captured for shipment to the supervisory control system. An economical method has been devised and partially tested for this purpose, which will be

transparent to the original system. These signals, among others, will be monitored through hardware purchased from Data Translation.

Actuators will be commanded by an Allen-Bradley SLC-5/03 Programmable Controller. This equipment must take commands from the Pentium, perform the operations requested, and inform of status. The appropriate development software is provided by ICOM; custom software is under development.

Custom actuator modules have been devised, and assembly will progress in phase with mechanical components for control of torch angles, standoff, etc. These will be implemented manually, with provision for automatic control as software and hardware are readied.

Communication

Communication to programmable controllers and the expert advisory system will be through buffered serial interface. The expert advisory system will serve as the central point of communication to all diagnostic systems. Preliminary testing indicates proper interface operation, but complete testing awaits further advances with the programmable controller software.

Expert system advisor

Criteria and procedures, based on previous work and environment, were developed for selecting expert system shells. These are flexible enough to adapt to different environments and other software products. We contacted several vendors for evaluation copies of their expert system shell products. Of the seven responding, only two passed the initial evaluation phase. After the detailed evaluation phase "level 5 object" from Information Builders, Inc. was purchased for the development of the advisor.

It was reported in the 1993 *Annual Technical Progress Report* that an expert system controller would directly control the plasma torch. However, since the last report period the implementation strategy of the control system has been changed. Our present plan is to control the torch initially with a conventional controller and use the expert system as an advisor to the control system. The advisor would use the torch operation information from the conventional control system and the diagnostic

instruments to arrive at the control recommendations. As we gain more confidence in the behavior of the two systems, the responsibility of controlling will be shared by both, and the level of control with each system will be adjusted automatically depending on the situation.

At present, we are developing a prototype of the advisor. We will be investigating the possibility of integrating fuzzy logic and neural network into the control system. We will also be working on the communication protocols with the conventional controller and the diagnostic instruments.

Task 1. Subtask 3. Diagnostics

Robert L. Cook

1.3.1 Emission Spectra

Leslie Bauman, David L. Monts and Weishun Wang

A wealth of information on density of species and plasma temperatures can be obtained by classical emission spectroscopy on the plasma torch. During the past year, three different spectroscopic systems were used to characterize the emission spectra of the various gases for the plasma torch under a variety of conditions. These spectral coverage extended from about 200 nm to 1000 nm, i.e., from the ultraviolet through the visible into the near infrared. The systems used included a scanning spectrometer with a 0.6 m focal length monochromator and a photomultiplier detector for moderate-resolution time-averaged survey spectra from 200 to 900 nm. The Multiwavelength Emission/Absorption Spectroscopy system was employed for time-resolved and also spatially-resolved plasma emission spectra from 370 to 520 nm. The third system was the Silicon Diode Array (SiDA) which is a low resolution system capable of recording spectra from the ultraviolet to the infrared. Emission spectra were primarily taken in the red region with this system. These diagnostic systems are described more fully in the 1993 *Annual Technical Progress Report*.

Plasma emissions for nitrogen, air, argon, and helium were recorded during the previous fiscal year and again following amelioration of leaks into the plasma arc vessel. The latter spectra were considerably 'cleaner' for the atomic species without the air impurity. The assigned emission lines and bands have been cataloged for use as an aid in developing diagnostic systems for monitoring the plasma operation.

Spatially resolved emission scans of argon, nitrogen, air, and helium plasmas were recorded using the area detector capabilities of the MEAS system. The software for the vidicon/optical multichannel analyzer (OMA) control was revised for multiple contiguous tracks. In the preliminary experiments, the arc was imaged directly onto the monochromator slit of the MEAS with a simple converging lens of focal length 50 mm to give an image size reduction of about $-1/16$ for about a 6 mm high inverted image of the 4 inch (~ 10 cm) arc, which nicely matched the vidicon detector size. The optics were simply adjusted to give a strong signal on the vidicon after the arc was struck. The spatially resolved

spectra were then recorded by scanning the vidicon detector in 12 horizontal tracks vertically displaced to cover the arc length. The arc emissions covered about 10 tracks so that each track is an integration of about 1 cm of height roughly along the arc axis. The spectra were also 1 millisecond time-resolved exposures using the MEAS optical chopper/shutter system with a single slot chopper blade. The data collection was synchronized to the shutter firing and subsequent detector exposure. The spectra were taken in groups of 10 exposures for several sets of spectra over the 370 to 520 nm region to see if there were any significant shot-to-shot variations. The 1200 groove per millimeter grating was used to give a wavelength range of 35 nm across the 500 channels of the vidicon and a step of 15 nm was taken between each set. Each complete experiment required about six minutes of data collection.

Figures 1 to 7 illustrate a few of the recorded spectra. Four of these spectra were featured in a paper presented at the 1994 International Incineration Conference.¹ Interesting spectral variations over the arc length were seen that clearly illustrate that the emission spectrum observed is a sensitive function of the portion of the plasma viewed by the detection system.

The argon plasma showed the strongest continuum radiation in the upper half of the arc with CN emissions in the lower half. The argon lines are seen at all heights along the arc. The argon ion line at 435 nm is a strong signature above the continuum radiation and the neutral argon lines.

Helium lines were seen only in the top half of the arc which may explain the variations in helium line intensities reported in the 1993 *Annual Technical Report*. These spectra were recorded at a particular location midway along the arc and variation in the torch operating conditions could easily have moved the helium emissions in and out of view of the MEAS system. No helium ion lines were seen, placing an upper limit on the plasma temperature. Strong CN lines were also seen with helium. Occasional flashes were seen of a rich iron spectrum just above the crucible for all of the gases and is illustrated in Figure 4 for a helium plasma.

The air and nitrogen plasma emissions were very similar. The N_2^+ band at 391 nm was optically thick throughout most of the arc. The CN band was recognizable above the crucible. Weak iron lines at were seen

continuously for nitrogen and air operation. Atomic nitrogen lines were seen just below the torch tip. The two visible atomic oxygen lines were observed in the upper half of the arc length for air plasma.

After the demonstration of the MEAS instrument for recording temporally-resolved and spatially-resolved emission spectra, the experiments were repeated taking additional care to tilt the optical system to match the tilt of the torch axis and a back alignment through the monochromator was performed to verify that the system was viewing along the torch axis. Another set of experiments utilized the 600 groove per millimeter grating to give a view of 70 nm in a single exposure. The greater spectral range allowed time-resolved spectra viewing multiple atomic lines which may allow for a determination of plasma temperature through line intensity ratios. In addition, spectra were also recorded of nitrogen, helium and argon with small amounts of helium or argon since line intensity ratio analysis is not valid for optically thick lines. Analysis of the emission spectra is underway.

Spectra were also recorded of helium plasma with a charge coupled device (CCD) detector on a 0.32 m monochromator. These spectra have provided a preliminary temperature measurement using the 447 and 471 nm helium lines. Figure 8 illustrates the preliminary results over a time period of approximately one half hour.

The SiDA system has performed an extensive series of experiments collecting emission spectra of the DIAL plasma torch under a variety of experimental conditions in order to determine the best species to monitor to determine the temperature in nitrogen and air plasmas. Figure 9 illustrates the change in intensity in a nitrogen plasma as a function of wavelength when the plasma torch power was increased from 50% of its maximum value to 98%. This figure indicates that the atomic nitrogen transitions are the most sensitive to the change in power. The same trend is also found in the ultraviolet where again the intensity of the atomic nitrogen appears to be the most sensitive to the change in power.¹

The SiDA system has been collecting emission spectra by using a simple pickup lens to view approximately a 3.3 cm diameter area at a selected distance beneath the plasma torch. Careful analysis of the extensive sets of emission spectra that we collected reveals that the practice of viewing a selected portion of the plasma arc when operating in the transferred mode does not produce results that can be reliably used for

determination of temperature. Figure 10 shows that at 198 amps, the intensity of a group of atomic nitrogen transitions increases with increasing voltage between the plasma torch and the graphite billet beneath. Figure 11 shows data collected on the same day at the same location in the plasma arc, but at 175 amps; for this case, the relative intensity of the same group of atomic nitrogen transitions decreases with increasing voltage. This is the opposite trend to that in Figure 10. The reason for this discrepancy can be understood by considering the results of the MEAS and the MCI systems. The MEAS system has clearly shown (see Figures 1-7) that there is a spatial distribution of species along the length of the plasma arc. The MCI system has extensively documented (see this report) that at a fixed wavelength, the distribution of intensity along and across the plasma arc is non-uniform and changes when the operating conditions (current, voltage, pressure) of the plasma arc are changed. Thus, the distribution of species viewed at 198 amps is different from that viewed at 175 amps even though the viewing location is exactly the same for the two cases. This implies that in order to extract an accurate average plasma temperature for the plasma arc, it is necessary to image the entire length of the plasma arc onto the detector.

References

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Figure 1. Spatial distribution of argon plasma emission as simultaneously recorded by the MEAS system.

Figure 2. Spatial distribution of argon plasma emission as simultaneously recorded by the MEAS system.

Figure 3. Spatial distribution of helium plasma emission as simultaneously recorded by the MEAS.

Figure 4. Spatial distribution of helium plasma emission as simultaneously recorded by the MEAS.

Figure 5. Spatial distribution of nitrogen plasma emission as simultaneously recorded by the MEAS.

Figure 7. Spatial distribution of air plasma emission as simultaneously recorded by the MEAS.

Figure 8. Preliminary measurement of helium plasma temperature from the line intensity ratio of the 447 and 471 nm lines.

Figure 9. Relative change in intensity with power vs. wavelength for a nitrogen plasma.

Figure 10. Relative intensities of selected atomic N transitions in a 6" nitrogen plasma as a function of plasma torch voltage. The plasma arc current is 198 amps.

Figure 11. Relative intensities of selected atomic N transitions in a 6" nitrogen plasma as a function of plasma torch voltage. The plasma arc current is 175 amps.

1.3.2 Laser Doppler Velocimeter

W. P. Okhuysen and O. P. Norton

Laser Doppler velocimetry (LDV) is a nonintrusive method for measuring flow velocity. A beam of coherent laser light is split into two beams of roughly equal intensity. These two beams are then manipulated so that they cross at the point where the velocity is to be measured. The beams are also brought to a focus at the crossing point, so the beam crossing region is very small. This focal volume is ellipsoidal, with a major axis typically 1 - 2 millimeters long and minor axes typically 100 - 200 microns across.

When a particle in the flow passes through the beam crossing region, it scatters light from both laser beams into a detector, which is arranged to receive this scattered light. Because the particle is moving, the scattered light is slightly Doppler shifted. Further, because the two beams are coming from slightly different directions, the amount of Doppler shift is slightly different for the light scattered from each incident beam. When these two signals combine at the detector, the result is beating--the formation of a ripple signal whose frequency is proportional to the component of the particle velocity in a particular direction.

Thus, the LDV technique is ideally suited to the investigation of flow patterns. It is an accurate velocity measurement technique, with excellent spatial resolution. During this past year we have made extensive use of our LDV instrument. In this report, we will present a brief summary of the results.

LDV measurements on the DIAL plasma torch

DIAL operates a mid-sized plasma torch in our laboratory for research purposes. In January of 1994, the LDV instrument was used to measure the velocity profile in this torch.

The LDV optics were arranged to measure the axial component of the velocity--the velocity component parallel to the torch axis--and were mounted on a traversing mechanism so that the measurement position could be moved horizontally across the plasma jet issuing from the torch tip.

The torch tip was positioned 5 inches from a block of graphite, so that the torch plasma would impinge directly on this surface. This graphite block also served as one electrode, since the torch was operated in transferred arc mode. The measurement volume for the LDV instrument was positioned so that it was located a constant 1.6 inches below the torch tip.

It was necessary to seed the flow with some small alumina particles to obtain a signal. Figure 12 shows some typical results obtained during this experiment. Here the torch current is fixed at 140 A, and the torch gas is argon. The supply pressure to the torch is being automatically cycled between 22 and 55 psig. This causes the torch operating voltage to vary from 140 to 160 volts. We measured the axial velocity at various horizontal positions to construct the mean velocity profile shown in Figure 12.

Off-site measurements

During this past year, we have made three trips with the LDV instrument. Two trips were made to the DOE/Industry Center for Vitrification Research at Clemson University's School of Environmental Systems Engineering. These trips were made in July and September 1994.

The July 1994 Clemson trip was to measure the velocity in the off-gas riser of a stirred melter. Figure 13 shows several mean velocity profiles measured in this 2 inch diameter pipe.

The September 1994 Clemson trip was to measure the velocity in the off-gas riser from an EnVitCo glass melter. Figure 14 shows several mean velocity profiles measured there.

In October 1994, we carried the LDV instrument to Butte, Montana to measure the velocity in a plasma torch facility, the PACT-6 operated by WETO. Figure 15 shows a mean velocity profile measured in the pipe which carried hot gas from the plasma torch vessel to the secondary combustor in this facility.

Future plans

For the immediate future, we plan to make more extensive velocity measurements in DIAL's plasma torch facility. In addition to the axial

velocity component, we plan to also measure the swirl component of the velocity, since the gas is swirling as it exits from the torch tip.

Figure 12. The LDV measurement location was 1.6 inches below the torch tip and was moved horizontally across the jet of plasma issuing from the torch. The torch gas is argon. The axial component of the velocity was measured. The solid symbols show the mean velocity, and the open symbols the RMS velocity, a measure of how much the instantaneous velocity fluctuates about the mean.

Figure 13. The mean velocity results from several traverses made in the off-gas riser from the stirred melter at Clemson. These measurements were made on July 28, 1994. Each traverse is identified by the time interval during which the data were taken. During two of the traversals, the FTIR system was extracting a sample. The final traversal was made after the feed to the melter had been interrupted and then restarted.

Figure 14. Mean velocity profiles measured in the off-gas riser from the EnVitCo melter at Clemson on September 13, 1994.

Figure 15. A mean velocity profile measured in the pipe carrying gases from the plasma torch to the secondary combustor in the PACT-6 facility at WETO in Butte, MT. This profile was measured between 15:48:26 and 16:47:30 on October 20, 1994.

1.3.3 Coherent Anti-Stokes Raman Spectroscopy

Fang-Yu Yueh and Jagdish P. Singh

The initial CARS measurements were performed in the MSU/DIAL plasma torch. The CARS laser beams were aligned inside the mobile electronic laboratory which is ~40 feet away from the plasma torch chamber. The experimental setup of the measurement is shown in Figure 16 and described in an earlier work.² In brief, the CARS laser beams from the transmitter were sent to the test port with several turning prisms and focused to the test point with a 100 cm focal length lens. The CARS signal was collected with an optical fiber and sent back to the data acquisition/analysis system in the mobile laboratory. All the measurements were performed at a height ~1 inch above the graphite base. The torch was operated on nitrogen. The N₂ CARS spectra were recorded at different positions away from the arc center by translating the field lens position. Figure 17 shows the typical spectra and the test run conditions of this set of measurements. Each spectrum is an average of 200 laser pulses. The signal to noise ratio and the spectral resolution of those data are not very good. To improve the CARS signal strength and spatial resolution, the mobile CARS transmitter was moved from the mobile laboratory to the south side of the torch chamber. With this setup, CARS spectrum can be collected from a single laser pulse (10 ns). Figure 18 shows the recorded single shot CARS spectra. It clearly shows the turbulent nature of the test medium. The temperature inferred from the data recorded with the 100 cm lens are generally colder than expected due to the poor spatial resolution. To improve the spatial resolution, a 30 cm focal length quartz lens was mounted inside the plasma torch chamber. A high temperature CARS spectrum was then recorded. Figure 19 shows the spectra recorded 0.5 inch below the collimator and 1 cm away from the arc center. However, attempts to record the spectrum from the center of the arc have not been successful. Work to improve the sensitivity of the system will continue.

To extract accurate temperature from the CARS torch data, an accurate theoretical model needs to be generated. The theory of CARS can be found from some review papers.^{3,4} A versatile computer code to calculate the CARS spectra of molecular species for combustion diagnostics is available⁵ using the formulation developed by Yuratich⁶ and modified by Kataoka et al.⁷ and Teets.⁸ A nonlinear least squared fitting program has also been developed for analyzing multiplex CARS spectra.^{9,10} To reduce the analysis time, a library of CARS spectra is generally pregenerated for later analysis. However, plasma is a high temperature, nonequilibrium

environment, and the CARS model developed for combustion analysis must be modified to include the effect of thermal nonequilibrium to be used for plasma analysis. In particular, the population fraction needed to be modified to include the independent rotational and vibrational temperatures. Typical spectra of CARS at various rotational and vibrational temperatures were generated using the modified CARS model and are shown in Figure 20.

Studies of CARS fitting techniques were made to find an efficient and accurate way to analyze CARS data from the plasma. Various quick fit and spectral shape fit methods were evaluated for extracting the vibrational and rotational temperature of the plasma. The study was performed with the simulated CARS data which have included the effect of thermal nonequilibrium. Various fitting methods for extracting both the vibrational and rotational temperatures from N_2 CARS data were tested and compared.

The quick-fit methods use the temperature sensitive parameters which are determined from only parts of the experimental spectrum. Various quick fit methods¹¹ were tested. To reduce the time needed to generate the library at particular rotational and vibrational temperatures for the quick-fit analysis, libraries at different rotational and vibrational temperatures were generated beforehand from 1000 - 7000 K in 500 K interval. The simulated CARS data were then generated using this library to find the temperature dependence of various parameters. The width of the fundamental band at 1/4, 1/2 and 3/4 full height were found mainly sensitive to rotational temperature. Therefore, those three parameters were evaluated for rotational temperature measurement. Figure 21 shows the temperature dependence of the bandwidth of the N_2 fundamental band. When the peak height of the hot band ($V = 1 - 2$) is higher than the 1/4 peak height of the fundamental band, the parameter of FW1/4H cannot be obtained. Therefore, FW1/4H can only be applied to the data with the rotational temperature below 3000 K. The width of the fundamental band depends slightly on the vibrational temperature as temperature increases. As long as the vibrational temperature is not too high above the rotational temperature, the bandwidth can be used to determine the rotational temperature directly.

The peak height ratio of the hot band ($V = 1 - 2$) and the fundamental band measured from the simulated N_2 CARS data depends on both rotational and vibrational temperatures. Therefore, it can be used for

vibrational temperature measurement if the rotational temperature was predetermined from the bandwidth measurement. Figure 22 shows the temperature dependence of the peak height ratio of the hot band and the fundamental band. A second order polynomial was used to derive the relation of temperature and various parameters from those curves. Those functions will then serve as a table for vibrational temperature determination.

Initial tests show that the inferred rotational and vibrational temperature from the quick fit method has an accuracy ~6%. These quick fit methods can provide a near real time analysis and are suitable to be used to investigate the thermal equilibrium condition in a plasma environment.

In order to obtain more accurate temperatures, spectral shape fitting method was also explored. To reduce the time in generating the library and fitting, the CARS model was modified to separate the contribution from each vibrational band by using the approximation of $N_{v,J} = N_J N_v$. The population difference $\Delta N_{v,J}$ can then be written as $N_J \Delta N_v$. With this simplification, a single temperature CARS library can be used to extract both T_r and T_v by properly adjusting ΔN_v . Figure 23 shows a typical fit of a single shot CARS torch spectrum using this model. The results of this fitting method are compared with the temperature used in the simulated data to determine the reliability of this fitting method. In general the vibrational temperature inferred from this method has an accuracy of 2.5%. The inferred rotational temperature has a little poorer accuracy. Figure 24 shows the inferred rotational temperature along with the temperature used in the simulated data. This method will give a reasonable temperature for rotational temperature below 2000 K. This is because at relatively low temperature the approximation used in this model is reasonably good. At a higher temperature, the inferred temperature error increases due to an increasing difference between $\Delta N_{v,J}$ and $N_J \Delta N_v$. However, Figure 24 can serve as a calibration curve for accurate temperature determination with this model.

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Figure 16. Experimental configuration for the mobile CARS instrument.

Figure 17. (A) CARS torch spectra at various locations; (B) experimental parameters used to record the above spectra.

Figure 18. N₂ CARS torch spectra recorded from a 5" arc. The measurement point is 0.5" below the collimator.

Figure 19. Single-shot CARS torch spectra recorded with a 30 cm focal length lens.

Figure 20. Simulated nitrogen CARS spectra at various rotational and vibrational temperatures.

Figure 21. Rotational temperature dependence of the bandwidth of N₂ fundamental band.

Figure 22. Vibrational temperature dependence of the peak height ratio of the hot band and the fundamental band of N_2 .

Figure 23. Typical fit of a single-shot torch CARS spectrum.

Figure 24. Error in inferred rotational temperature as a function of Tr .

1.3.4 Multiwavelength Emission Absorption Spectroscopy

Leslie Bauman

The Multiwavelength Emission Absorption Spectroscopy (MEAS) system is a field proven nonintrusive diagnostic instrument capable of providing time-resolved average measurements of temperature and species density. The system is programmed for operation on any of the visible spectrum alkali doublets but could be used for any atomic or molecular species if the line strength is known.

The field system is configured around a 0.32 m focal length monochromator with exchangeable gratings and a vidicon detector controlled by an LSI-11/73 computer. Key milestones for the MEAS concern replacing the early 1980s components with more modern, robust and faster components. During the past year, the main replacement components were purchased and integrated including a 0.5 m monochromator with computer controllable triple grating turret (Acton Research Corporation Spectro-Pro), a charge coupled device (CCD) detector (Princeton Instruments, Inc. TEA/CCD-1024EMUV1 with ST-130 controller) to replace the vidicon and a 66 MHz 486 PC (Dell Dimension XPS 466V with UltraScan video monitor) to replace the old computer. The user interface for the new computer remains to be devised and written. Current use of the system entails using the CSMA software package for data collection and post-test analysis with C programs.

The MEAS system is a very useful general purpose spectroscopic system and the components were selected to maintain the general purpose nature of the instrument. The new monochromator was also purchased with a lateral exit port for a photomultiplier tube detector for scanning operation if desired. The computer controllable grating turret will allow rapid choices of the system resolution and spectral range.

The CCD detector is thermoelectrically cooled and so is easily transportable as it does not require liquid nitrogen. The CCD detector is an area detector with 1024 by 256 pixels of 27 micron diameter designed for spectroscopic application as compared to the vidicon 512 by 512 25 micron pixels. The controller/software allows for many different scan patterns including full surface imaging. Standard operation of the system will be in two-track scans for the emission and absorption signals. The built-in shutter has been mounted at the entrance slit of the monochromator and

will replace the shutter now used in the field system. The other optical components will be unchanged from the current field system.

During the year, the computer monitors for the field system failed and of necessity the original video board of the PC was replaced with one that supports a terminal emulation package. Replacing the old computer monitor for the field MEAS entailed considerable time revising the MEAS software package for the emulator. The LSI computer is still used but the PC now serves as the monitor, and serial transfer of data between the two computers facilitates further data analysis and display on the PC.

Part of the activities concerned surveying the absorption spectrum of the plasma torch with plans to perform these experiments with a Xenon arc lamp as a source of white light. Short and long-term stability testing revealed that the lamp would not be useful for a standard for emission absorption measurements but, with a concurrent reference measurement, the lamp could be used for the survey scans. The routines for the absorption scans were written for the LSI computer and vidicon detector using the second track for the lamp reference signal. A multi-track fiber optic cable was used to view the lamp and the lamp through the plasma on the two tracks of the vidicon detector. Survey absorption scans were run of Ar, He, nitrogen and air plasmas using using a 5 inch arc length with the Xenon arc lamp beam collimated across the arc at a midway position. The arc lamp beam diameter was approximately 1 inch. No significant absorptions were seen due to the high temperature and optical depth of the plasma. Current plans are to repeat the air and nitrogen arc studies with the lamp focused through the outer sheath of the arc. Figure 25 illustrates one of the absorption scans for a nitrogen plasma and shows that the arc is optically thick throughout the visible spectrum.

One major problem in applying an emission absorption technique to a rapidly fluctuating flow is the error that arises due to noncoincidence of the two signals. A study was completed demonstrating that sample averaged measurements can have dramatically increased measurement uncertainty because of rapid fluctuations and noncoincident detection but the average measurements reveal the true flow averages. A paper presenting this study has been accepted for publication in the *Journal of Quantitative Spectroscopy and Radiative Transfer*.

Figure 25. Absorption spectrum for a nitrogen arc at 95% of maximum power.

1.3.5 Pyrometer Systems

Ping-Rey Jang and David Monts

Temperature measurement tests in the DIAL plasma hearth have been completed using the Ratio Pyrometer (RP), Two-Color Pyrometer (TCP) and Multiwavelength Pyrometer (MWP) systems (Figure 26). In these tests, the plasma torch's graphite block electrode (work piece) has been used as a surrogate for plasma torch processed material.

The RP, TCP and MWP systems obtain temperatures from the intensity of the blackbody radiation spectrum; the presence of atomic or molecular transitions prevent a spectral region from being used for accurate temperature measurements assuming blackbody radiation behavior. To test the affect of the hot plasma torch gases on our ability to measure temperatures, a series of tests were performed using the MWP system to record the emission spectrum of the graphite work piece every 30 ms with the plasma torch on and immediately after the plasma torch had been turned off. Emission spectra recorded with the plasma torch on and with the plasma torch off are shown in Figure 27. Strong spectral interference from the torch arc emission exists throughout the visible spectral response regions for all three pyrometer systems. The initial results from an emission study of the torch arc emission using an FTIR spectrometer indicate a spectral interference free region exists in the 1.9 - 2.5 μm range (Figure 28); this region includes the wavelength region monitored by the TCP 2.17 μm detector.

The TCP 2.17 μm detector has been used to monitor the work piece temperature, assuming that the graphite spectral emissivity is 0.625 at 2.17 μm . To investigate the operating characteristics of the plasma torch, a series of parametric tests have been performed with the plasma torch's operating parameters being systematically varied and the plasma torch's performance monitored by several DIAL instruments, including the TCP system. In Figures 29 and 30, graphite work piece temperature vs. torch output power is compared with the variation of torch gas pressure and torch arc length, respectively. The measured temperature results do follow the torch output power variations caused by the changes of the torch operation parameters.

Three field measurement trips were completed during 1994. Because of the nature of the measured targets (joule melters at Clemson University's Environmental Systems Engineering Department's Vitrifica-

tion Laboratory ESE/CU) or because of the location of the measurements (viewing the slag pour with the view of the plasma torch blocked at MSE's Western Environmental Technology Office facility WETO/MSE in Butte, Montana), these measurements do not have the spectral interference evident in measurements on DIAL's plasma torch. Pyrometry temperature measurements were successfully performed during all three tests, providing valuable data to the test facilities.

During the first trip to ESE/CU in July 1994, measurements were performed on the Stir Melter™ glass melter. The RP was used to monitor the glass stream temperature from the melter's pour exit. The TCP was employed to measure the molten glass temperature and emissivity inside the Stir Melter system through the melter's camera port. The MWP was utilized to measure the molten glass temperature and emissivity inside the Stir Melter system through the melter's camera port as well as the glass stream temperature from the melter's pour exit. Typical measurement results for this trip are shown in Figures 31 - 33. The MWP observed emission from gas-phase atomic Li, K and Na while monitoring the melter's glass stream; the MWP did not observe any atomic emission when monitoring inside the Stir Melter system through the camera port.

During the second field trip to ESE/CU in September 1994, measurements were performed on the EnVitCo cold-top glass melter. The RP was used to measure the temperature of the molten glass bath inside the EnVitCo melter through a quartz window on the melter's cover, as well as to make temperature measurements of the molten glass stream pour. The TCP was utilized to measure the molten glass surface temperature and emissivity inside the melter with the top cover opened and the insulation board removed. The cover was closed between each of the TCP measurements to reduce the heat loss. The MWP was employed to measure the temperature of the EnVitCo's glass stream. The MWP did not observe any atomic emission in this set of tests. Figures 34 - 36 show typical results from this test.

During the third field trip, DIAL's pyrometer systems were employed to measure the slag temperature of the RETECH PACT-6 plasma arc centrifugal treatment system at WETO/MSE during the 95-75HOUR-1 test in October 1994. The RP was used to measure the temperature of the slag pour. After exiting the centrifugal plasma arc treatment chamber, the slag falls vertically through a shrouded pour channel and into a barrel. The RP viewed the slag stream in the gap between the pour channel shroud and

the top edge of the slag barrel holder. Due to the moving/swirling slag streams and limited observation area (~0.5 in. high, 2 ft wide), the temperatures measured fluctuated significantly and were discontinuous. Figure 37 presents a temperature plot recorded during Segment 2 of the test when WETO/MSE was processing a mixture of metal and soil. During the last portion of the data in Figure 37, a piece of slag was hanging in the field of view and cooling off. The TCP low temperature detectors were set up to measure the slag temperature at the top of the receiving barrel through the barrel observation port. Since the slag volume level never reached the limited observation region, only the wall of the receiving barrel's temperature was measured. Typical results are shown in Figure 38. The temperature spikes were due to the splash of molten slag falling into the observation region. Starting with the last pour of Segment 2 of the test, the TCP high temperature detectors were set up to measure the slag temperature in the pour channel from a port just underneath the PACT-6 plasma arc chamber. Because of the slag stream movement and the uneven temperature distribution across the slag stream surface, temperatures measured fluctuated significantly and were discontinuous as shown in Figure 39. The MWP detector was used to monitor the slag temperature at a second port just underneath the PACT-6 as shown in Figure 40. Only when the plasma torch was near the exit throat of the plasma torch treatment chamber could the MWP observe emission from atomic K, Ba, Na, N and O; otherwise, no atomic emission was observed. For more details on these field operations, refer to individual field trip reports.¹²⁻¹⁴

Development of a Two-Color Infrared Pyrometer will be the major task during FY 95. As mentioned above, temperature/emissivity measurements inside a plasma torch vessel cannot be accomplished with the current pyrometer systems due to spectral interference from the torch arc emission (Figure 27). This fact became even more obvious during the field trip to WETO/MSE where slag temperature while the material is being thermally processed is a important operational parameter. Initial investigations to identify spectral interference free regions are in progress.

In order to enable the MWP system to monitor multiple locations in a nearly simultaneous manner, development of an optical fiber switcher is needed and is in progress. The expected completion date for this development is December 94. Continuation of pyrometry field measurements is also expected during FY 95.

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Figure 26. Pyrometer systems measurements on plasma torch graphite block.

Figure 27. Torch arc emission spectral interference.

Figure 28. FTIR torch arc emission spectrum in air.

Figure 29. Graphite block temperature vs. torch power during gas pressure variation test.

Figure 30. Graphite block temperature vs. torch power during arc length variation test.

Figure 31. Ratio Pyrometer temperature measurement on ESE/CU Stir Melter system glass stream.

Figure 32. Two-Color Pyrometer temperature/emissivity measurement inside ESE/CU Stir Melter system.

Figure 33. Multiwavelength Pyrometer temperature/emissivity measurement inside ESE/CU Stir Melter system.

Figure 34. Ratio Pyrometer temperature measurement inside ESE/CU EnVitCo melter on the surface of molten glass bath.

Figure 35. Two-Color Pyrometer temperature/emissivity measurement inside ESE/CU EnVitCo melter on surface of molten glass bath.

Figure 36. Multiwavelength Pyrometer temperature measurement of ESE/CU EnVitCo melter's molten glass stream pour.

Figure 37. Ratio Pyrometer temperature measurement at WETO/MSE during Segment 2 of 95-75HOUR-1 test.

Figure 38. Two-Color Pyrometer temperature measurement on WETO/MSE PACT-6 at wall of slag receiving barrel.

Figure 39. Two-Color Pyrometer temperature measurement on WETO/MSE just beneath PACT-6 plasma arc treatment chamber.

Figure 40. Multicolor Pyrometer temperature measurement on WETO/MSE PACT-6 at the throat pour chamber (#2).

1.3.6 Fourier Transform Infrared Spectroscopy

Jeff Lindner

The DIAL FTIR spectrometers were used to support a number of facility experiments during this reporting period. Initial studies centered on evaluation of the emission spectra along with products resulting from operation of the DIAL 75 KW plasma torch. These results were delineated in the FY 93 Annual Report.¹⁵ Subsequent measurements revealed essentially identical results. Further field testing was conducted at the DOE/Industry Center for Vitrification Research at Clemson University (on two occasions) and at the Western Energy Technology Office (WETO) at Mountain States Energy in Butte Montana. A number of necessary system integration tasks were completed in order to accomplish these tests.

The initial field experiments at Clemson were aimed at evaluating the off-gas arising from the Stir Melter system. In this and all of the other downstream FTIR experiments a "dry" gas conditioning system was employed. In brief, a fraction of the gas stream was routed to the long path gas cell by first removing the particulates, using filters, and then by condensing the moisture by cooling the flue to 0°C. This method appears well suited for the determination and quantification of a number of species; however water-soluble organics and acid gases may condense with the water. To eliminate this problem a high temperature White cell has been obtained and a future project involves the development of a "wet" extraction system.

Details of the three field measurement were provided in reports and will not be described in detail here. A typical transmission spectrum of the off-gas from the stir-melter is shown in Figure 41. Molecules identified include CO₂, CO, H₂O, NO, NO₂, HCN, CH₄ and SO₂. Of some interest to facility engineers was the presence of methane. During these experiments an auxiliary methane torch was used to reduce the viscosity of the glass at the tap. Figure 42 shows the CH stretching region for methane. The top trace is a sample of the air inside the vitrification laboratory, the middle trace is the off-gas when the torch was operating, and the lower trace corresponds to a period when the torch was off. The spectra indicate that the majority of the methane observed in the off-gas arises from leakage of incomplete combustion products from the torch into the melter. In a similar manner, inquiries made to gas distributors indicated that sulfur is present in methane in trace concentrations. Thus the origin of the SO₂ in

the melter effluent was also identified. The NO, NO₂ and HCN are products from nitrate feed components.

The second field experiments at Clemson evaluated the effluent from the EnVitCo melter. Figure 43 illustrates two processed absorption spectra. The upper trace is a spectrum wherein the transitions arising from water and CO₂ have been subtracted. The lower spectrum continues the processing by removing CO and CH₄. Other molecules identified include NO, NH₃ and C₂H₄. In contrast to the measurements on the stir-melter the methane and ethylene have been identified as pyrolysis products from the melter. No auxiliary torch was used during these experiments. Measurements were performed at different feed rates to the melter. Figure 44 illustrated the change in absorbance at two different feeds and also indicates the stability of the FTIR measurement protocol.

In contrast to the complicated gas stream observed from the melters, the spectra collected at the MSE plasma torch facility was relatively simple, Figure 45. Part of this contrast resulted from the fact that the input feed stream contained little or no organics. Components identified include NO, NO₂, HONO and CO₂. All of these torch products have also been observed in the effluent from the DIAL 75 KW plasma torch.¹⁵ An interesting experiment to evaluate the efficiency of the ammonia injection catalytic unit was conducted. Sample lines were run from port location up and downstream of the SNCR. The main purpose of these experiments was to characterize any leakage of NH₃, commonly referred to as ammonia slip, through the unit. The spectra presented in Figure 46 show the NO₂ and NO absorbance bands for the gas stream prior to the SNCR (top trace) and the results observed downstream of the unit at different ammonia injection levels. All of the spectra are plotted on a common scale; consequently it appears that the SNCR unit is capable of almost total reduction of both the NO and NO₂. Ammonia was not observed in the gas stream following the catalytic unit.

A second FTIR unit was located at an upstream port location directly after the torch furnace but before the secondary combustor. The purpose of these experiments was to quantify the passive radiation from the molecules in the high temperature gas stream. A series of emission spectra collected when the centrifugal furnace was rotating, when the rotation velocity of the furnace was slowed during a glass pour, and when rotation resumed, is shown in Figure 47. When the glass is tapped, feed to

the melter is stopped. Lines observed in the spectra arise from H₂O, NO and CO₂. During the pour the NO rotational lines from the R branch are isolated; whereas these lines are interfered with by water transitions when the feed is injected. Theoretically the intensities of the NO rotational lines will follow a Boltzman distribution and work is currently in progress to retrieve average (line of sight) temperatures. The CO₂ fundamental is at a maximum intensity during feed injection and drastically decreases during a pour. The shape of this band depends on concentration and temperature and further analysis of this band is possible using some existing models.¹⁶ Separation of the H₂O and NO lines in the spectra collected will also permit assignment of the intensity of the CO₂ band to a concentration or temperature effect.

The above results indicate the potential power of FTIR spectroscopy as a diagnostic tool for the evaluation of waste remediation processes and for characterization of facility component operating envelopes. Some work, however is required for simplifying the experimental protocols such that direct interfacing with an operations system is possible. Towards this end a large portion of the work planned for FY 95 will be directed towards the development of the high temperature gas conditioning system and the implementation of advanced data processing or chemometric methods for rapid quantification of multiple component spectral signatures.¹⁷ Both surrogate waste and nuclear tests are planned at the ANL-West Treat facilities in FY 95, and some considerations for the actual experimental configurations will be needed.

One task, which was not completed during FY 94, was the recovery of particle size distributions from FTIR scattering experiments. Reasons for the delay in this milestone include some mathematical difficulties associated with the inversion formalism and the large effort spent on field studies. The potential benefit to facility diagnostics is, however, large since, in principle, a single FTIR spectrum can be used for the quantification of entrained particles as well as providing molecular speciation and quantification.

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Figure 41. FTIR transmission spectrum of the gas effluent from the Clemson University Stir Melter system.

Figure 42. CH stretching region for methane observed in the Stir Melter system spectra. The data indicates that the source of the methane arises primarily from the auxiliary methane torch used to heat the glass tap.

Figure 43. FTIR spectra obtained from the gas stream of the Clemson University EnVitCo melter.

Figure 44. Measured absorbance values at two different melter feed rates of the EnVitCo melter.

Figure 45. Absorbance spectrum of the off-gas from the MSE Plasma Torch Facility.

Figure 46. Spectra describing the reduction of NO_x compounds by the ammonia injection catalytic unit during the MSE tests.

Figure 47. FTIR emission spectra collected at a port location between the plasma torch and secondary combustor.

1.3.7 Stimulated Raman Scattering

Jagdish P. Singh and Fang-Yu Yueh

A theoretical study of the SRS signal was performed. This study provides helpful information for setting up various laboratory experiments. The shift in the pump laser frequency ($\omega_p - \omega_s$) calculated from an SRS spectrum can be used to infer electron density of the plasma by the equation $\omega_p - \omega_s = (n_e e^2 / m_e \epsilon_0)^{0.5}$. The calculated wavelength shift as a function of electronic density for various laser frequencies is shown in Figures 48 and 49. There is a limitation of this method which is the laser intensity required to drive the Raman instability. The laser intensity threshold was calculated for various experimental conditions. The laser intensity threshold for two different plasma lengths was also calculated for various plasma temperatures and is shown in Figures 50 and 51.

The experimental set up for SRS is shown in Figure 52. A frequency doubled Nd:YAG laser (532 nm) beam is focused on stainless steel and aluminum targets to study the laser produced plasma. The backward SRS signal is also collimated with the same lens. A glass slide beam splitter is used to reflect the SRS signal to the detection system. The SRS signal is passed through different filters to reduce the background due to the pump laser. The filtered SRS signal is focused on the entrance slit of a spectrograph which is 5 m from the target. The signal is detected by a Princeton Instrument (PI) intensified diode array detector. Figure 53 shows the 532 nm laser line. The spectra of the backward reflected signal from the stainless target is shown in Figure 54. The spectral peak position with respect to the 532 nm line changes from pulse to pulse. This might be due to pulse to pulse variation of the laser produced plasma. The maximum shift in the peak position is about 18.9 cm^{-1} which corresponds to a plasma density of $\sim 5 \times 10^{15} \text{ cm}^{-3}$. The inferred plasma density is lower than the expected plasma density in a laser produced plasma. This raises some doubts on the observed SRS peaks. To exclude the possibility of the observed peak is from the emission of stainless, spectra were also recorded with an Al target which is similar to the spectra from the stainless target. Further study is continuing to understand the origin of the shifted peak in the laser produced plasma.

Figure 48. Calculated Raman shift as a function of electron density for 532 nm pump laser beam.

Figure 49. Calculated Raman shift as a function of electron density for 1064 nm pump laser beam.

Figure 50. Calculated SRS laser intensity threshold for various electron temperatures. A parabolic electron density profile ($n = n_0 \cdot (1 - x^2/L^2)$) with $L = 5$ mm was used in this calculation. (Flagged symbol for a 1064 nm pump laser beam; unflagged symbol for a 532 nm pump laser beam).

Figure 51. Calculated SRS laser intensity threshold for various electron temperatures. A parabolic electron density profile with $L = 10$ mm was used in this calculation. (Flagged symbol for a 1064 nm pump laser beam; unflagged symbol for a 532 nm pump laser beam).

Figure 52. Instrument diagram for SRS electron density measurement.

Laser line (Nd:YAG, 532 nm)
(121305---1 & 2)

Figure 53. The unshifted 532 nm laser beam profile.

Figure 54. The backward SRS signal from a stainless target.

1.3.8 Far Infrared Absorption Spectroscopy

Leslie Bauman

Far Infrared Absorption (FIA) spectroscopy was proposed as a nonintrusive measure of electron density in a plasma. The measure is made by recording the optical absorbance and relating the measured optical depth which arises from electron free-free transitions to the electron density using a collision frequency model. Such a technique can provide a continuous, real time monitor of the plasma electron density and electron conductivity or can be used as needed to provide an independent verification of other diagnostic measurements of electron density.

Preliminary milestones for application of this technique to the plasma torch included design, construction and testing of Teflon windows, and testing the detection system for torch interferences. The Teflon windows were constructed but never tested and the interference study was not carried out because of the failure of the far infrared laser. Efforts to repair the laser entailed a protracted wait for components from a supplier with eventual replacement of the far infrared output window. Replacement of this component was expected to restore operation of the laser; however, the infrared pump laser was then below power specification and its grating was replaced. The project was canceled before the final realignment of the laser.

1.3.9 Multicolor Imaging System

Russell K. Lengel

There were three major thrusts in the development and use of the multicolor imaging system this year. The system was used to collect many more images of the DIAL plasma torch, but now the measurements were geared more toward changing and understanding the torch properties than the imaging system. Also this year, the components for a three color system were specified, ordered, and received. Finally, the imaging system was taken on three field trips to provide images of molten glass streams from the joule melters at the Vitrification Laboratory at Clemson University (two trips) and from the PACT-6 plasma arc facility at WETO in Butte, Montana.

For the torch measurements, first a series of plasma torch runs were made at various conditions, and images were taken at all torch conditions and at several different wavelengths for each condition. The major variables for the torch were the current and the plasma length. In general, for all of the gases studied (argon, helium, nitrogen and air), as the torch current was increased, the intensity increased, but not linearly. Proportionately more light was given off at higher powers. For all conditions, but especially for helium and for the longer plasma lengths, the attachment point was much less stable at the lower currents.

Then, a series of torch runs were made in which the power, pressure and plasma length were varied systematically for argon, nitrogen, helium, and air fill gases. At each condition, a representative image was taken. It was found that there was a great deal of variation in the images during the five to ten minutes spent at each operating condition. However, by viewing a series of images it was fairly straight forward to choose which ones to store for later analysis. These images will be compared to other data taken during these tests, and hopefully will be useful in the torch control schemes being developed by the expert systems group here at DIAL.

In July we performed our first field measurements at the vitrification laboratory of Clemson University, concentrating on their Stir Melter system. By using a 75 mm focal length lens equipped with a +1 diopter close-up lens for the working distance of 740 mm, it was possible to image the molten glass exiting the Stir Melter system with sub-millimeter resolution. The drops from the melter ranged in diameter from 7.7 mm

near the exit of the melter to 0.6 mm at there narrowest point. The use of a 900 nm interference filter in the optical train limited the image to the thermal emissions from the glass stream. Also, the combination of this filter and the temperature range of the glass, 760 - 1050°C, made it possible to calibrate the camera system with a blackbody source so that image intensities could be converted to absolute temperatures. There were definite hot and cold spots in individual drops as well as more regular temperature variations.

In September we completed a second field trip to Clemson to take images of the melt stream and melt surface of the EnVitCo melter operated by the Vitrification Laboratory of the ESE department. The melt stream from this melter is quite small, 1.3 mm with a resolution of .2 mm, and uniform in diameter along its length. The temperatures determined with the calibrated camera also showed great uniformity both radially and along the 78 mm length of the stream viewed by the camera. Images taken of the stream at two different wavelengths showed that for the temperature and wavelength range used for these measurements, the emissivity of the glass is close enough to one to allow absolute temperatures to be determined from one color images. Images of the melt surface showed a great deal of temperature variation, with the center of the melt being considerably hotter than the edges, and there were also distinct hot and cold spots.

The multicolor imaging system was part of a group of diagnostic instruments used to make measurements at the PACT-6 plasma torch melter operated by WETO in Butte, Montana. The imaging system was used to provide thermal images of the molten glass stream at two locations on the PACT-6. The first location was looking up into the throat of the melter. The glass exiting at this point, during the middle sections of the approximately 30 second glass pours, was usually quite hot, up to 1500°C, showed gradual and localized thermal distributions, and was broad in spatial width, up to 100 mm. The other imaging location was at the base of the system, where the stream could be viewed through the 18.5 mm gap between the exit of the melter and the top of the receiving barrel. The stream at this location was cooler, below 1250°C, more uniform in temperature, and much narrower, usually around 10 mm in diameter. We hope to make more measurements on this system in the future.

1.3.10 Laser Optogalvanic Spectroscopy

David Monts

Laser optogalvanic spectroscopy (LOGS) will provide the capability to monitor the concentration of off-gases in order to ensure that the vitrification process treatment system and subsystems (scrubber, etc.) are operating efficiently. Species of interest among the off-gases include gas-phase, elemental, toxic trace metals with appreciable vapor pressure (such as As, Cd, Ni, Sb).

When a pulsed laser is tuned into resonance with a transition, there is a transient increase in the ionization rate due to laser-enhanced electron impact ionization (and/or to multiphoton ionization). This LOGS signal is detected by a high voltage electrode (see Figure 55). The LOGS detection circuit transforms the transient LOGS current pulse into a voltage pulse, which a gated integrator monitors only during a selectable time window after the laser pulse. The LOGS spectrum is produced by recording the LOGS signal as a function of laser wavelength. Since LOGS utilizes electrical rather than optical detection, it will provide the capability of operating even in particle-laden or optically-thick media. Moreover, since collection of ions is more efficient than the collection of fluorescent photons, LOGS has greater sensitivity than optical detection techniques. Identification and characterization of species present is performed by applying standard spectroscopic techniques to the analysis of the LOGS spectrum. Time-resolved species concentrations are attained by tuning the laser into resonance with an atomic transition, then monitoring the LOGS signal intensity at that wavelength; periodic calibration of the LOGS signal using a known concentration of the species of interest is used to validate the concentration values.

A series of experiments were performed to probe the reason why the LOGS signal intensity in a flame increases with increasing oxide coating on the electrode. It was found that the oxide coating on the electrode increased the resistance of the circuit, requiring the constant-current power supply to supply a higher voltage to maintain the current at the set value. The increasing voltage of the electrode increased the efficiency of collection of the cations generated by the LOGS process. Experiments were performed to determine whether the LOGS peak height and/or the LOGS baseline changed with time; this was done by scanning the dye laser once an hour and recording the resulting LOGS spectrum of a K transition. The maximum intensity and line width (full-width-at-half-

maximum) of the K LOGS spectra were found to increase with time. The LOGS background level did not change with time. Controls were used to ensure that the observed changes were associated with the effect of the oxide coating on the LOGS signal intensity and not due to the change of other experimental conditions. The conditions used in these studies telescoped into a six-hour experiment changes that would occur over weeks or months in a flame if less reactive material is used for the electrodes. (In a glow discharge cell, the rate of change is expected to be much slower than in a flame.) The results clearly show that periodic calibration of the LOGS signal is required in order to ensure accuracy. A study on the effect of particles on the LOGS signal intensity in a bench-top flame was completed, as was a study on the behavior of the LOGS signals of K, Rb and of Cs generated by multiphoton ionization. The results of our LOGS research in flames were presented in three conference papers.¹⁸⁻²⁰ A new LOGS preamplifier using current technology was designed, constructed, and successfully tested.

Based on a suggestion made at the October 1993 Quarterly Progress Review meeting by Dr. Kevin Carney of Argonne National Laboratory-West, it was decided that the use of a glow discharge cell (GDC) offered significant advantages over the use of multiphoton ionization for detection of metals in the off-gas. A portion of the off-gases will be routed via a slipstream through a GDC, and then the gas will be returned to the gas stream. With the assistance of Dr. Carney, a GDC has been installed at DIAL and a metal hydride generator for production of the volatile metal hydrides of arsenic, tin, selenium, and lead tested. An ultrasonic nebulizer has been acquired and installed in order to enable us to volatilize for metallic elements (such as Ni and Cd) that do not form volatile metal hydrides. The ultrasonic nebulizer can also be used with the inductively coupled plasma-atomic emission spectroscopy (ICP-AES) system that we are assembling with assistance from ANL-W. The ICP-AES will be used in the calibration of LOGS and LIBS, and will ultimately also be attached to the DIAL test stand to provide an on-line monitor of selected metallic species. A library of hollow cathode lamp spectra has been acquired to facilitate tuning the laser into resonance with an optical transition of the elemental metallic species of interest. A pulsed solenoid valve system (see Figure 56) for introducing limited quantities of metal hydride gas into a static pressure GDC has been designed, constructed, and successfully tested. A portable GDC test bed was constructed and installed; this will enable the GDC system to be shared by the LOGS and LIBS systems.

A study of the effect of cell pressure on the LOGS background signal in the GDC has begun. Initial work has concentrated on observation of argon LOGS signals in the visible region before beginning the study of RCRA metals.

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Figure 55. Schematic of Laser Optogalvanic Spectroscopy apparatus.

Figure 56. Pulsed solenoid valve circuit for use with glow discharge cell.

1.3.11 Differential Absorption Laser Spectroscopy

David Monts

Differential Absorption Laser Spectroscopy (DALAS) can provide the capability to monitor the concentration of species at the (sub-) ppm level. DALAS is a general purpose technique that can be applied to a wide variety of species. Of concern among the off-gases are pollutants such as SO_2 and Cl_2 .

DALAS obtains a line-of-sight average concentration from application of the Beer-Lambert law by monitoring the transmitted intensity of two laser wavelengths: one which the species of interest strongly absorbs, and the other is a nearby wavelength that the species does not absorb or only weakly absorbs. The two wavelengths are attained by utilizing a custom two-wavelength dye laser that produces the on- and off-resonance wavelengths on alternating laser pulses. Both wavelengths follow the same path through the sample onto the photodetector. The on- and off-resonance signals are each monitored by dedicated gated integrator modules before being sent to a computer for data acquisition and display.

Construction and testing of the second stage amplifier for the custom dye laser was completed. Progress was slowed by the Nd:YAG laser, which is shared by the DALAS and LOGS projects, being in need of repair for almost the entire first quarter. A multiple-pass (White) cell for decreasing the limits of detection by increasing the sample path was obtained. Components for the associated vacuum system were obtained, and construction of the vacuum system began.

1.3.12 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, 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.²¹ 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.^{22,23} 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 considers 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. Accordingly, we have implemented the cross-correlation technique in a system that uses the attenuation of laser light by particles or droplets as the raw measured variables.

Theory

One key to the cross-correlation velocity measurement technique is the signal processing. Experimentally, two signals are recorded which fluctuate in time; call them $x(t)$ and $y(t)$. The central idea of this technique is that the two signals have some common content, but one signal is shifted in time with respect to the other. (The downstream signal lags behind the upstream signal.) The problem is, given two experimentally recorded signals, $x(t)$ and $y(t)$, to find the value of this time shift.

Let $x(t)$ be the signal measured upstream and $y(t)$ be the signal measured downstream. The first step is to compute the mean values of these signals from

$$\mu_x = \frac{1}{T} \int_0^T x(t) dt$$

and

$$\mu_y = \frac{1}{T} \int_0^T y(t) dt$$

where T is the sampling period. Next, find the root mean square of the fluctuations of each signal about its mean from

$$\sigma_x = \sqrt{\frac{1}{T} \int_0^T (x(t) - \mu_x)^2 dt}$$

and

$$\sigma_y = \sqrt{\frac{1}{T} \int_0^T (y(t) - \mu_y)^2 dt}.$$

The cross-correlation function of the two signals is defined as

$$R_{xy}(\tau) = \frac{1}{T - \tau} \int_0^{T-\tau} (x(t) - \mu_x)(y(t + \tau) - \mu_y) dt$$

and defines a function of τ . A useful form of the cross-correlation function can be found by normalizing this result by the root mean square of the fluctuations. The normalized cross-correlation function is defined as

$$\rho_{xy}(\tau) = \frac{R_{xy}(\tau)}{\sigma_x \sigma_y}.$$

These cross-correlation functions have properties that make them useful. First, if the signal $y(t)$ is a perfect copy of $x(t)$, only shifted in time by a lag τ^* , then both R_{xy} and ρ_{xy} will have maxima at the point $\tau = \tau^*$. Furthermore, the normalized cross-correlation function ρ_{xy} will have a value of one at this maximum. Further, if $x(t)$ and $y(t)$ have some common content, but are not exactly the same, then the peak value of ρ_{xy} will be less than one.²⁴

Thus the cross-correlation method gets its name from the signal processing algorithm used to identify the lag time τ^* . We compute the cross-correlation function from the measured signals $x(t)$ and $y(t)$, and the value of τ where this function reaches a maximum will identify the time required for the fluctuations to convect from the upstream measurement location to the downstream location. Further, the value of ρ_{xy} at this point will indicate the degree to which the fluctuations are preserved as they are convected between the measurement locations.

Experimental setup

A schematic of the test bed is shown in Figure 57. Air to the test bed is supplied from a 1.75 peak HP commercial wet/dry shop vac 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 58 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. The laser beam is first expanded using a 10X beam expander. The two parallel beams are then generated when this expanded beam goes through a two slit mask. The two slits which are 0.15 in. apart, center to center, have a width of 0.01 in. each. The two beams are attenuated when they pass through the water-injected air flow. Each of the attenuated beams is then transmitted through a 632.8 nm optical filter in the detector housing before they are measured.

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.

The signal from each of the detectors is gathered using a high speed Data Acquisition System (DAQ). The DAQ consists of a Data Translation DT 2841-L board installed in a Gateway 2000, 33 MHz, 40486 PC. This acquisition board has a throughput of 750 KHz, a range of 5 V and 12 bit resolution. This Data Translation board is connected to a plug-in DT2878 Advanced Processor board installed in the PC. Data is transferred directly from the acquisition board to the processor board using a 16 bit high speed data port, which bypasses the PC bus. The processor board provides 25 Mflops peak rate execution, has 2 Mbytes of on-board data memory, and it has 32 bit floating point data formatting. Algorithms for this processor board are generated using a software package called DSPworks. This package includes subroutines for performing advanced math calculations on the processor board, including the computations of FFT's and inverse FFT's that are used in the determination of the correlation coefficient.

A FORTRAN program on the PC generates the algorithm for the velocity determination process and downloads it to the processor board. The processor board then sets the measurement frequency and triggers the acquisition board to pass on the measured data points. The processor board performs all computations on the data up to the point where the data has to be rearranged from the calculations of the inverse FFT. This final step is performed by the PC processor. Raw voltage data from the detector are requested and transferred to disc as necessary.

We have set up the system so that there is a real time display of the normalized cross-correlation coefficient of the data on the top half of the screen, which is refreshed with every block of data measured and analyzed. This helps in determining the signal quality, as well as indicating the reliability of the data. The bottom half of the screen gives a real time display of the velocity as a function of time. This velocity data and peak correlation coefficient are periodically stored on disc for later analysis. Provision has been made for altering measurement frequencies as well as size of data sets. The largest data set that can currently be acquired in a single shot for data analysis is 16,384 points (8,192 each channel) for both the channels of detector data. There are also support programs available to aid in laser and detector alignment which are used for setup. We are satisfied with the measurement system and software and feel it is robust and reliable.

Results

Measurements of velocity were made at a distance of 0.23 in. from the exit of the air delivery tube. The water droplet injection was done 2.6 in. upstream of the exit. Figure 59 shows a typical plot of the raw signals from the detectors, at a data acquisition frequency of 500 KHz with 4096 points acquired from each channel. This velocity level in the airstream was the highest one investigated. Signal 1 is the output of the upstream detector and Signal 2 is that of the downstream detector. One can see a delay in the attenuation of Signal 2 with respect to Signal 1. The mean baseline value of the signals from the two detectors is different because of the positioning of the two slit mask in the expanded laser beam. The mean values would be nearly equal if the mask were centered in the beam. The centering of the mask is not necessary for system operation.

Figure 60 shows a plot of the computed normalized cross-correlation coefficient between the two beams for the same data set. The peak

value for the coefficient is slightly to the right of the zero time for correlation, indicating that Signal 2 lags Signal 1. Were there no time delay for correlation, then the peak value of the coefficient would be at a time of 0.0, and if the upstream signal lagged the downstream one, then the peak would occur at a negative time value. The slit spacing divided by the time for correlation is the velocity of the airstream measured by the system. Generally, the plots for correlation showed strong, very distinguishable peaks as shown in Figure 60. Typically, the peak values for the cross-correlation coefficient were in the 0.5 to 0.9 range, and there was no difficulty in picking them out. This plot is displayed on the screen with every set of data measured.

Figure 61 shows a real time velocity plot obtained at maximum air flow through the system. This plot is continuously updated on the bottom half of the display screen. The larger gap in the data, at a time of 1.6 minutes, is caused by a raw data set being saved to disc. A plot of the correlation coefficient of the data is also presented on the second y-axis. With the current version of the program we can obtain about 20 measurements of velocity per minute at 500 KHz when 8192 points of data are acquired. This measurement frequency increases when the data sets for measurements are smaller and when transfer of raw data is minimized.

As can be seen, many measurements of velocity on this plot occur at around 13 m/s. Most of our velocity plots have this kind of pattern, where a significant portion of the measurements fall on a single value. In order to determine if this is a function of the size of the data set being analyzed, we doubled the number of points acquired to 16,384 points for the same valve settings. A plot of the velocity with time for this flow is shown in Figure 62. A similar pattern is observed, which indicates that data set size is not the cause of the observations. The number of observations of velocity for this, double-in-size data set dropped by half, to about 11 per minute. Figure 63 shows a plot of the velocity and cross-correlation coefficient for the lowest air flow setting on the system.

In order to determine the validity of the velocity measurements, comparisons were made on the flow stream using a laser Doppler velocimeter (LDV) available at DIAL. The LDV was used in forward scatter mode and velocity measurements were made at different locations across the flow stream. A profile of the velocity from the traverse is shown in Figure 64. The cross-correlation system measurements for this flow setting at different measurement frequencies are also shown here. The CCS

values are offset from one another only for clarity. CCS velocity measurements are in the 13 m/s range whereas the LDV velocity in the core of the flow stream is around 10.5 m/s. We are still in the process of investigating the cause for this difference in measurement. In none experiment, we set the water droplet sprayer further back in the airstream. For the same flow setting, we measured a core velocity with the LDV of 11.5 m/s. There was not, however, enough attenuation of the CCS laser beams to offer any correlation.

Figure 65 shows the effect of data set size on velocity at different measurement frequencies. Over the range of frequencies selected, the velocity measurements are relatively the same. This indicates that the data set size is sufficiently large, and that the chosen frequencies are in range for the beam spacing used and for the flow velocity.

In practice one would like to go to as small a data set size as needed, while still obtaining good correlations, so that velocity determinations are maximized. For the same reason a higher data acquisition frequency is also desired. It must also be remembered that, for a given beam spacing, there is only a certain range of frequencies that can be utilized to measure a given velocity. Given this, the range of the instrument, in theory, can be increased by spacing the two beams further apart, provided there is enough attenuation of the laser beams that can be correlated. We are in the process of assembling a variable beam spacing system that should also use the laser beam power more effectively. We are still in the process of determining whether the velocities obtained from this system are cross sectionally averaged velocities, or peak velocities. Once these questions are answered, the next step is to determine the operating envelope of this system, especially in terms of the minimum attenuation needed for obtaining reliable data. The addition of the variable beam spacing should also enhance the range of the system. We are, however, very encouraged by the measurements obtained by the CCS, and have confidence that this PC-based velocity measurement system will find many applications.

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Figure 57. Schematic of test bed.

Figure 58. Cross-correlation system schematic.

Figure 59. Raw signal from optical detectors.

Figure 60. Normalized cross-correlation coefficient as a function of time for correlation.

Figure 61. Velocity and correlation coefficient as a function of time for high flow rate setting.

Figure 62. Measured CCS velocities and correlation coefficient for larger data set size at high flow rate setting.

Figure 63. Measured CCS velocity and correlation coefficient for low flow setting.

Figure 64. LDV velocity profile and cross-correlation measurements.

Figure 65. Measured CCS velocities for two different data set sizes, at different measurement frequencies.

1.3.13 Gas Analysis System (GAS)

Porter H. Mitchell and Robert A. Green

During this reporting period, gas sampling and analysis methods for the HP5890 Gas Chromatograph were being developed and will soon be operational. We are investigating a new method which uses two columns with a back-flush technique to analyze the spectrum of permanent gases, light hydrocarbons, halogenated compounds and higher boiling point aromatics. The gas sample is deposited on the first column, which is either a capillary or packed glass column capable of separating the permanent gases and light hydrocarbons. The permanent gases, $C_1 - C_3$ hydrocarbons, and water are allowed to elute from the column, and detected using the thermal conductivity detector (TCD). The higher boiling point materials are retained at the head of this first column. After detection of the last light hydrocarbon, the first column is back-flushed, that is carrier gas flowing through the column is reversed, and the higher boiling point compounds are deposited on the second column. Using temperature programming, the higher boiling point halogenated and aromatic compounds are eluted and detected using the flame ionization detector (FID).

The sampling of the gas stream from the torch will be made before and after the secondary combustor. The sampling ports and sample tubing will be maintained above 100°C to prevent water condensation and subsequent dissolution of volatile compounds. The sample tubing is Teflon lined stainless steel to prevent loss of halogenated species through reactions with the metal tubing.

Qualitative/quantitative analysis will be performed after standardization with known materials. Samples of pure materials, identified in previous post-torch gas effluents including 34 chlorinated phenols, anthracenes, and other high boiling point compounds, have been acquired and will be used as standards.

Future work includes GC calibration and analysis method refinement. Specifications for post-GC mass spectrometer will be developed and manufacturer data accumulated.

The SO_2 analyzer was received from the factory after being repaired and recalibrated. It was then reinstalled and successfully tested. Further progress was made on the Method 5 equipment revitalization in prepara-

tion for the upcoming WSRC tests. The selection criteria for the GAS software was developed and final selection of the software is anticipated by 20 November 1994.

The DIAL gas analysis system was reassembled and made operational. This system consists of conventional gas analyzers which can measure SO₂, CO, CO₂, O₂, NO_x and combustibles. All analyzers are rack mounted and the system is plumbed to allow the introduction of calibration gases and gas sample to each of the analyzers. All pressures and flow rates can be adjusted from the front panel of the rack. Data is logged to a personal computer for later analysis and archiving.

A gas sample conditioning system was constructed to extract a gas sample and perform the necessary particulate filtering and water condensing required by the gas analyzers. This system was located such that it can be quickly switched from operating on DIAL's plasma torches to the combustion test stand. The complete system is fully operational and is routinely used at DIAL in support of instrumentation testing and development.

In support of tests to be conducted for Westinghouse Savannah River Center, DIAL began work on performing EPA Method 5 particulate analysis. Some hardware was on hand and some was recently procured. Significant progress has been made in this area and efforts will continue.

Future work includes the routine operation of the GAS and maintenance of the hardware. New software will be written to receive the data from the gas analyzers and then to display the information in a user-friendly manner. This software will be more functional and easier to use than the current software. A method to evaluate software of this type was developed by modifying the procedures used to select expert systems for plasma torch operation. This procedure will be written up in a report for use by others. The purchase of additional analyzers to expand the spectrum of gases analyzed will also be evaluated for possible addition to future budgets. The expansion of DIAL's analytical techniques into other EPA methods will be investigated with the intent of developing capabilities to perform these tests at MSU.

1.3.14 Laser-Induced Breakdown Spectroscopy (LIBS)

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

DIAL has two systems to perform the various LIBS measurements. Both instruments provide data from solid or gas phase samples. One system is mainly used to record spectra in the laboratory, while the other system is a rugged, compact, portable and versatile instrument used for field measurements.

The experimental arrangement of the LIBS system was described in an earlier report.²⁵ A frequency doubled Nd:YAG laser (Continuum) beam is focussed to produce a spark at the sample. The emission light from the spark is coupled to an optical fiber. Various optics arrangements are used to focus the laser beam and to collect the LIBS signal in different LIBS measurements. The other end of the fiber is attached to a spectrograph. An intensified diode array detector or a vidicon detector from Princeton Applied Research Corporation (PARC) is attached to the exit of the spectrograph. A high voltage pulse from a pulse generator is used to operate the detector in the gate mode. A detector controller is used to control the detector and to transfer the data to a data acquisition/analysis computer.

Spectra were recorded to study the LIBS spectra of aerosol. Figure 66 shows the Cr LIBS spectrum recorded with an aerosol generator. To record Ag and Cu spectra simultaneously, a mixture of Ag and Cu salt solution was injected into the aerosol generator. The recorded spectrum was fitted with computer simulated LIBS spectra to infer the relative concentration of the elements, as shown in Figure 67.

The LIBS spectra was calibrated by making measurements with metal hydrides in a stainless steel sample cell. A known concentration of metal hydride was generated in a hydride generator and injected into the sample cell. Spectra were recorded with different buffer gases. Figures 68 and 69 show the typical spectra with 100 ppm and 1 ppm Sn solution with helium as the buffer gas. One ppm solution concentration is equivalent to 0.15 ppm (v/v). Similar spectra were recorded with various metal hydrides at different conditions.

To study the LIBS spectra of vitrified glass, the spectra were recorded from various vitrified glass samples. The experimental setup used for the measurement is described elsewhere.²⁵ Figures 70, 71 and 72 show the

spectra recorded with the various glass samples from Clemson University and MSE. The spectra clearly show the difference in the composition of the various samples. Spectra were also recorded in different spectral regions. These spectra were used to infer the relative concentration of the different elements.

The mobile LIBS system was used to perform the LIBS measurements at Clemson University's Stir and EnVitCo melters and also at WETO/MSE. These field measurements are summarized below.

LIBS measurements at Clemson University Stir Melter system

DIAL's LIBS group recorded and identified the LIBS spectra observed from the molten glass of the Stir Melter system at Clemson University during a five day test run, July 25 - 29, 1994. The LIBS spectra emitted by the molten glass droplets were recorded between 320 and 770 nm. By comparing the measured wavelengths and relative intensities with the standard tabulations of atomic emission spectra, most of the observed emission lines can be identified.

Some of the recorded spectra used for analysis in the field tests are shown in Figures 73 and 74. Besides identifying the species, attempts were made to calculate the concentration ratios of various species based upon one particular element. The relative concentrations of the identified elements were obtained by fitting the observed LIBS spectra with the theoretical spectra and also by comparing the intensity of the spectral lines. Plasma temperature is an important parameter which affects the observed LIBS spectra. By assuming LTE and using Boltzmann's plot, plasma temperature was obtained. The temperature was found to be 7500 K. The concentration ratios were computed by using the spectra recorded during the test run with the inferred plasma temperature. Twenty LIBS spectra of each observed wavelength region (about 40 nm), recorded at the same condition for comparison, were analyzed to obtain the element concentration ratios. The average ratios and their standard deviations were inferred from the twenty spectra in each spectral region. By analyzing the data recorded on July 25 and 28, several problems were found which can affect the accuracy of the analysis. Emission lines of Ca covered all the recorded spectral regions and were used as a concentration reference in the glass sample analysis. However, the Ca lines were found to be self-absorbed in most of the recorded spectral regions. Therefore, it cannot be used as a concentration reference in many of those spectral regions. In that case, the

concentration ratio must be calculated using two low concentration elements which might also reduce the accuracy of the results. Table I lists the analysis of LIBS spectra of the Stir Melter system. Because of the difficulty in finding a single reference element for all the spectral regions, the concentration ratio may have a different reference element depending on the spectrum used.

Table I. Relative mole fraction inferred from LIBS data of Stir Melter system.

C ratio- Date	f_{Cr}/f_{Mg}	f_{Fe}/f_{Mg}	f_{Na}/f_{Ca}	f_{Li}/f_{Ca}
7/25/94	6.6×10^{-2} (5.3×10^{-3})	1.26 (4.5×10^{-1})	0.153 (2.1×10^{-2})	0.85 (6.3×10^{-2})
7/28/94	6.7×10^{-2} (5.6×10^{-3})	0.66 (2.3×10^{-1})	0.18 (3.0×10^{-2})	9.31×10^{-1} (5.0×10^{-2})

Several differences were found from the LIBS spectra recorded at the Stir Melter system and that recorded with the glass sample at MSU. Higher self absorption of calcium in some wavelength regions was observed in the Stir Melter system spectra. This affects the accuracy of the inferred concentration ratios. The signal to background ratios of the LIBS melter data are smaller, which can also affect the concentration ratio measurement.

LIBS measurements at Clemson University EnVitCo melter

The arrangement of various components of the LIBS system was modified for the measurement of the EnVitCo melter, based on the previous experience from the Stir Melter system measurements.²⁶ The laser beam was 35 cm below the melter outlet. To avoid the problems of the self absorption in the Stir Melter system measurements, the detection system was moved from the DIAL mobile laboratory which was 80 feet away from the Melter, to a place closer to the Melter and used a UV optical fiber 5 meters long to improve the detection sensitivity. The spectra were also recorded at low laser power. The alignment of the laser beam was very critical due to the limited space available near the melter outlet. The laser beam had to be aligned at an angle to pass between the container of the molten glass and the steel frame which support the melter. To make

the system more compact, the spectrograph, detector controller and HV trigger pulse generator were kept in a box with the laser head and optics.

The LIBS spectra of the EnVitCo melter were collected during the September 13, 1994 run. Figures 75 and 76 show the typical spectra recorded during that run at different spectral regions. Assignments of the elements are also marked on the figures. The LIBS data were analyzed by comparing the experimental data with the simulated data. Figures 77 and 78 show the results of fitting from two different spectral regions. The relative mole fractions of Cr, Ni, Al and Pb, with respect to the mole fraction of Fe, were obtained from these two spectral regions. Because the spectroscopy data of some emission lines were not available, those lines were excluded from the fitting. By comparing the linewidth of simulated data with that of the experimental data, we found the problem of self-absorption still existed in some strong emission lines which could produce a larger error in concentration of that element.

Table II. Inferred element concentration ratios of the Clemson EnVitCo molten glass.

Element	Cr	Ti	Ni	Pb	Al	Si
C/C _{Fe}	0.023	0.017	0.071	0.01	13.3	28.6
σ	0.0079	0.0047	0.057	0.00431	2.54	2.23

Table II shows the analysis of LIBS spectra of the EnVitCo molten glass. Elements such as Cr, Ti, Ni, Pb, Al and Si can be found from two different spectral regions which were analyzed. The averaged inferred concentration and its standard deviation of those elements were listed. The standard deviation of Ni is higher compared to other elements due to the relatively weak signal in one spectral region and the problem of interference from other nearby lines.

LIBS spectra were also recorded in the EnVitCo off-emission on September 19, 1994. Figures 79 and 80 show typical spectra at the center wavelengths of 248 and 285 nm. Similar spectra were recorded from 230 to 460 nm. Some of these spectra have similar S/N as the spectra of molten glass. The spectral lines from the off-emission were narrower than the lines observed with molten glass. The elements identified in the off-emission were Al, B, Ba, Ca, Cr, Cu, Fe, Mg, Mo, Na, Ni, Si and Ti. Special

attention was paid to assignment of Mo lines because it was not listed in the feed. Mo was observed in both molten glass and off-gas measurements.

LIBS measurements at WETO/MSE

Figure 81 shows the experimental setup of the LIBS system which has been modified to optimize the signal for the off-emission measurement.²⁷ A frequency doubled Nd:YAG laser (Continuum Surelite I) beam is focused with a 30 cm focal length lens. The laser beam was aligned to an optical port before bag house. The same port was used to collect the LIBS signal. A beam dump was mounted on the opposite port across the gas stream to dump the laser energy. The emission from the Spark is collected with an UV optical fiber of 1 mm core diameter and 1 m long and couple to an Instrument SA Inc. HR 460 spectroscopy. The detection system is the same as described previously.

LIBS spectra were recorded in various spectral regions during the three test run segments. 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. Figures 82, 83 and 84 show some of the identified spectra at center wavelengths of 267, 359 and 431 nm. The strongest Cr lines were in the spectral regions of 431 and 359 nm. There were also some Fe lines near the Cr lines. Therefore, the relative concentration of Cr and Fe can be inferred from these two spectral regions using the intensity ratio. Figure 85 shows the histogram of the inferred Cr/Fe concentration ratio obtained from these two spectral regions. The spectra at 431 nm was recorded two minutes after the 359 nm spectra. The results from these two spectral regions were in reasonable agreement. In most cases, 20 LIBS spectra were collected under the same experimental conditions. To compare the measurements with different sample numbers, 100 spectra were also recorded under the same conditions in some spectral regions. The histogram from these two sample numbers were compared. The distribution of the 100 sample number data were closer to a Gaussian distribution than the 20 sample measurement. However, the mean value and the standard derivation of these two sets of measurements were very close. The results of this statistical study are shown in Figure 86. The concentration of Cr can be readily compared in the three segment runs with the data collected under the same experimental setup. The intensity of the Cr 428.98 nm lines was plotted at different segment tests and shown in Figure 87. The concentration of Cr

decreased from Segment 1 to Segment 3. Also, the Cr concentration dropped during pouring (no feed).

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 in the same spectral region as shown in Figure 88. CN formation was readily observed from the spectra of the laser spark of air. Since CN was not found from the FTIR measurement, the observed CN band in the 418 nm region is believed to be due to the formation in the high density plasma produced by the laser spark. Atomic emissions from N were found from the recorded LIBS spectra in the spectral region 743 nm. A strong C line at 247.86 nm was also identified from the observed LIBS spectra as marked in Figure 89. This line was used to monitor the C concentration at different run conditions. The intensity of this C line at different segment measurements was plotted in Figure 90. The carbon concentration was decreased about two times from Segment 1 to Segment 2.

The Ni lines can be found from some of the spectra recorded near 302 nm.²⁷ 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 can 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 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_2CO_3 concentration in the feed was increased from 0 to 4% in Segment 3 than that in Segment 2, the measurement shows that most of the Na has gone to the slag. The Na observed in Segment 2 is due to the presence of Na in the soil.

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Figure 66. Cr LIBS spectrum in aerosol.

Figure 67. Comparison of theoretical LIBS spectrum with an experimental spectrum recorded from Cu and Ag seeded aerosol.

Figure 68. LIBS spectrum of 100 ppm Sn from hydride generator.

Figure 69. LIBS spectrum of 1 ppm Sn from hydride generator.

Figure 70. Laser-induced breakdown spectroscopy of Clemson University glass sample.

Figure 71. LIBS spectrum of MSE vitrified glass, low Fe and Na.

Figure 72. LIBS spectrum of MSE vitrified glass, high Fe, low Na.

Figure 73. Observed LIBS spectrum from Clemson Stir Melter system near 437 nm.

Figure 74. Observed LIBS spectrum from Clemson Stir Melter system near 528 nm.

Figure 75. LIBS spectrum of melt glass, Clemson EnVitCo melter, 9-13-94.

Figure 76. LIBS spectrum of melt glass, Clemson EnVitCo melter, 9-13-94.

Figure 77. Fitting of the EnVitCo molten glass LIBS spectrum ($C_{Cr}/C_{Fe} = 0.02$, $C_{Ti}/C_{Fe} = 0.014$, $C_{Ni}/C_{Fe} = 0.014$, $C_{Pb}/C_{Fe} = 0.008$).

Figure 78. Fitting of the EnVitCo molten glass LIBS spectrum ($C_{Cr}/C_{Fe} = 0.021$, $C_{Al}/C_{Fe} = 13.46$).

Figure 79. Clemson EnVitCo off-gas LIBS spectrum.

Figure 80. Clemson EnVitCo off-gas LIBS spectrum.

Figure 81. LIBS experimental setup.

Figure 82. LIBS spectrum, WETO/MSE before baghouse, 10-17-94.

Figure 83. LIBS spectrum, WETO/MSE before baghouse,10-17-94.

Figure 84. LIBS spectrum, WETO/MSE before baghouse, 10-17-94.

Figure 85. Inferred $f(\text{Cr})/f(\text{Fe})$ from data recorded in spectral regions of 431 nm (top) and 359 nm (bottom).

Figure 86. Inferred $f(\text{Cr})/f(\text{Fe})$ from the 20 sample data (top) and the 100 sample data (bottom).

Figure 87. MSE off-gas LIBS measurements, Cr LIBS intensity @428.98 nm.

Figure 88. LIBS spectrum of MSE off-gas during Segment 1 test run showing CN.

Figure 89. LIBS spectrum of MSE off-gas during Segment 1 test run showing C, Si and Fe+ lines.

Figure 90. MSE off-gas measurement, C LIBS intensity @ 247.86 nm.

Task 1. Subtask 4. Torch Operation/Correlations

Russell K. Lengel, David Monts and O. P. Norton

A series of torch runs were made in which the power, pressure and plasma length were varied systematically for argon, nitrogen, helium, and air fill gases. At each condition, a representative image was taken. It was found that there was a great deal of variation in the images during the five to ten minutes spent at each operating condition. However, by viewing a series of images it was fairly straight forward to choose which ones to store for later analysis. These images will be compared to other data taken during these tests, and hopefully will be useful in the torch control schemes being developed by the expert systems group here at DIAL.

Efforts by the Emission Spectroscopy group, reported above, concentrated on recording emission spectra in order to correlate the observed emission intensities with torch operating conditions so that the temperature of the plasma could be determined and operation of the plasma torch be optimized. Comparison of emission spectra recorded by the SiDA system indicate that of the various species present in nitrogen and air plasmas, the atomic nitrogen transitions are the most sensitive to changes in plasma torch power. Spatially-resolved emission spectra recorded by the MEAS system reveal dramatic changes in intensity and species present along the length of the plasma arc. These results, in conjunction with those of the MCI system, indicate that the entire plasma arc must be imaged in order to obtain reliable determinations of the average plasma temperature.

We have performed a series of experiments on DIAL's PT-50 plasma torch. In these experiments, the variation in torch voltage was measured while systematically varying the torch current and gas delivery pressure (which controls the flow rate of gas through the torch). These experiments were repeated for arc lengths (distance from the torch tip to the graphite workpiece) of 3" and 6", and using nitrogen, air, argon, and helium as the process gas. The results of these measurements were correlated in terms of the first and second Yas'ko numbers, which are dimensionless quantities.

Task 1. Subtask 5. Product Evaluation

Robert A. Green

This subtask was initially conceived as developing the capability for DIAL to perform product evaluation/characterization tests of material treated in plasma processes. After some tests procedures were investigated, it was decided that other facilities within the EM-50 area already had this capability. During a quarterly review, it was decided that DIAL need not duplicate these tests at this time. Emphasis then shifted to the development of a glass melter to allow testing of DIAL instrumentation to be performed on the product and the development of a method to measure the internal temperature of the glass in a melter.

In order to test DIAL instrumentation for use at Clemson University, an effort was undertaken to design and construct a melter capable of melting glass samples. The melter would allow the sample to drip through the bottom of the vessel simulating the flow from an actual melter. A design was developed, but equipment necessary to construct the melter could not be obtained in time to support the Clemson tests. The melter may be constructed during the next fiscal year to allow further instrumentation testing at MSU.

Another task was the development of a probe system capable of measuring the internal temperature of the glass melt. The concept is to use the lightpipe sensor enclosed in a ceramic sheath to make the measurement. The ceramic would be inserted into the glass melt and allowed to come to equilibrium. The lightpipe sensor would then be used to measure the temperature of the inside of the ceramic sheath which would act as a blackbody. Initial modeling was conducted to determine if this was indeed feasible and some initial designs were discussed. This task will continue into the next fiscal year.

In recognition of the change in direction of this subtask, it has been combined with Special Projects in FY 95. Work will continue and be reported under that subtask.

Task 1. Subtask 6. Modeling

O. P. Norton

Electrical conductivity calculations. The electrical conductivity of the plasma is important when modeling a plasma torch. In this last year, we have improved our calculation of the electrical conductivity.

The electrical conductivity is determined from the electron number density and the electron mobility. The electron number density is found from the same equilibrium calculation described in last year's report. However, we have improved the calculation of the electron mobility, which depends on the momentum transfer cross-sections for collisions between electrons and the other species in the plasma.

Previously, these cross-sections were assumed to be constants, following the method described by Rosa.²⁸ In the past year, we have implemented an improved electron mobility calculation method following the method of Frost²⁹ (see also Mitchner and Kruger³⁰). In this method, the dependence of the cross-section on the collision energy is specified, and is then integrated over a Maxwell-Boltzmann distribution of electron energies. Figure 91 shows some results from this calculation, showing the computed electrical conductivities of air, nitrogen, argon, and helium as functions of temperature at one atmosphere of pressure.

Flow field modeling

During this past year we have made considerable progress on a first-principles model of the plasma torch system. The flow field is found using the techniques of computational fluid dynamics (CFD). The solution of the CFD model specifies the distributions of velocity, density, pressure, and temperature in the computational domain. Then, using the results of the electrical conductivity model described previously, the local electrical conductivity is found. From the local electrical conductivity, and the specified electrical boundary conditions, the voltage and current distribution in the plasma is found. Then, from this the Joule heating term (I^2R) is evaluated, which is then fed back into the CFD model as a heat source in the energy equation. This Joule heating is important, since this term is responsible for heating the gas so that it will conduct electricity.

Figures 92, 93, and 94 show some of the first results we have obtained from this model. In each figure, the computational domain is represented as a square. This square is a domain in r - z coordinates (r being the radial coordinate and z the axial coordinate in a cylindrical coordinate system). This square represents a 3 inch by 3 inch area. We have modeled the flow external to the torch, where the hot plasma issues from a circular opening in the torch tip and then impinges on flat workpiece which is three inches away. Due to the symmetry of the problem, we assume that there is no variation in θ , the angular coordinate. The figures are aligned so that z is horizontal and r is vertical.

The orifice at the torch tip, from which the plasma issues, is at the lower left. The workpiece is on the right. On the bottom is the symmetry axis $r = 0$. The fluid is free to flow out of the computational domain across the line $r = 3$ inches, which is at the top of the figure.

Figure 92 shows the computed velocity distribution in the torch jet. The plasma enters from the left as a 0.475 inch radius jet with a z velocity of 150 m/s. The fluid properties were given values appropriate for an air plasma. Figure 93 shows the temperature distribution computed by the model. The plasma exiting the torch tip was given a maximum temperature of 8000 K, so the 12000 K temperatures seen in the solution show the effects of Joule heating as the current flows through the gas. Figure 94 shows the voltage distribution calculated by the electrical solver. In this step, the workpiece was assumed to have an electrical potential of zero volts, and the exit plane of the torch was assumed to be another equipotential surface. This voltage was varied as the solution progressed to fix the total current between the torch and the workpiece at 150 A.

One item of particular interest is the heat flux distribution on the workpiece surface, since this is what one is trying to heat with the plasma torch. Figure 95 shows the calculated heat flux distribution from the CFD solution. This is purely a convective heat flux distribution, gas radiation has not yet been added to the model.

Future plans

In the short-term future, we plan to focus on two areas. First, after some measurements of the swirl velocity become available, we plan to add a swirling component to the calculation described above. We know that the gases in the torch are deliberately swirled, but the amount of swirl is

unknown to us. In our calculation, we need to specify the velocity of the gas exiting the torch as a boundary condition. When swirl measurements are available, we will add this to the calculations.

We will also be working on the problem of radiative heat transfer in the torch system. This may or may not be a significant heat transfer mechanism. We have obtained a program from NASA called NEQAIR2, which has an extensive spectroscopic data base and can compute the spectral emission and absorption coefficients for hot air plasmas.^{31,32} This will give us the ability to predict the radiative heat transfer from the plasma when air or nitrogen is used as the torch feed gas.

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Figure 91. The computed electrical conductivity for plasmas formed from air, nitrogen, argon, and helium at one atmosphere of pressure.

Figure 92. A flow field solution for the flow between the tip of the torch and workpiece. The flow exits the torch tip (on the left) and impinges on the workpiece, represented as a flat surface (the right boundary). The solution is shown in a 3"x 3" section of the r-z coordinate plane, with z horizontal and r vertical. At each point, an arrow is drawn which represents the local velocity vector.

Figure 93. Temperature (K) contours in the r - z plane from the CFD flow field solution.

Figure 94. Contours of electrical potential in volts. 150 A is flowing from the torch (on the left) to the workpiece (on the right).

Figure 95. The computed convective heat flux to the workpiece.

Task 1. Subtask 7. Torch Design

Bert Nail

An audio sensor was installed in the PT-50 torch vessel, designed to monitor the resonance in the inner electrode. Experiments underway are designed to produce data that may be correlated to torch attachment point or arc rotation rate. Both of these are important in plasma torch design and operation.

Task 1. Subtask 8. Field Operations

Robert L. Cook

1.8.1 Field Operations

Robert L. Cook

DIAL's mobile instrument laboratory was employed during the weeks of July 25 - 29 and September 12 - 16, 1994, to support a series of measurements at the Clemson University Environmental Systems Engineering Vitrification Laboratory. At Clemson, exploratory measurements on the Stir Melter and EnVitCo melters focused on determination of the melt temperature, the melt discharge temperature, thermal images of the melt discharge, off-gas compounds, the heavy metals in the molten glass, and the off-gas local flow velocity and velocity profile exiting the melters.

DIAL's mobile instrument laboratory was also employed during the week of October 17 - 21 to support a series of tests at the Western Energy Technology Office (WETO) operated by MSE in Butte, MT. The diagnostic measurements on the Plasma Arc Centrifugal Treatment System represent 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 earlier with representatives of WETO and Clemson to identify the measurement locations and other specifications.

1.8.2 Field Operations (ANL-West Project)

Jeff Lindner

Some limited FTIR experiments were conducted in support of ANL-West. These studies were concerned with the determination of absorption cross-sections for HCl. Results indicated that physical absorption of the gas on the cell walls was occurring but that this effect could be accounted for by performing the measurements rapidly (within 10 minutes) or by continuously flowing the gas through the cell. Planned experiments on speciation from the combustion of chlorinated organics was, however, not completed. These experiments have been delayed so as to coincide with the installation of the air pollution control system on the DIAL test facilities. Since this delay additional interest from Dr. Kevin Carney at ANL-West has been expressed in the destruction of waste using

an inductively coupled plasma. This unit was obtained by ANL-West and is being modified for operation on air by workers at Ames Laboratory. It is expected that the unit will be shipped to DIAL in early 1995 and thereafter can be used as a test bed or as an analytical instrument. Work will also continue with ANL-West for supporting plasma hearth testing at the Treat facility.

Task 1. Subtask 9. Downstream Emission

Jeff Lindner

During this reporting period milestones on the analysis of the effluent from the plasma torch using FTIR and incorporation of the gas analyzers for on-line monitoring of the torch off-gas were completed. Milestones on incorporating a gas chromatograph for online measurement of the test facility effluent and for determination of SO₂ in the gas stream of the DIAL combustion test train by DALAS were not accomplished. Additionally, milestones relating to support of plasma torch operations with surrogate waste streams and the establishment of the limits of detection for all of the downstream techniques were not finalized.

Delay of the gas chromatograph milestone was a direct result from a delay in obtaining the unit from the manufacturer. This unit is now in operating condition and the necessary components for direct interfacing to the test facility effluent are on order. The DALAS experiments were reconsidered and a change in work scope was made. Test facility experiments using surrogate waste streams are scheduled for early FY 95 and the large plasma torch unit (200 kW) along with the new air pollution control system will be employed. These results will be gathered with the individual diagnostic instruments. In a like manner limits of detection are being determined.

Task 1. Subtask 10. Special Projects

R. Arun Kumar and Bert Nail

We have primarily looked at the application of different viscometry techniques, in order to determine if there were any commercial viscometers available that could be used, or modified for use, to make *in situ* measurements of viscosity of molten glass. Data was provided to us by Westinghouse Savannah River Corporation (WSRC) on the Frit compositions as well as all the other relevant physical and chemical properties of the expected glass melt. The properties were provided as a function of temperature. We have searched the literature for relevant references and techniques. We have obtained catalogs from some of the major companies who sell viscometry units. We also specifically investigated one relatively new product that is marketed for the measurement of viscosity of glass. It uses an oscillatory technique as compared to a direct rotational technique used by most other manufacturers. Some of the information provided by this and other manufacturers was also in the form of relevant publications.

There does not appear to be any instrument that can be taken off the shelf and used directly to measure the viscosity of the glass melt in the melters. Some of the measuring heads can be utilized with a specially designed refractory rod to make viscosity measurements. Since the torque measured by the measuring head is directly proportional to the depth of insertion into the melt, a differential method of measurement is recommended.

We have also done a survey of the literature regarding the use of different materials as wetted surfaces in a glass melt. This would be necessary in case a rotational viscometry technique or other indirect intrusive measurement method were to be used to measure the melt viscosity.

WSRC and others have already determined that electrical conductivity/resistivity of the glass melt is a good indicator of the viscosity. This is true, provided that the relationship of one to the other is known *a priori*. As an example, for the case of a high Fe Frit-165 mixture the viscosity-conductivity relationship is nearly the same as that of an the average Frit (TDS-3A). The high Al Frit-165 has a relationship different from the average. On the other hand the viscosity-density relationship of

the high Al Frit-165 falls nearly on top of the average frit. So it appears that under these circumstances a resistivity measurement is very useful for a high Fe melt and a density measurement is very useful for a high Al measurement as a measure of the viscosity.

A report, which is to include all the references and some relevant catalogs, is being prepared and will be sent to WSRC. We are also in the process of looking at some methods that can be used to measure the electrical resistivity. We may also include a real time density measurement technique if it is found to be needed.

Task 1. Subtask 11. Diagnostics/National Effort

R. Daniel Costley

Photo-acoustic technique for measuring velocity and temperature of gas flows simultaneously

This technique involves creating a plasma spark in the gas with a pulsed laser via a breakdown mechanism. An acoustic disturbance is produced which propagates upstream with the velocity $c_0 - v_f$ and downstream with the velocity $c_0 + v_f$ where c_0 is the sound speed and v_f is the gas flow velocity. HeNe laser beams are positioned both upstream and downstream from the spark. The change in density at the acoustic wavefront causes a change in the index of refraction, which in turn causes the beams to deflect. It is a simple matter to detect this deflection with a photo-detector and an oscilloscope. The gas flow velocity and the sound speed can be determined from the arrival times of the acoustic disturbance and the separation distances of the beams from the spark. The temperature can be determined by knowing the sound speed as a function of temperature. The instrumentation for this technique appears to be simple, robust, and therefore relatively simple to implement in the field. In preliminary, room temperature experiments in the laboratory, we were able to measure flow velocities ranging from 1 m/s to 7 m/s. We were also able to measure the temperature to within 1°C.

Several possible applications of this technique come to mind. One is monitoring the flow velocity and temperature in off-gas systems for process control type applications. Similarly, it could also be used in conjunction with EPA method 5 diagnostics to determine the flow velocity so that off-gas samples can be extracted properly. At present, this function is being performed with a Pitot tube, which tends to get clogged in gas streams containing particles. The Pitot tube is also not very effective in measuring low flow velocities. This technique could potentially be used in flame diagnostics or in fluids.

TASK 2: ADVANCED COMBUSTION CONTROL & PROCESSES

Task 2. Subtask 1. Real Time Combustion Controller

Jeff Lindner

The Real Time Combustion Controller (RTCC) was initially developed with the thought of nonintrusively measuring the infrared emission intensities of major gases resulting from combustion. Previous work in these laboratories using FTIR spectroscopy for high temperature infrared signature analysis indicated that specific relationships exist between the radiance of a given molecule and the combustion stoichiometry.³³

The combustion efficiency can be defined as

$$E = [\text{CO}_2] / ([\text{CO}] + [\text{CO}_2])$$

where the square brackets denote concentration. In practice, the combustion efficiency will attain a maximum value of 1 under conditions of complete combustion. The combustion stoichiometry, ϕ , is defined as the ratio of air to fuel in the combustor. For a simple hydrocarbon fuel, if the stoichiometry has a value of 1, complete combustion will result and the major products will be CO_2 and H_2O . At stoichiometry values less than 1 complete transformation of the fuel will not occur and additional combustion products such as CO , CH_4 and other hydrocarbons can result. In a like manner, at air to fuel ratios greater than 1, the combustion temperatures will be reduced and this can reduce downstream heat recovery. Control of the air to fuel ratio of a combustor dictates the efficient use of the fuel and plant economics as well as the environmental impact associated with fuel (waste) conversion.

Conventional measurement of the combustion efficiency relies on the determination of CO_2 and CO concentrations from standard monitors. In practice, a gas sample is extracted from a downstream location such as a stack and then routed to the gas analyzers. The two main disadvantages of this practice are the potentially long residence times of large scale facilities and the fact that many facilities now employ multistage combustion schemes for control of NO_x formation. Thus, rapid changes in input flow

rates cannot be accounted for and the conventional analyzers only provide an overall combustion efficiency for the plant.

The RTCC eliminates these restrictions by passively measuring the infrared radiation arising from H_2O , CO_2 and CO . This measurement is rapid and the framework for relating the observed signals to the combustion conditions is now well established. The instrument has been designed and thoroughly tested on the laboratory bench. Appropriate software has been written for processing the detector signals and for integrating these signals into a control scheme. Actual experiments wherein the system controlled the fuel input to the DIAL 500 KW combustion test facility have been accomplished (see below).

The RTCC has been shown to permit control of the test facility combustor using the measurement approach of nondispersive infrared emission spectroscopy. A previous review of the pertinent patent literature revealed that the RTCC was a novel device; consequently, an application was filed with the U.S. Patent Office.³⁴

Figure 96 is a block diagram of the control instrument. Radiation emanating from the molecules in the high temperature gas stream is modulated using a mechanical chopper and then routed, using suitable optics, to bandpass-filtered thermoelectrically-cooled infrared detectors. The spectral regions have been chosen based on the previously mentioned infrared emission (FTIR) measurements on the test facility.³³ At the present development of the technology a single detector is used for each molecule, however, it may be possible to minimize the instrument size through the use of multiple element detector packages. The modulated signal is amplified with a unique electronic design and then sent to the control computer.

In developing the control scheme it was noted that although the single molecule emission signals vary systematically with combustion stoichiometry both the CO_2 and H_2O signals achieve a maximum value at complete combustion. A plot, therefore, of CO_2 (or H_2O) signal against the air to fuel ratio is somewhat parabolic in shape. Thus, measurement of the signal below or above a stoichiometry of 1 may result in a similar value. The CO signal decreases from a maximum value at low stoichiometries to some noise level in the absence of CO (as combustion becomes complete). Consequently it was determined that ratioing the emission signals would permit for a simpler control scheme.

Experiments detailing the anticipated errors in the signals and ratios were conducted in the laboratory using a stable infrared blackbody source. A plot of the signal stability against time is given in Figure 97. Standard deviation errors ranged from 0.34% to 0.84%. Corresponding ratios are shown in Figure 98 and here the average errors were less than 0.9%.

The next stage of development was actual measurements on the combustion test facility. The variation of two of the three signal ratios with stoichiometry is shown in Figure 99. The two curves intersect at an air to fuel ratio around 1. Further subtraction of the curves results in a function which takes on positive values at stoichiometries less than 1 and negative values at stoichiometries above 1. The control scheme software was developed to automatically and rapidly step the fuel flow from one extreme of the operating envelope to the other while quantifying the ratios and the subsequent control parameter. In this manner the control curve can be determined without prior knowledge of the fuel and facility characteristics as well as whenever desired by the operator.

Once the control curve has been established an operator can enter the desired control value and the RTCC will step the fuel flow to achieve a stoichiometry within the error range of the desired set point. Control is established rapidly. Figure 100 illustrates evaluation on the 500 KW test facility combustor. In this experiment control of the air to fuel ratio was initially with facility operators where the stoichiometry was set to 1. Control of the facility was then relinquished to the RTCC and a control value specific for an air to fuel ratio of 0.85 was entered into the software. The plot shows the rapid and logical changing of the air to fuel ratio (via the fuel flow to the combustor) followed by attainment of a relatively constant signal or stoichiometry. Deviations in the fuel input are accounted for by the RTCC as the signal returns to the preset value and, in so doing, adjusts the fuel flow accordingly. Adjustment of the stoichiometry from a low to high value is shown in Figure 101. As in the preceding plot slight variations in short term fuel fluctuations are accounted for.

Future studies using the RTCC technology will be aimed at extending the control device to waste fuel fired combustion processes and to secondary combustion to plasma hearth units. Work is also continuing on transfer of the concept to the private sector.

References

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Figure 96. Block diagram of the RTCC.

Figure 97. Laboratory bench testing of the stability of the RTCC detectors.

Figure 98. Corresponding detector ratios from bench testing of the RTCC.

Figure 99. Plot of signal ratios against the stoichiometry.

Figure 100. Example of the RTCC control of the DIAL 500 kW combustion test facility combustor.

Figure 101. Example of combustor control using the RTCC.

Task 2. Subtask 2. NO_x Control Using Staged Fuel Injection

R. Arun Kumar

Introduction

NO_x formation in a fossil fuel fired combustion facility is primarily a function of :

- a) the stoichiometric (air/fuel) ratio of operation,
- b) the peak gas temperature reached,
- c) residence time of the gas stream at the high temperatures,

and to a lesser extent parameters like the fuel bound nitrogen and other catalytic components that may be present. Staged air combustion is one technique whereby the maximum gas temperatures reached in the primary combustion zone are lowered thus lowering the NO_x produced. Another way to accomplish the same result is by staging the introduction of fuel instead of air. Experiments were conducted on the combustion test facility at DIAL/MSU to study the NO_x formed using this staged fuel combustion. Measurements with staged air combustion on the same test bed were also made.

Facility

Figure 102 shows a schematic of a computer controlled fuel oil fired combustion facility operated by DIAL at Mississippi State University. The test train burns fuel oil No. 1 and air. Nominal flow rates to the system are 0.063 Kg/s (500 lbm/hr) of air and 0.0042 Kg/s (34 lbm/hr) of fuel. The air entering the combustor can be preheated up to 1100 K or cold air combustion can be performed with the aid of an ignition device. Downstream of the combustor, the test facility has a constant internal diameter of 0.2 m (8 in.). A number of ports are available on the facility to access for optical instrumentation, gas sampling, and secondary gas/liquid injection. The upstream sections of the test train have various degrees of refractory lining to reduce heat loss. These lined sections have cooling water tubes wrapped around them. The downstream, annular sections of the test stand have no refractory and have cooling water flowing in the annulus. The gas from the test stand goes through a quencher and scrubber before being

exhausted. A bank of measuring devices complement the test stand, and they are interfaced to a real time computer measurement system.

Theory

In the case of fuel oil/air combustion, theoretically, the peak temperature obtained is at a slightly fuel rich condition. In practice however, maximum flame temperatures are obtained under slightly air rich conditions. This is due to the better fuel and oxidant mixing which is necessary for efficient combustion. The peak flame temperatures obtained decrease about this slightly air rich point. In general the NO_x produced follows this trend, with the maximum production occurring at the slightly air rich stoichiometry (ϕ). Figure 103 shows the peak production of NO_x at different stoichiometric conditions for the combustion of fuel oil #1 and air. The air preheat temperature was 600 K. The maximum NO_x concentration of 500 ppm measured was at a stoichiometry of 1, but in reality can be inferred to be somewhere between 1.0 and 1.05 (slightly air rich). NO_x formation decreases around this point for all other stoichiometries. Figure 104 shows the dry gas CO, CO_2 and O_2 concentrations for the same combustion situation. Under fuel rich conditions ($\phi < 1$) elevated CO levels are found with no excess oxygen measured. At near stoichiometric conditions ($\phi = 1$) CO_2 concentrations are a maximum, CO levels are lowered and there is some slight excess oxygen measured. Under air rich conditions the oxygen levels increase and CO is immeasurable.

Traditional methods for reducing NO_x production primarily involve lowering the flame temperatures. This can be accomplished by steam or other inert gas injection. Another method that has been successfully employed is staged air combustion. In this technique gas combustion in the primary combustion zone is very fuel rich with a stoichiometric (air/fuel divided by the theoretical air/fuel required for complete combustion) ratio approaching 0.80. Once the gas temperature has lowered, due to heat exchange with boiler walls, secondary air is added to bring the stoichiometric ratio up to above 1 (air rich), which consumes the CO that produced in the primary zone. Exhaust gaseous concentrations of CO, CO_2 and O_2 are nearly the same as those obtained with single stage combustion. The lowered peak temperatures however, result in lower NO_x gas production and emission. There is a loss in system efficiency due to the lower peak temperatures obtained. This method of staged air injection has

been employed in many energy generation processes, of which MHD (magnetohydrodynamics) is one example.

Figure 105 shows the NO_x production from the combustion of fuel oil and air for this type of secondary combustion with the injection of secondary air into a fuel rich primary combustion stream. The gas concentration measurement is done on the exhaust gas stream. The graph shows the NO_x concentrations measured as a function of the primary zone, fuel rich combustion stoichiometry. Secondary air injection was performed at a distance of 9 ft from the primary combustion zone and air was added to maintain a secondary stoichiometric ratio of 1.05 at all conditions. As can be seen the lower the primary zone combustion stoichiometry (more fuel rich) the lower the exhaust gas NO_x production. This is due to the lower primary gas combustion temperatures attained. Figure 106 shows the CO , CO_2 and O_2 measurements in the exhaust gas (after secondary combustion), and serve as a check on the secondary combustion stoichiometry which was maintained at a $\phi = 1.05$ for all the conditions. As can be seen, on the expanded scales, the concentrations are all fairly constant, and as expected. The CO levels are very low and the O_2 levels are indicative of a slightly air rich condition.

One possible alternative to the staged air injection technique of reducing NO_x is to stage the injection of fuel into the combustion process. This technique could have potential benefits in certain situations. In the case of liquid fuel and air combustion the secondary fuel pumping, metering and control can be performed more easily than can be done on air. Lower primary zone gas temperatures are to be expected due to the excess air available to be heated up. These lower gas temperatures should lead to lower primary and overall NO_x production.

To investigate the NO_x formation for these conditions a water cooled injection probe was designed. A fuel atomization (with nitrogen) unit was added to the system to aid in more efficient fuel distribution into the combustion stream. Secondary fuel injection into the air rich primary stream was done at the same location as in the staged air case (9 ft from the inlet). Figure 107 shows a plot of the downstream NO_x measured for different air rich upstream conditions. The downstream stoichiometry was maintained at 1.05, as can be seen from the measured downstream gas concentrations shown in Figure 108. As expected, the higher the initial gas stream stoichiometry (more air rich), the lower the gas stream tempera-

tures attained and thus the lower the NO_x produced. It can be seen that in the instance of the conditions and fuel/oxidant used on the DIAL facility the staged fuel combustion method can also be used as a significant method in reducing the amount of NO_x formed. By delaying the injection of 20% of the fuel the NO_x produced reduced from a previously measured value of 460 ppm (Figure 103) using single stage combustion to a value of 308 ppm using staged fuel combustion. As can be seen by delaying the injection of 16% of the fuel (from 32.738 lb/hr down to 27.36 lbm/hr) to the combustion stream a 25% reduction in the NO_x level is attained.

Figure 102. Schematic of the DIAL MSU combustion test facility.

Figure 103. Baseline NO_x concentrations.

Figure 104. Baseline CO, CO₂ and O₂ concentrations.

Figure 105. NO_x concentrations for staged air combustion.

Figure 106. CO, CO₂ and O₂ concentrations for staged air combustion.

Figure 107. NO_x concentration for staged fuel combustion.

Figure 108. CO , CO_2 and O_2 concentrations for staged fuel combustion.