In Situ, Real Time Measurement of Melt Constituents in the Aluminum, Glass, and Steel Industries

Final Report

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Executive Summary

Energy Research Company (ERCo), with support from DOE's Industrial Technologies Program, Sensors and Automation has developed a Laser Induced Breakdown Spectroscopy (LIBS) probe to measure, in real time and in-situ, the composition of an aluminum melt in a furnace at an industrial plant. The compositional data is provided to the operator continuously allowing the operator to adjust the melt composition, saving energy, increasing production, and maintaining tighter compositional tolerances than has been previously possible.

The overall objectives of this project were to: -- design, develop, fabricate, test and project future costs of the LIBS probe on bench-size experiments; - test the unit in a pilot-scaled aluminum furnace under varying operating conditions of temperature and melt constituents; -- determine the instruments needed for use in industrial environment; -- compare LIBS Probe data to readings traditionally taken on the furnace; -- get full-scale data to resolve if, and how, the LIBS Probe design should be modified for operator acceptance.

Extensive laboratory tests have proven the concept feasibility. Elemental concentrations below 0.1% wt. have been accurately measured. Further, the LIBS system has now been installed and is operating at a Commonwealth Aluminum plant in Ohio.

The technology is crosscutting as it can be used in a wide variety of applications. In the Sensors and Automation Program the application was for the secondary aluminum industry. However, this project spawned a number of other applications, which are also reported here for completeness.

The project was effective in that two commercial systems are now operating; one at Commonwealth Aluminum and another at a PPG fiberglass plant. Other commercial installations are being negotiated as of this writing.

This project led to the following conclusions:

1. The LIBS System has been developed for industrial applications. This is the first time this has been accomplished. In addition, two commercial installations have been completed; one at Commonwealth and another at PPG.
2. The system is easy to operate and requires no operator training. Calibration is not required. It is certified as eye safe.
3. The system is crosscutting and ERCo is evaluating seven applications, as reported in this report, and other applications to be reported later.
4. A business plan is being completed for each of the near term markets. ERCo is committed to achieving continued commercial success with the LIBS System.
5. A world wide patent has been issued.
6. The energy savings is substantial. The annual energy savings, by 2010, for each industry is estimated as follows:
    - Secondary Aluminum – 1.44 trillion Btu's
    - Glass – 17 to 45 trillion Btu's
    - Steel – Up to 26 trillion Btu's

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1. Introduction

1.1. Problem Statement

In the production of aluminum, steel, and glass products, the feedstocks are melted and then formed into the final product. The composition of the material is closely controlled in order to ensure material properties meet specifications. Since the composition can only be changed while the material is in a molten state, current practice is to remove a small sample of molten material from the furnace for analysis by a laboratory. The results of the analysis, for example, the percentages of iron, chrome, and nickel in a stainless steel melt, are used by the furnace operator to add or remove elements from the melt in order to bring the composition to within the desired material's specification. In the steel and aluminum industries specifically, where melting scrap of unknown composition is typical, these analyses allow the smelter to produce alloys to within their respective specifications. Usually multiple analyses are performed on the same melt. For the glass industry, the glass feedstock (batch and cullet) elemental concentrations are tightly controlled by the vendor and the glass product is tested after being formed.

There are two problems with these methods. First, by sampling the material off-line, the furnace idles and productivity comes to a halt while the material is transported to the laboratory and the analysis is performed. Second, the material that is removed from the melt may not be representative of the entire melt. If alloying materials were added to the melt and the melt was not sufficiently mixed, the melt may be inhomogeneous, and changes made on the basis of the analysis of the sample may not bring the material into specification.

These two problems lead to excessive melting time, quality control problems, wasted feedstock, increased energy used and emissions, and product that may need to be remelted or discarded.

At Energy Research Company (ERCo) we have solved these problems by developing an instrument that can measure in real time and in-situ the elemental concentrations of a large number of industrial process materials. The concept is described in Chapter 2, laboratory development results are given in Chapter 4, and field installations in Chapters 6, 5, and 7.

1.2. Teaming members

The following organizations were involved in the work reported here.

- DOE
  - Industrial Technologies Program – Funded the Sensors and Automation and the Glass work.
  - National Energy Technology Laboratory – Funded the coal work.
- The New York State Energy Research and Development Authority - Funded the steel work.

- ERCo – The prime contractor, and owner of the intellectual property.
- PPG – The largest fiberglass manufacturer in the US. PPG hosted the glass batch work.
- Fenton Glass – Assisted in the glass work.
- Commonwealth – An aluminum manufacturer; hosted the installation at their Uhrichsville, OH plant.

1.3. Goals and Objectives of Project

Project Objectives

The overall objectives of this project were to: -- design, develop, fabricate, test and project future costs of the LIBS probe on bench-size experiments; - test the unit in a pilot-scaled aluminum furnace under varying operating conditions of temperature and melt constituents; -- determine the instruments needed for use in industrial environment; -- compare LIBS Probe data to readings traditionally taken on the furnace; -- get full-scale data to resolve if, and how, the LIBS Probe design should be modified for operator acceptance. More detailed phase specific objectives are stated within the sections covering each phase.

Phase 1 Objectives

The goals of this project were:

- Design, develop, and fabricate the LIBS Probe
- Test the LIBS Probe in an aluminum melt and determine its sensitivity for the elemental constituents of interest.
- Test various sheathed fiber optic designs (how many), immersed in the melt, and decide on the best one.

Phase II Objectives

In Phase II, the LIBS Probe wase tested in a ¼-scale pilot aluminum furnace at ERCo's facility.

The goals of this project were:

- Test the unit in a pilot-scaled aluminum furnace.
- Test the unit under varying aluminum furnace operating conditions. The temperature and melt constituents will be varied.

Phase III Objectives

In Phase III, further development of the LIBS Probe were conducted on a full-scale commercially operating aluminum furnace. The main objective of these tests was to obtain data on the operation of the LIBS system under special conditions of large scale industrial furnaces, so the data can be used to further redesign and develop the LIBS system. Several iterations of testing, redesign, and modification were needed to establish a stable design. Specific objectives of this phase were as follows:

- Determine the requirements for how robust the instrument needs to be while operating in an industrial environment.

- Compare the readings from the LIBS Probe and compare to actual readings traditionally taken on the furnace.
- Gather user information on how the LIBS Probe design needs to be modified for operator acceptance.

All project objectives and goals have been achieved as is discussed in the following sections.

2. Technology Solution

2.1. LIBS Description

ERCo has developed a laser instrument to measure the elemental concentrations of industrial melts, in-situ and in real time. Termed LIBS for Laser Induced Breakdown Spectroscopy, the concept is shown in Figure 1 and Figure 2 shows the LIBS components. It is an optical atomic emission technique in which a high energy plasma is formed using a laser pulse. A pulsed laser is repetitively fired through a fiber optic cable, which is placed in the melt via the probe. A small amount of melt absorbs the laser light and is rapidly vaporized and ionized. Light from the spark is gathered by another lens and focused on a second fiber optic cable that carries the signal to the spectrometer. The spectrometer resolves the light into different wavelengths and sends the signal to the computer for analysis. The wavelengths observed uniquely identify the elements present (Al, Cu, Mn, Si, Na, Ca, Mg, Ba, B, Al, Fe, Sc, Mn, Cr for instance) and the emissions' strength are used to determine the concentration of each element.

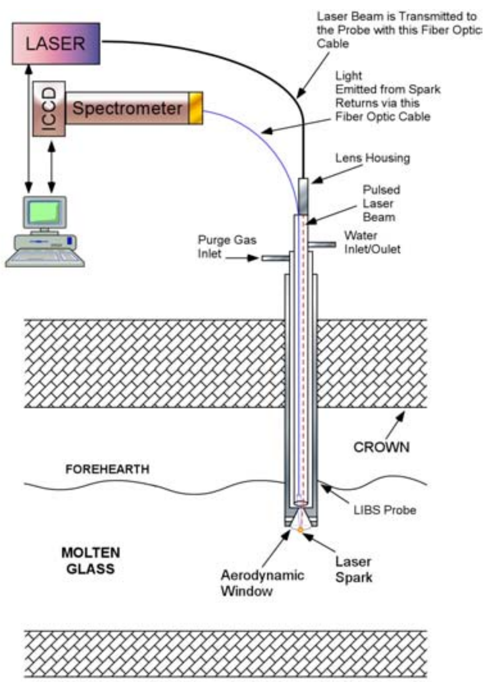
Figure 3 shows a section of typical LIBS spectra taken in ERCo's laboratory from two aluminum alloys, 1100 and 2024, showing spectral lines from a number of minor elements in the alloys. These lines are identified from tables of emission lines for the different elements. To convert LIBS spectra to concentration measurements, the areas under spectral peaks for different elements are measured and correlated to actual concentrations. For instance, in Figure 3, the 2024 alloy has about 4 to 5 % copper, while the 1100 alloy has .05 to 0.2% copper. The peak and area of the copper line is consequently larger for the 2024 than for the 1100. This difference is characteristic of all elements and their relative concentrations and is used by ERCo to quantify absolute concentrations.

The spark size is about 1 to 2 mm in diameter. Since the system takes a measurement about once per second and since the probe can be moved vertically and laterally, the measurements will represent the true composition of the melt and will measure spatial as well as temporal variations.

Figure 4 is a schematic of the concept as applied to the Aluminum Industry. Figure 4 B shows the application in which the sensor is used to measure during a pour, for in-line alloying applications. There are several applications for the proposed technology within the aluminum industry as follows.

1) In-Line Alloying

The simplest application is for selective in-line alloying during a pour. In this application, the fiber optic would be situated directly on top of the melt in the trough as it is being poured from the furnace (see Figure 4 B). Only one or two selected elements would be measured, say Mg, Mn. These elements would be alloyed in the trough as the melt is being poured and would be controlled by the readings from the proposed sensor, (the balance of the alloying would have been previously accomplished in the furnace in the conventional manner).



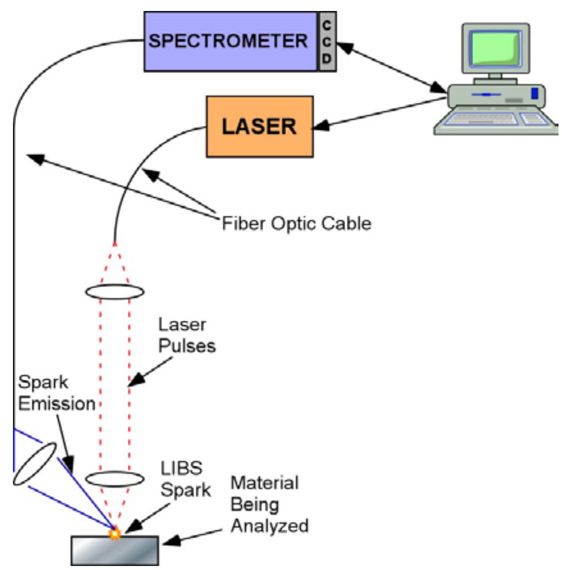
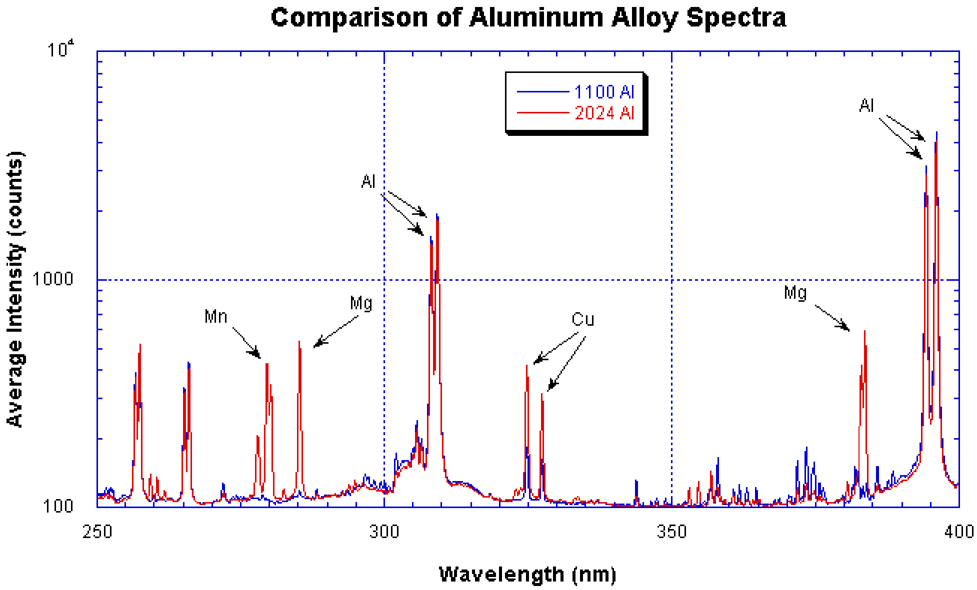


Figure 1 – Left - Schematic of a Probe in Glass Furnace

Figure 2: Right - Schematic of Basic LIBS System

2) Continuous Furnace

The largest benefit for the application of the proposed sensor comes from its use in converting the operation of a conventional batch furnace into a continuous furnace. The implications of this are significant and could result in a new operating paradigm for the aluminum industry. Large production increases, energy savings, emission savings, and greatly reduced prices are possible. In this application, the fiber optic is again positioned immediately above the melt in the trough as the melt is being poured. However, all the elements of interest are being read and controlled. The furnace is continuously and simultaneously pouring and charging. The furnace alloying takes place in the furnace, also on a continuous basis. As the instrument records the concentration of any of the elements, the operator either manually or automatically adjusts the feed to keep the alloy within specification. The benefits of a continuous furnace are significant and include energy reduction, production increase, and emission reduction.



ALLOY	COMPOSITION							
	Al	Si	Mg	Cu	Zn	Fe	Mn	Cr	Ti
AA1100	99	0.95*	-	0.05 – 0.2	0.1*	0.95*	0.05*	-	-
AA2024	bal	0.5*	1.2 – 1.8	3.8 – 4.9	0.25*	0.5*	0.3 – 0.9	0.1*	0.15*

* - indicates maximum allowable composition
bal – indicates element is present as balance of alloy

Figure 3 - Spectra from ERCo's Laboratory LIBS Setup

3) Semi-Continuous Furnace

The approach of a continuous furnace may be difficult to achieve in the near term as it requires feeding the furnace in a dramatically new fashion. A more evolutionary step would be to operate the furnace in a semi-continuous fashion. The goal here would be to achieve one or more additional pours per day. In this application, the fiber optic would be immersed in the melt, inside the furnace. See Figure 4 A. It is anticipated that since the measurement is instantaneous and continuous, the furnace operator will be able to adjust the melt in less time resulting in one or more additional pours.

4) VFM Rapid Melter

ERCo, under sponsorship of DOE, has developed a Vertical Floatation Melter (VFM) that can process scrap aluminum in a rapid and energy efficient manner. This is much different than a conventional furnace as the scrap aluminum is melted continuously while immersed in the flue gases. The VFM would be an excellent candidate for use of the proposed sensor as it is already designed to operate in a continuous fashion[1].

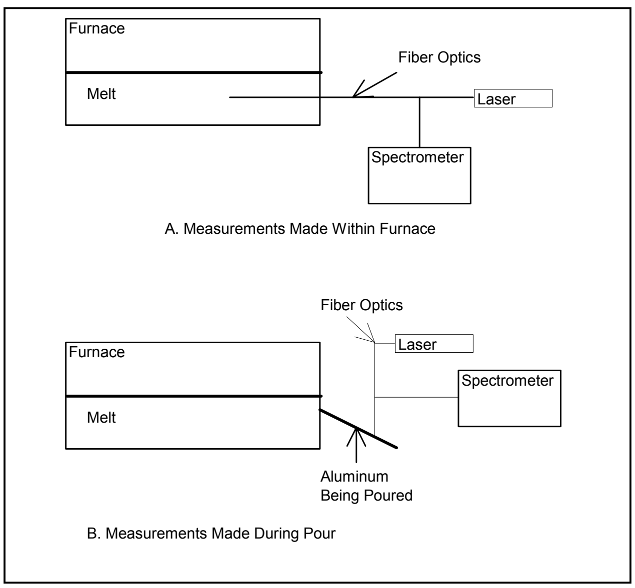


Figure 4 - Schematic of Concept for Use in the Secondary Aluminum Industry

5) Diagnostic for Conventional Furnaces

An interesting application is to use the proposed sensor as a diagnostic tool to better understand furnace internal melt thermal and mass transfer so as to improve furnace modeling. Depending on the researchers needs, the proposed sensor would be used to probe the interior of the melt both spatially and temporally. Similar to item 3 above, the sensor would be immersed and it would also be moved to different locations within the melt. A spatial and temporal map of the exact composition could be determined and

[1] De Saro, R "The Development of an Innovative Vertical Floatation Melter and Scrap Dryer for Use in the Aluminum Processing Industry Final Report", The U.S. Department of Energy Award Number DE-FC02-95CE41186, 24 August 2004.

correlated to any independent variables under consideration. Also, existing computer models could be calibrated using the sensor.

2.2. Technical Breakthroughs

ERCo has made several technical breakthroughs that now allow the technology to be commercially saleable. See Chapter 8 for a detailed discussion.

- Calibration Free Equipment (C-LESS) – By modeling the plasma, the concentration values can be determined without ever calibrating the instrument. This allows the system to be easy to operate and does not require any operator training.
- Software Development – Along with the C-LESS technology, the LIBS System requires only single button operation, making it easy to operate at a plant.
- Probe – A probe has been developed to be used immersed in aluminum melts. Other probes, for steel and glass melts, are under development.
- Eye Safe – By using a series of safety interlocks, the LIBS system has been certified to be eye safe and no safety training is required.
- Continuous furnace – The use of the LIBS system, since it provides real time continuous data on the melt chemistry, allows a batch furnace to be converted to a continuous furnace with a commensurate increase in productivity.

2.3. Energy Savings for Glass, Steel, and Secondary Aluminum Industries

The annual energy savings, by 2010, for each industry is estimated as follows:

- Secondary Aluminum – 1.44 trillion Btu’s
- Glass – 17 to 45 trillion Btu’s
- Steel – Up to 26 trillion Btu’s

3. Crosscutting Technology

The LIBS technology developed by ERCo is a crosscutting technology in that it has a large number of applications. The underlying technology for each of the applications is the same, as described above, with each application dictating somewhat different packaging and ancillary equipment. The applications either developed or under development by ERCo are:

- Molten aluminum (Installed at Commonwealth Aluminum)
- Molten glass
- Molten steel (Demonstration to be conducted at Crucible Specialty Metals)
- Glass batch (Installed at PPG)
- Coal for electric utility power plants (Demonstration to be conducted at Brayton Point Power Plant).
- Alloy sorting

These are described in this report. Other applications are also being pursued and will be reported in future reports.

4. Laboratory Development

4.1. Experimental Setup

Preliminary tests were conducted in ERCo's laboratory to develop the LIBS technique. A photograph of the probe installed in the laboratory furnace is shown in Figure 5. A crucible containing molten aluminum is inside the furnace, and the probe is lowered through a hole in the furnace cover into the melt to a depth of approximately 2".

ERCo's LIBS apparatus consists of three Q-switched, 20Hz Nd:YAG lasers, two of which operate at 1064nm with a maximum pulse energy of 50mJ. One of these is fiber coupled. The third laser is frequency quadrupled with maximum pulse energies of 45mJ @ 266nm, 200mJ @ 532nm, and 155 mJ @ 1064nm. All lasers are manufactured by Big Sky Laser of Bozeman, MT. In addition, ERCo's laboratory contains two spectrometers: a 300mm Czerny-Turner type spectrograph manufactured by Acton Research coupled to a PI-MAX intensified CCD camera and gated using a ST-133 programmable timing generator, and an ESA 3000 Echelle-type unit from LLA Instruments. The laboratory also contains two calibrated light sources, a deuterium lamp and a quartz-tungsten-halogen lamp, certified by Optronic Laboratories, two broadband sources, a xenon lamp and a quartz-tungsten halogen lamp both manufactured by Oriel Instruments, and a mercury lamp.

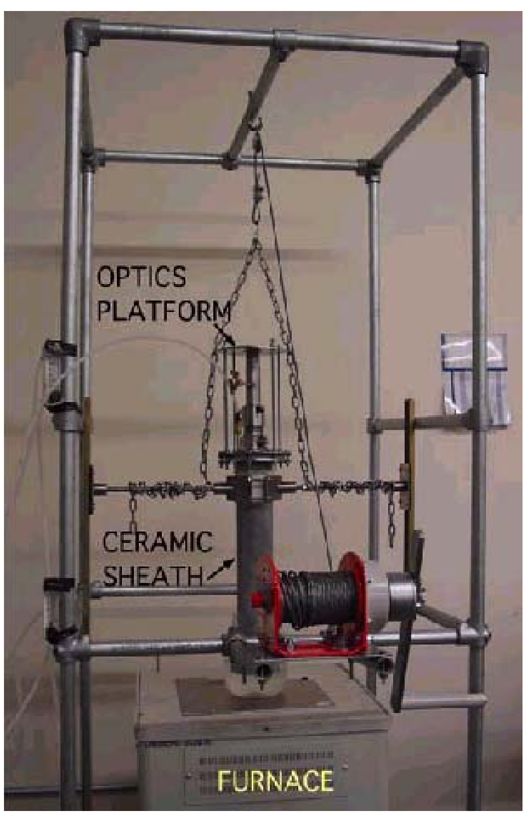


Figure 5: Photograph of a Full-Scale LIBS Probe Installed in a Laboratory Furnace

4.2. Molten Aluminum

Aluminum samples were purchased from Belmont (New York, NY) along with their elemental specifications. The samples were melted in the furnace, and the probe was inserted into the melt for the LIBS analysis. The following tables show the results and the reported values as supplied by Belmont. ERCo's C-LESS technique was used to arrive at the concentration numbers. The difference between the LIBS measurement and the actual concentration as reported by Belmont is also shown. The results agree well in all cases. For instance, for the 3105 alloy, Mn is measured at .508% and the Belmont value is 0.52% for a relative difference of only 2.3%. The differences from all the tests span a range of 0.0% to 2.3%.

Table 1 - 3105 Alloy

	Mn	Mg	Si	Al
Reported	0.52%	0.57%	0.02%	98.89%
LIBS Meas.	0.508%	0.568%	0.02%	98.92%
Difference	2.3%	0.35%	0.0%	0.03%

Table 2 - 5052 Alloy

	Cr	Mg	Al
Reported	0.26%	2.4%	97.34%
LIBS Meas.	0.258%	2.42%	97.32%
Difference	0.39%	%	0.02%

Table 3 - 3004 Alloy

	Mg	Mn	Al
Reported	1.15%	1.42%	97.34%
LIBS Meas.	1.13%	1.44%	97.31%
Difference	1.7%	1.4%	0.027%

This raises the question of how close should the LIBS values be to the reported values? Since a spark spectrometer is used for the reported values, and in-fact is the conventional tool used throughout the aluminum industry, and since it must be calibrated, its accuracy is only as good as the accuracy of the calibration standards used for its calibration. The data from a number of calibration standards were collected from different sources and their errors were compared to the LIBS laboratory tests as described above. Figure 6 shows the calibration standards errors (B) compared to ERCo's LIBS measured errors

(A). The results are similar. When the concentrations are 0.4% and higher, the errors are about 2 to 4% in both cases. As the concentration decreases, the error increases in about the same fashion. Hence, the differences reported in our lab work is about the same as the errors from the calibration standards, resulting in a LIBS accuracy about the same as can now be achieved with a conventional spark spectrometer.

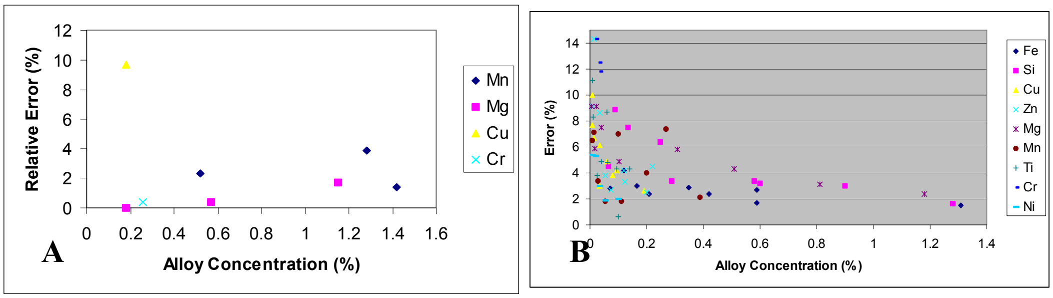


Figure 6 - Accuracy Comparison – LIBS (A) and Calibration Standards (B)

4.3. Molten glass

Preliminary laboratory tests were conducted on molten glass in ERCo's laboratory. One hundred grams of cullet from PPG were melted in a crucible at 1250 ^{o}C (2282 ^{o}F). PPG supplied the chemical composition, and after melting we sent the solidified glass to Monarch, an independent laboratory, for chemical analysis.

A probe was used and measurements were taken at the surface of the molten glass. As discussed in Section 8.3 we determined concentrations using our proprietary calibration free LIBS technique (C-LESS).

Table 4 shows the results. The range of concentrations, as reported by PPG and Monarch, is shown along with our experimental results. Most of the measurements agreed well with the reported values. Of the eight elements measured, three were outside the reported values, though by acceptably small amounts. Silicon was low by 0.81% (on a relative basis), Mg high by 5.2%, and Ba high by 2.8%. Generally, such measurements have uncertainties of 5 to 10% depending on the element and its concentration. Hence, these values, particularly since they are preliminary, are mostly within general industry requirements.

4.4. Steel

The LIBS system was used to measure elemental concentrations of solid steel samples. Again, ERCo's C-LESS techniques were applied to determine elemental concentrations. Figure 7 shows the results with Figure 8 showing the results with an expanded vertical scale. Comparing the LIBS result to the actual concentrations shows that the results are close with only Mo outside an acceptable range. This was early work and the techniques have been refined since then which will improve the Mo result.

Table 4 - Molten Glass Concentration Results

Element	Range of Reported Values		Measured By LIBS	Result	% Outside Range
Si	62.96%	61.51%	61.01%	Good	0.81%
Na	29.67%	20.72%	24.90%	Good	
Ca	5.36%	3.46%	4.87%	Good	
Mg	2.71%	2.42%	2.85%	Out	5.2%
Ba	4.66%	0.00%	4.79%	Out	2.8%
Fe	0.04%	0.020%	0.02%	Good	
Sr	0.04%	0.00%	0.03%	Good	
Mn	0.1%	0.00%	0.08%	Good	

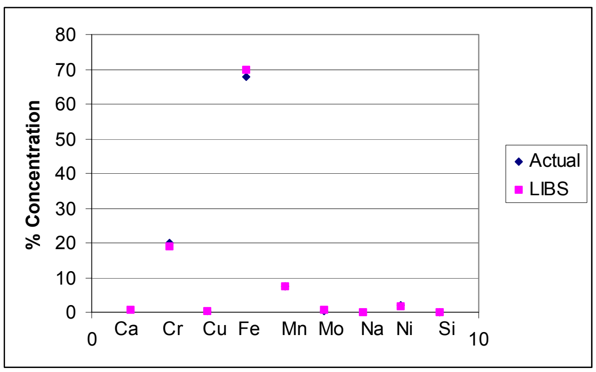


Figure 7 - Steel Results

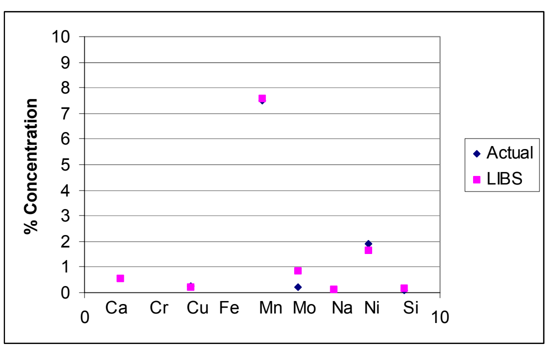


Figure 8 - Steel Results with Expanded Scale

4.5. Coal

A sensor based on LIBS technology can be used on dry feedstocks and can be integrated into conventional coal feed equipment as shown in Figure 9. As the coal moves along the belt, the laser samples it as it passes beneath the focal spot, and a fiber optic cable attached to a spectrometer captures the emissions from the LIBS spark.

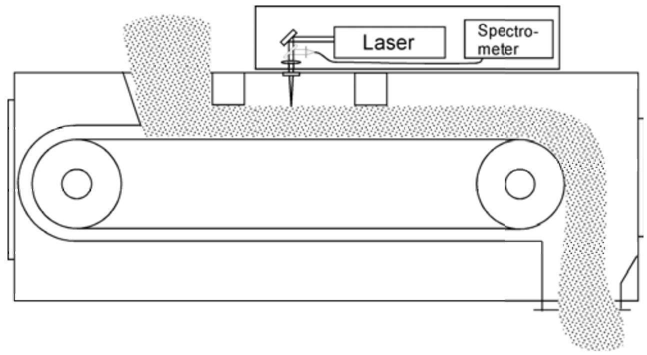


Figure 9 - Schematic of LIBS System

The LIBS sensor can be incorporated into the gasifier process using either dry pulverized coal or coal slurry. As seen in Figure 10, the LIBS sensor will continuously monitor the coal feed prior to gasification. For gasifiers using dry feedstocks, the coal composition will be measured immediately prior to gasification. For gasifiers fed by coal slurry, the sensor can be installed in the pipe leading to the pump that feeds the gasifier.

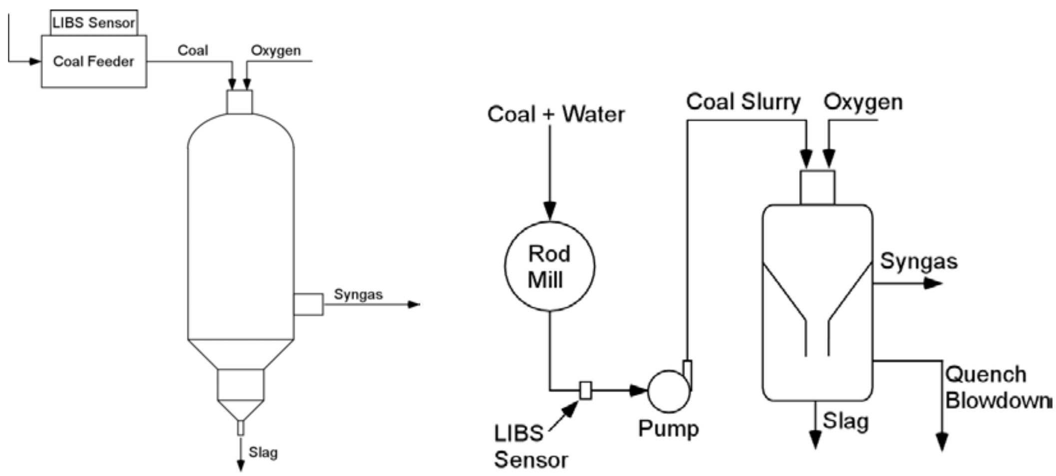


Figure 10 - Schematic Drawings Illustrating Where a LIBS Sensor Would Monitor Gasifier Feedstocks

Pressed pulverized coal samples were placed in ERCo's laboratory chamber shown in Figure 11. The top of the chamber was replaced with a 3" diameter optical quality glass window though which the laser pulses passed on their way to spark the coal. The light from the resulting plasma was viewed through this window by the two fiber optic cables.

The chamber was filled with argon. The use of argon eliminated interference from elements in the air, such as nitrogen, oxygen, hydrogen, and carbon. Nitrogen gas can also be used when coal bound nitrogen measurements are not being made. A pressure of half an atmosphere was used because lower ambient pressures tend to raise the signal to noise levels in LIBS experiments[2]. The laser emitted coincident UV, visible, and near infrared laser pulses from right to left in the photograph.

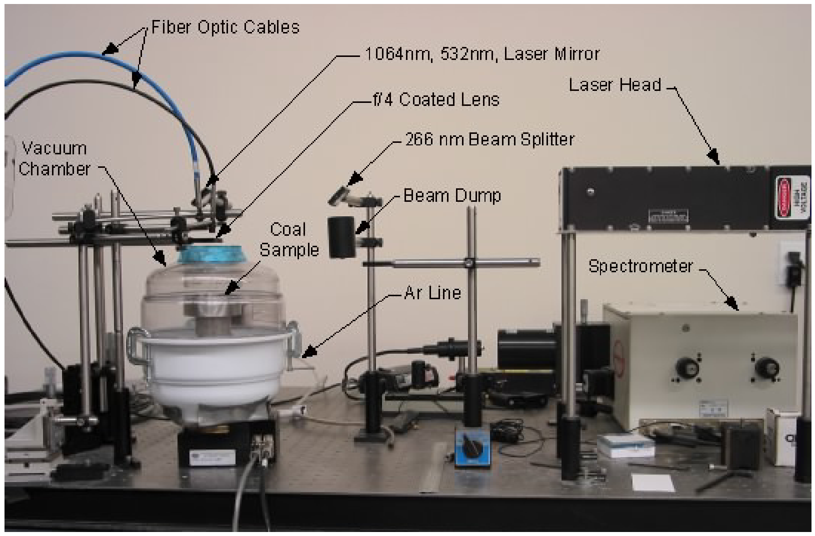


Figure 11 - Experimental Setup for Performing LIBS Measurements in ERCo's Laboratory

The light emitted from the resultant spark was viewed by lenses on the ends of the two fiber optic cables. One fiber optic cable was connected to a conventional Czerny-Turner scanning spectrometer system and the other to a broadband Echelle spectrometer. The Echelle spectrometer is capable of viewing the spectrum from 200-780nm at once. The Czerny-Turner spectrometer has better resolution at longer wavelengths and can view wavelengths further into the infrared.

Each sample of coal was sparked 75 times at different locations in the sample. During the testing the moisture content was not controlled, and likely changed due to changing ambient conditions.

In order to convert LIBS spectra to concentration measurements, the areas under spectral peaks for different elements are measured and compared to calibration curves. A small section of a LIBS spectrum from a coal sample is seen in Figure 12. The useful peaks in this spectrum are identified using published lists of atomic emission lines[3]. After the peaks are identified, the area under each peak is measured. Using Figure 12 as an example, if a different coal sample was analyzed that had more aluminum relative to silicon, its spectrum would contain relatively more area under the aluminum peak as compared to the silicon peaks.

[2] Iida, Yasuo, "Effects of atmosphere on laser vaporization and excitation processes of solid samples", Spectrochimica Acta, **45B**, 12, pp.1353-1367, 1990

[3] An searchable online database of emission lines can be found at: http://physics.nist.gov/cgi-bin/AtData/lines_form

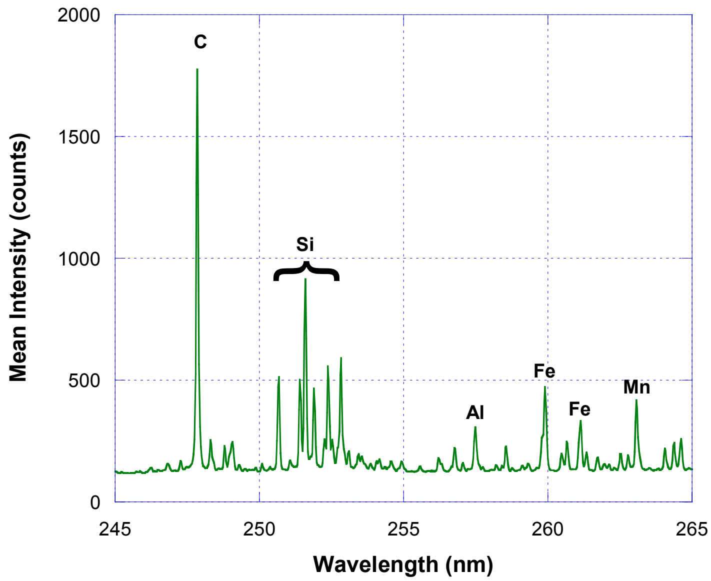


Figure 12 - Sample LIBS Spectrum from Coal Sample

(Elemental Concentrations in sample: C=75.13%, Si=2.3%, Al=1.6%, Fe=1.1%, Mn=77ppm)

The calibration curves presented below demonstrate that LIBS signals closely track elemental concentrations over a wide range of elements.

A. Hydrogen, Nitrogen, Carbon and Sulfur

H, O, and N were observed simultaneously using the Czerny-Turner spectrometer with the highest resolution setting in the far visible-near infrared part of the spectrum where these elements emit. Carbon was measured using the Echelle spectrometer.

The accuracy of the technique can be seen in Figure 13 through Figure 16. These figures depict the accuracy of the fit for the different samples. The actual elemental ratio is on the x-axis and the predicted ratio using the calibration curve fit is on the y-axis. Ideally, these two values would be identical, and the data points would fall on the 45^o line shown. The majority of the data points fall close to the 45^o line indicating that the measurements are generally accurate.

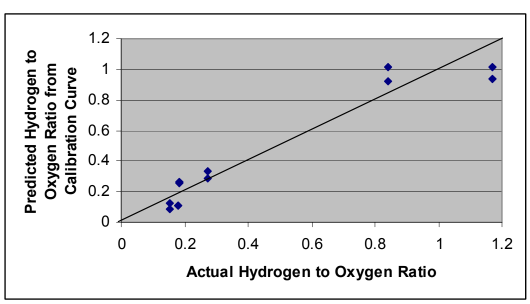


Figure 13 - Hydrogen to Oxygen LIBS Accuracy Curves

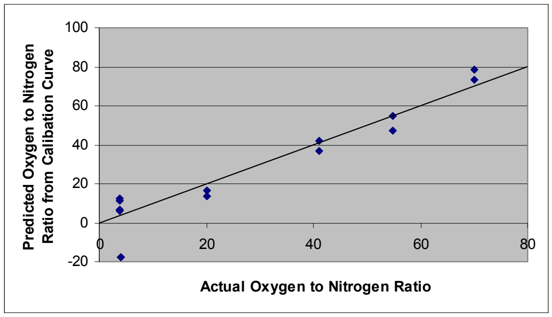


Figure 14 - Oxygen to Nitrogen LIBS Accuracy Curves

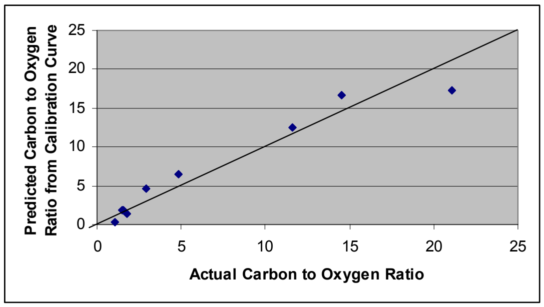


Figure 15 - Carbon to Oxygen LIBS Accuracy Curves

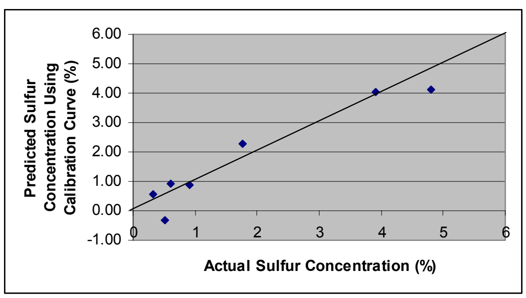


Figure 16 - Absolute Sulfur Accuracy Plot

B. Unburned Carbon in Fly Ash

ERCo acquired samples of fly ash from a mid-western coal fired power plant for analysis with the LIBS apparatus. In Figure 17 below, a strong carbon peak from an ash sample is seen. The signal-to-noise ratio for this peak is in excess of 500, indicating that samples with much lower carbon content can be successfully analyzed.

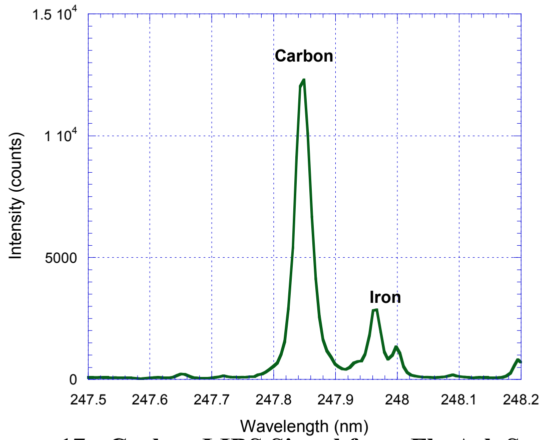


Figure 17 - Carbon LIBS Signal from Fly Ash Sample

4.6. Alloy Sorting

Another application comes about from the mixed materials that are typically recycled by consumers and wasted product from industrial plants. LIBS can be used to sort mixed waste so as to separate high value alloys for resale. Because each aluminum alloy is comprised of different elements at different concentrations, the spectral "fingerprint" of the type seen in Figure 18 is unique to each alloy. In order to identify an unknown piece of metal, it is sparked by the LIBS apparatus and the resulting light is analyzed by the computer system and compared to a database of these "fingerprints". If a match is found in the database, the metal is identified.

Figure 19 contains a schematic drawing of the optical layout to perform the LIBS experiments. The sample to be analyzed is placed below the focusing lenses. The laser is fired, either through a fiber optic cable as shown, or through the air, and the pulse of light creates the plasma. Light from the plasma is collected by a second fiber optic cable, which transmits the light to the spectrometer system for analysis by the computer.

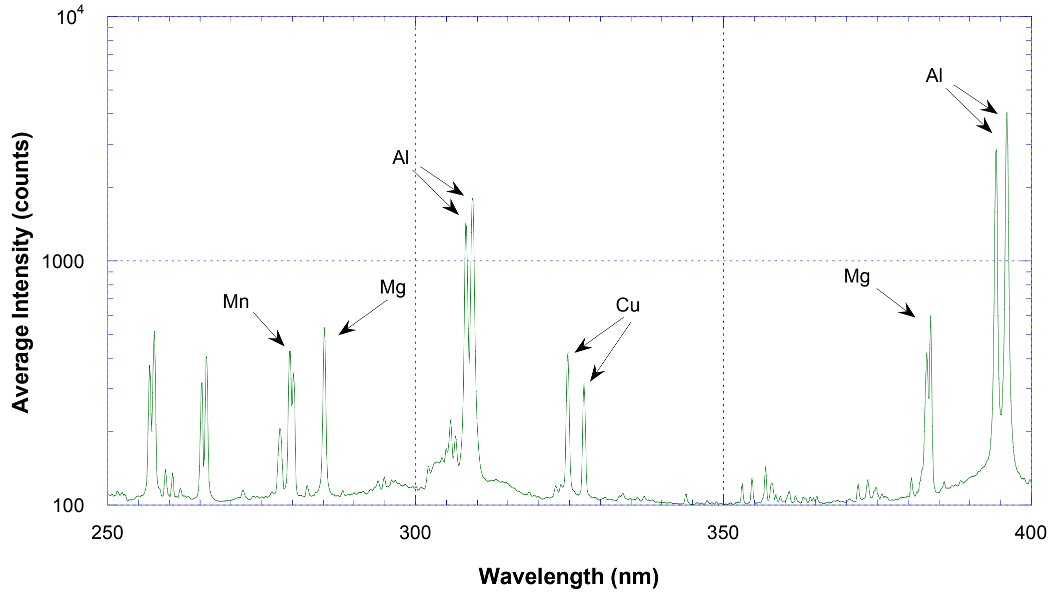


Figure 18 - LIBS Spectrum from 2024 Aluminum Alloy as Measured in ERCo LIBS Laboratory

The locations of the peaks reveal which elements are in the material, while the height of the peak is correlated to the concentration of the particular element. (Mn=Manganese, Mg=Magnesium, Al=Aluminum, Cu=Copper)

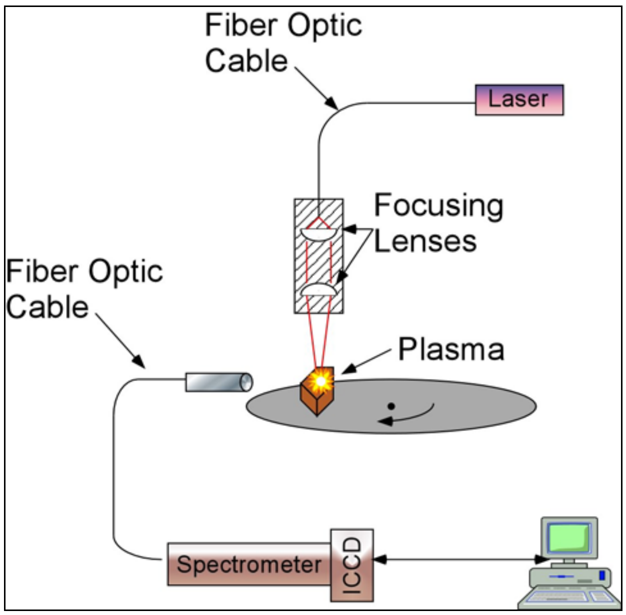


Figure 19 - Schematic Drawing of Optical Setup for LIBS Experiments

The pulse of laser light is focused down onto the material being analyzed. The light from resulting LIBS spark is sent to the spectrometer system via a fiber optic cable. A computer analyzes the light signal for comparison with a database of spectral "fingerprints".

ERCo acquired the following 12 metal plates for testing, shown in Table 5:

Table 5 - Wrought Aluminum Alloys and Other Metals Used in Initial Aluminum Sorting Experiments

Wrought aluminum alloys	1100, 2024, 3003, 5052, 6061 (2 samples), 7075
Steel Alloys	A-36 Carbon Steel, 304 Stainless Steel
Copper Alloys	260 Brass, 220 Bronze
Nickel Alloy	400 Monel

With the exception of the two copper alloys, the metal samples were visually identical.

Wrought aluminum alloys are classified by major alloying elements. The 1000 series are nearly pure aluminum, the 2000 series are alloyed with copper, the 3000 series with manganese, the 5000 series with magnesium, the 6000 series with magnesium and silicon, and the 7000 series with zinc.

The samples were rotated on a turntable to simulate the throughput of conveyor systems in a high production setting. This is shown schematically in Figure 19. Analysis of each piece was based upon single laser shots, since at commercial sorting speeds there will be time for only one laser shot per piece. A total of 800 single shot spectra from the samples were used to construct the library of spectral fingerprints. Next, single shot spectra were collected from the samples in a blind test to see if the sorting software could correctly match the spectra to the samples. The results are summarized in Table 6. These results are encouraging with nearly perfect identification. The handful of misidentifications can be attributed to LIBS sparks on portions of the plates that had small pieces of tape or sparks on seams between pieces of material.

Table 6 - Wrought Alloy Sorting Results – Samples in Motion

Aluminum 1100	99.875%
Aluminum 2024	100%
Aluminum 3003	100%
Aluminum 5052	99.625%
Aluminum 6061	99.250%
Aluminum 7075	99.875%
Non-Aluminum	100%

5. Aluminum Industry Installation

5.1. Introduction

ERCo has installed a full-scale LIBS system to measure in-situ and in real time the elemental concentrations of Commonwealth's aluminum melt in their Uhrichsville, OH plant, as shown in Figure 20. A probe is placed inside the melt and a laser is repetitively fired through a fiber optic cable and through the probe. A small amount of melt, at the probe tip, absorbs the laser light producing temperatures sufficiently high to heat and vaporize it into a gaseous plasma state.

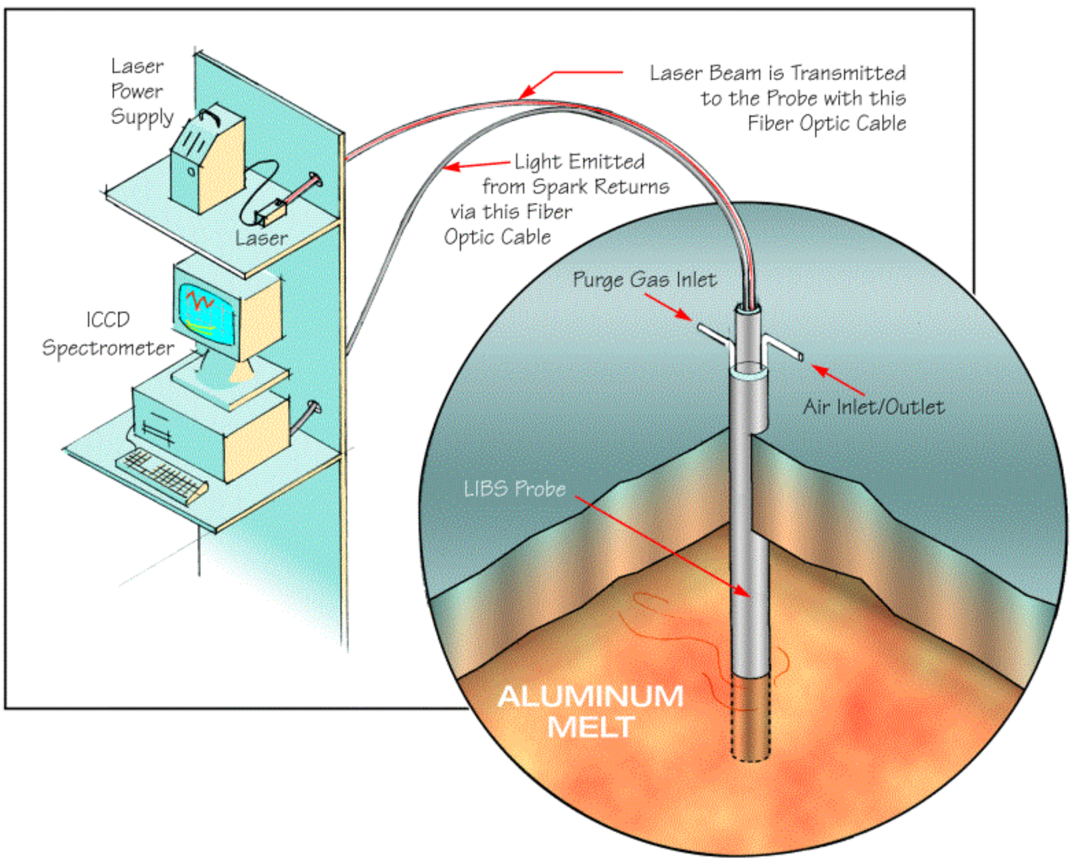


Figure 20 - LIBS Concept

The photo on the left of Figure 21 shows the LIBS probe installed in Commonwealth's filter bowl and the right side of the figure shows a close-up of the probe inserted in the melt. Figure 22 shows the cabinet which houses the laser, spectrometer, gas flow controllers, and ancillary components. It is located on a mezzanine overlooking the filter bowl.

The LIBS System is designed to be a single push button operation with no training required. The operator presses the on-button and, if all the interlocks are satisfied, the probe automatically extends into the melt and begins collecting data. Similarly, a single button ends the measurements and retracts the probe. Figure 23 shows the control screen the operator uses.

In addition, the LIBS System has been certified as being eye safe, so neither specialized laser safety training nor laser safety equipment are required.

Figure 21 - LIBS Probe Installed at Commonwealth

Figure 22 - Instrument Cabinet Located on the Mezzanine

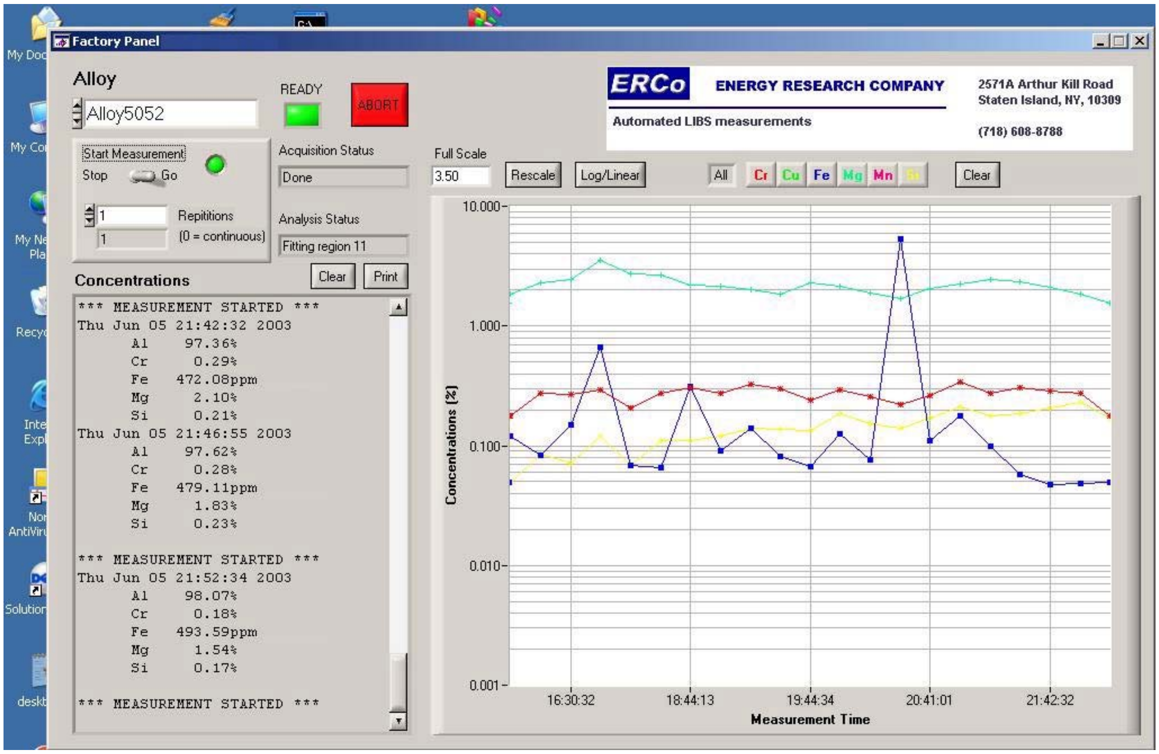


Figure 23 - Operator Control Screen

5.2. Test Results Using C-LESS Software

Table 7 shows a summary of the LIBS data for a typical day, November 6, 2003. Also shown, as a comparison, are samples periodically collected by Commonwealth and analyzed using a conventional spark spectrometer.

For the elements with concentrations of about 0.1% or higher, the difference between the LIBS measurements and the Commonwealth button samples is from 0.0 to 7.1%. The LIBS relative standard deviation (RSD)[4], a measure of the data variability, ranges from 4.5 to 11.6%.

Table 7 - 11/6/03 Data for 3105 Alloy

	Al	Cu	Fe	Mg	Mn	Si
LIBS Average	97.87%	0.17%	0.65%	0.47%	0.52%	0.28%
Commonwealth Average	97.56%	0.18%	0.65%	0.49%	0.56%	0.30%
% Difference	0.32%	5.6%	0.0%	4.1%	7.1%	6.7%
LIBS RSD	0.09%	5.06%	4.87%	11.61%	4.54%	6.29%
Commonwealth RSD	0.03%	3.51%	3.65%	1.53%	3.57%	2.25%

The following plots show the LIBS measurements over time as compared to the Commonwealth sample results.

[4] RSD is the standard deviation divided by the average.

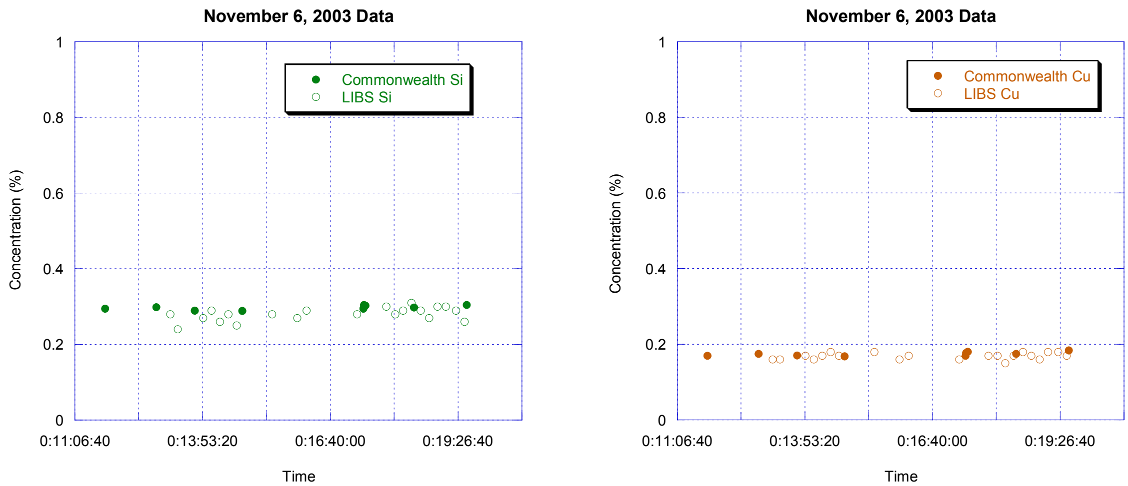


Figure 24 - LIBS and Commonwealth Button Data Differences for Si and Cu

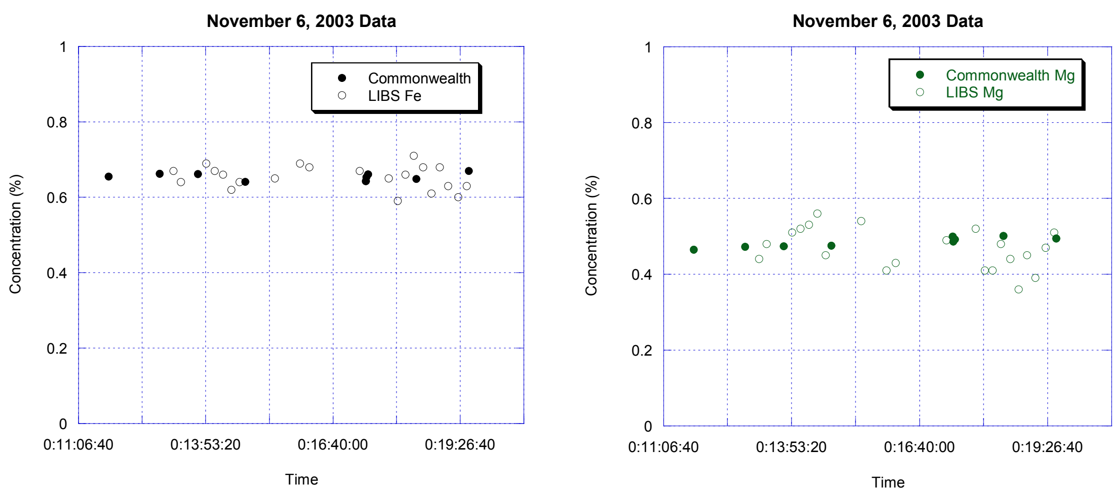


Figure 25 - LIBS and Commonwealth Button Data for Fe and Mg

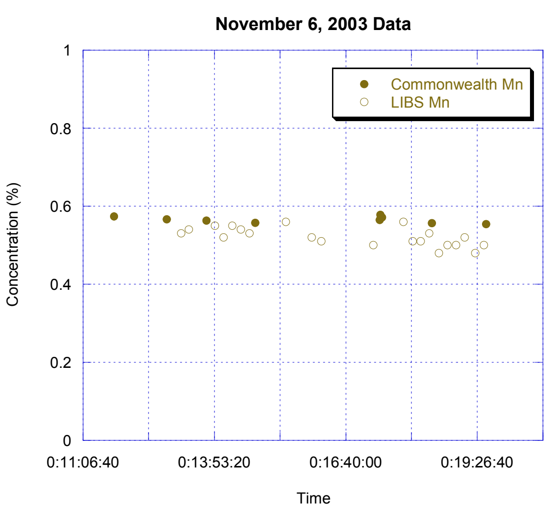


Figure 26 - LIBS and Commonwealth Button Data for Mn

5.3. Conclusions from the Commonwealth Installation

As in the laboratory testing, the results from the commonwealth installation show that the LIBS system is as accurate as the conventional spark spectrometer. Also, after well over 4000 hours of field and lab testing, the probe suffered no adverse affects. Finally, the LIBS system continues to be used by Commonwealth as a process tool.

6. Aluminum Furnace Mixing Measurements

Conventional aluminum melt furnace design has not changed much since there is little or no operating data available that would allow engineers to design more efficient furnaces. ERCo's LIBS probe can provide such data that could dramatically improve furnace designs. The ability to design aluminum furnaces from scratch should now be possible based on the LIBS data, which has never been previously available. The LIBS probe can provide data on mixing as alloys are added to a furnace, or on the effect of fluxes and other additions. For instance, when chlorinating to remove magnesium, or fluorinating to remove sodium, it is never known when the desired levels have been reached, so excess chlorine and fluorine are used. ERCo's LIBS probe can provide real time data on any of the elements of interest so that the fluxing can be discontinued once the desired level has been reached. It can also provide data on alternate methods of feeding alloy additions (both how and at what furnace location) to maximize mixing and minimize the furnace size.

Preliminary mixing tests were conducted in a pilot holding furnace of 6000 pound capacity shown in Figure 27. The photo on the right shows the LIBS probe inserted in the chamber. The furnace was charged with 2000 lbs of a nonstandard aluminum alloy containing copper, zinc, silicon, iron, manganese, and magnesium, and smaller amounts of titanium, nickel, and chromium. We added magnesium, chromium, copper, and manganese to the melt, using aluminum hardners, in the proportions shown in Table 8.

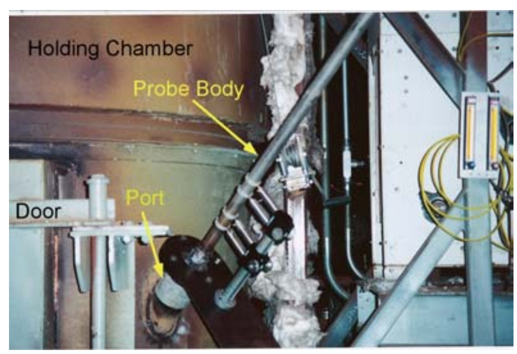


Figure 27 - Furnace Used for Mixing Tests

Table 8 - Change in Aluminum Composition from Alloying Operations

(all quantities in % by weight)

	Addition #1	Addition #2	Addition #3	Total Change
Copper		0.3%	0.2%	0.5%
Chromium		0.2%	0.2%	0.4%
Magnesium	0.1%	0.2%	0.2%	0.5%
Manganese		0.2%	0.2%	0.4%

In Figure 28, the increase in a magnesium peak with the addition of magnesium to the molten aluminum is seen. The first to the second Mg addition resulted in an increase of Mg from 0.1% to 0.2%. The intensities of magnesium's spectral lines went up by a factor of 2.6 in response to the change. From these measurements, the mixing time and its effect on the melt, at any location in the furnace, can be observed. In actual furnace operation, this type of measurement could minimize the use of fluxes and can determine the optimum use and location of aluminum pumps.

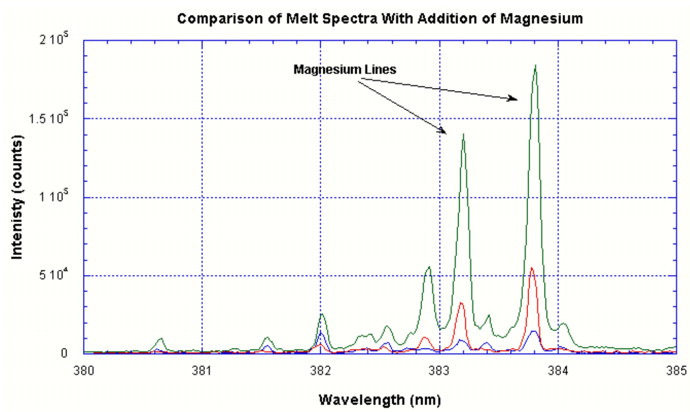


Figure 28 - Change in LIBS Spectrum with Addition of Magnesium to the Melt

7. Glass Industry Installation

7.1. Introduction

Compositional variability in batch minerals is thought to be a significant contributor to lost fiberglass production, as well as lost production in other glass industry sectors. While mining companies provide compositional data on their shipments of batch ingredients, these figures are from only one small sample pulled from the shipment, and may not be representative of the entire shipment. Furthermore, upon delivery to the glass plant silos each shipment is mixed in with remnants from prior shipments that are still in storage. The degree to which these shipments are mixed is unknown. Therefore, for precise knowledge of the minerals entering the furnace, the batch material exiting the silos should be tested. Currently, there is no instrument capable of rapidly measuring mineral compositions in this fashion.

ERCo has developed a laser-based analysis technology, termed LIBS, for this application. Under contract with the U.S. Department of Energy, and with PPG's support and guidance, a LIBS batch analyzer has been built to deliver mineral composition data within minutes of placing the sample in the instrument.

This report summarizes the results of extensive testing of ERCo's LIBS batch analyzer at PPG's Chester plant. High degrees of accuracy and repeatability were achieved in this test. PPG personnel continue to operate the equipment and find it easy to use and the results well presented and easily understood.

7.2. Analyzer Components

ERCo's batch analyzer system components are shown in Figure 29. The analyzer is run by ERCo's LIBS software running on the Windows PC shown in the figure. The sensor hardware requires little maintenance and runs off an ordinary 110V electrical outlet.

A close up photograph of the sample chamber is shown in Figure 30 (left). The procedure for analyzing a sample involves placing a few grams of powdered batch material in a custom holder which is then placed inside the chamber door, as seen in Figure 30 (right). The sealed chamber prevents the laser light from escaping into the room, so laser safety training and eyewear are not necessary. The door is interlocked so that the laser will not fire with the door open. Inside the chamber are all the optics and mechanical hardware necessary to perform the LIBS measurements.

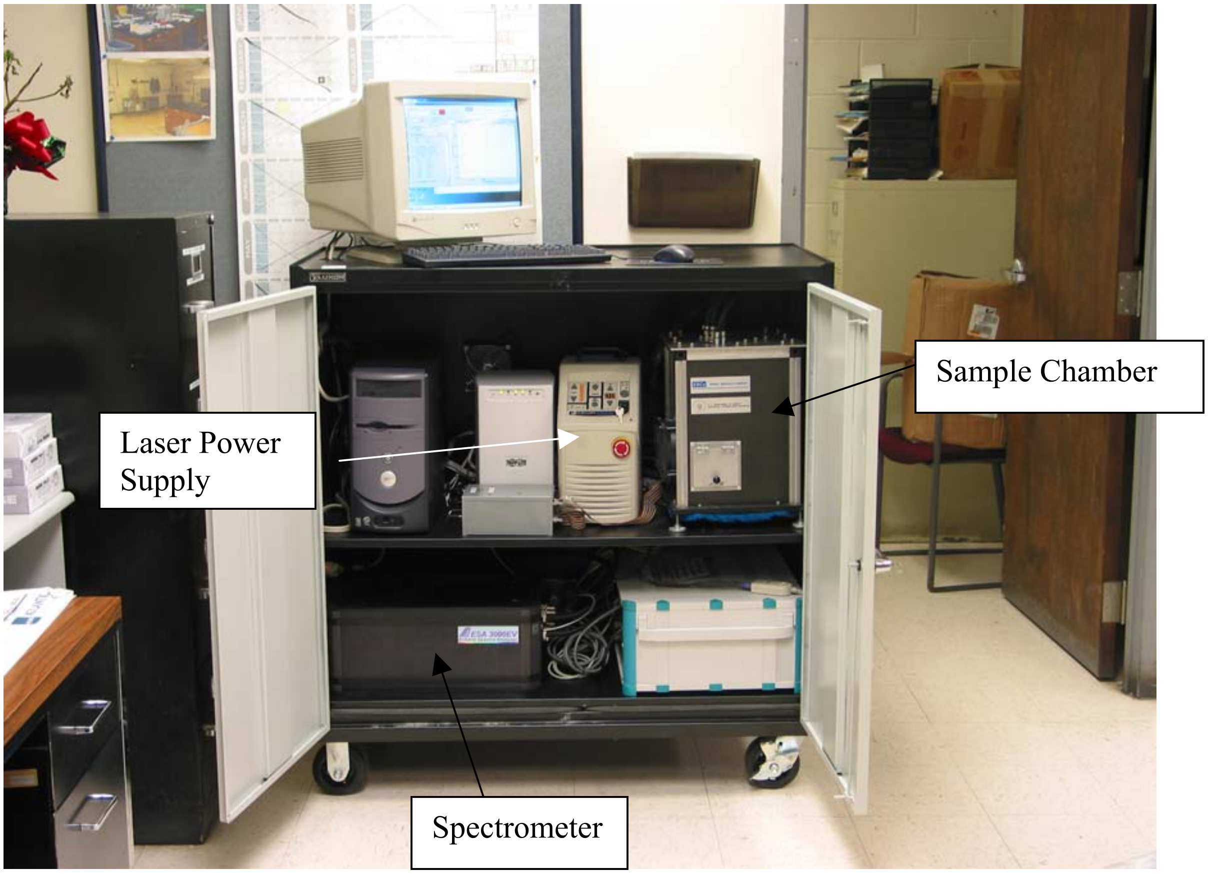


Figure 29 - Photograph of ERCo Batch Analyzer Equipment in PPG Chester Plant

Figure 30 - PPG Production Manager Kevin Streicher Placing a Sample into the Chamber for Analysis

7.3. User Interface

The analyzer is controlled from ERCo's LIBS software package, a "point and click" Windows program, operating on a PC, shown in Figure 31. This software package was instrumental in bringing LIBS technology out of the laboratory and into the plant environment. Our goal in developing this software was to enable non-specialist plant personnel to use the analyzer on a regular basis. We achieved this goal as PPG found the software package easy to use and that the results were provided in an easy to understand format.

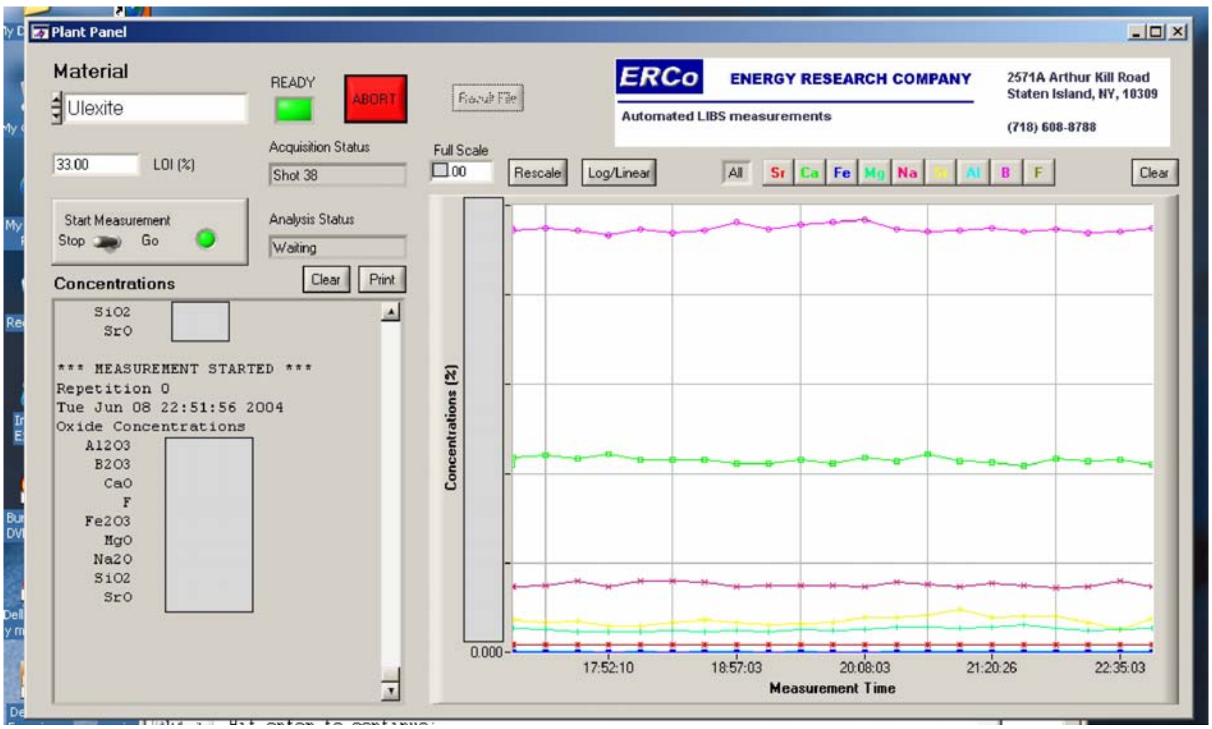


Figure 31 - ERCo's LIBS Software Control Panel

In order to operate the analyzer, the user selects the mineral being analyzed from the drop down menu in the upper left hand corner (ulexite is selected in the figure). Below this menu and the LOI input box[5] is a toggle switch. By clicking on the toggle switch, it moves from "Stop" to "Go" and the measurement is initiated. The laser is turned on and operated automatically, as is the spectrometer and all the other necessary hardware components, so that no further operator actions are necessary.

In the event that the analysis must be stopped for any reason, the red "Abort" button is provided on the screen. Additionally, if the door on the sample chamber is opened during an analysis, the laser is turned off and the analysis is immediately aborted.

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[5] The LOI value text box is a placeholder for future software upgrades. It is not used in the current version of the software.

After the data is collected and analyzed, the results are presented on the screen in the text window on the lower left and in the strip chart display on the right (all concentrations are blocked out as they are proprietary PPG data). In addition, the compositional data is saved in a text file that can readily be imported to any data analysis package or spreadsheet such as Excel.

The data in the strip chart can be viewed all at once, as shown in the figure, or data from one element at a time can be displayed by clicking on the element buttons immediately above the strip chart. Controls are provided for rescaling the y-axis and for switching between a linear and a logarithmic scale. In the single element views, two visible markers can be set to easily see if the data falls within a desired range.

7.4. Results

Powdered ulexite samples that were pulled from shipments to PPG over the course of the prior year were used in this test. Each sample was tested five times with the results shown in the figures below for each element. In each figure the blue diamonds are the data provided by the mining company and the purple squares are the LIBS analyzer results.

In each figure caption the average relative difference between the mining company results and the LIBS analysis +/- one standard deviation is given. The actual concentrations are proprietary PPG data, and are therefore blocked out.

The major constituents of ulexite are boron, calcium, and sodium. The first three graphs, Figure 32, Figure 33, and Figure 34, demonstrate the accuracy of the LIBS analyzer for these large percentage constituents. The average difference for between the supplier's data and the LIBS measurements was no greater than 2.75%.

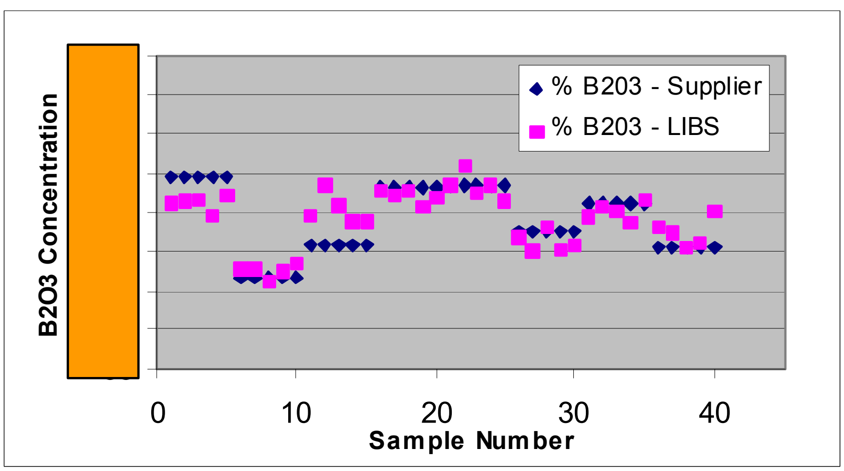

Figure 32 - Boron Average Difference: 0.54% +/- 0.43%

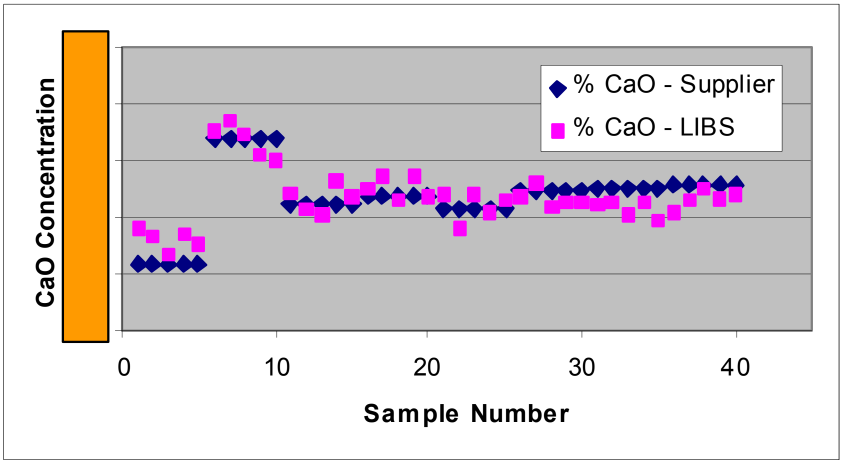

Figure 33 - Calcium Average Difference: 1.51% +/- 0.94%

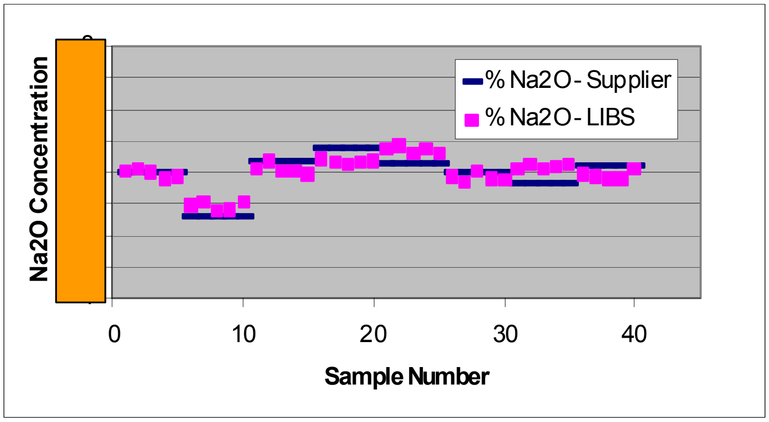

Figure 34 - Sodium Average Difference: 2.75% +/- 1.54%

Silicon and magnesium are present in much lower concentrations. As in the case of the major constituents, the LIBS analyzer closely tracked the reported data for these elements, shown in Figure 35 and Figure 36. The average difference for these minor elements was no greater than 5%.

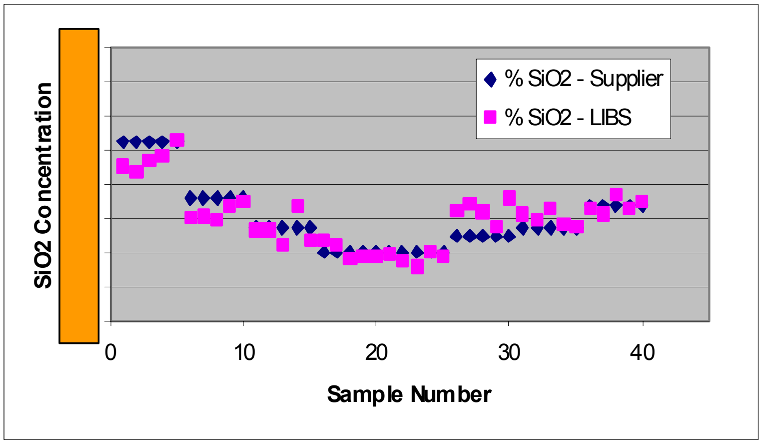

Figure 35 - Silicon Average Difference: 4.98% +/- 4.02%

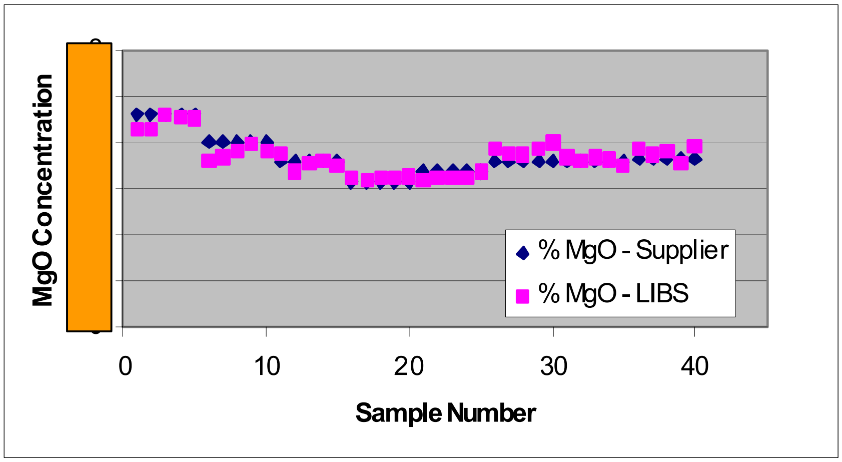

Figure 36 - Magnesium Average Difference: 4.06% +/- 2.72%

The last three elements, shown in Figure 37, Figure 38, and Figure 39, are all present in trace quantities. Even at these much lower concentrations, the LIBS analyzer was able to match the mining company data as well. Since the concentration percentages for these elements are so small, the absolute differences between the mining company values and the LIBS analyzer values are relevant, more so than the relative values. Therefore, the percentage difference is reported as absolute percent for these elements, and was no greater than 0.026%.

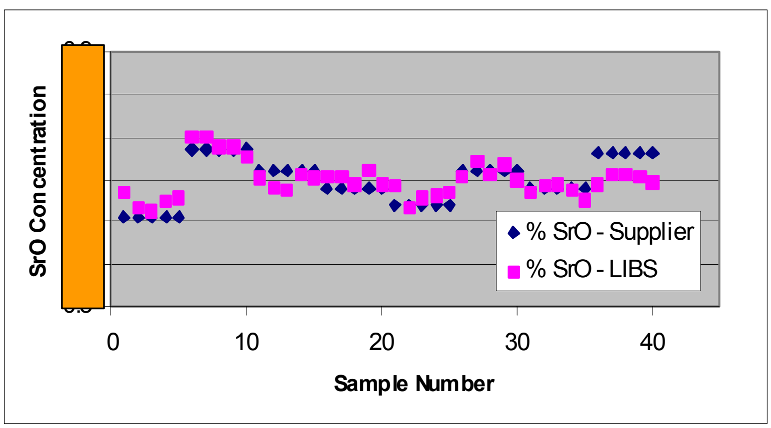

Figure 37 - Strontium Average Difference: 0.026% +/- 0.018%

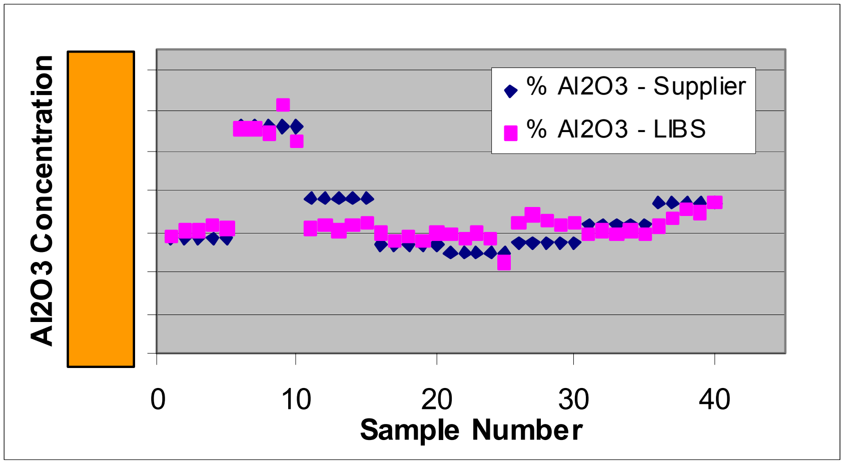

Figure 38 - Aluminum Average Difference: 0.007% +/- 0.004%

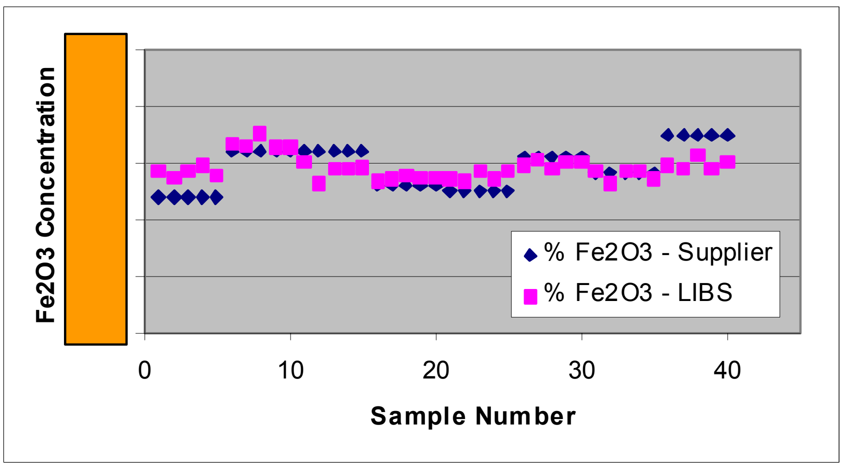

Figure 39 - Iron Average Difference: 0.003% +/- 0.002%

Following these tests, PPG provided two new ulexite samples without providing the elemental concentrations to ERCo. The mining company only provided boron concentrations for these samples, so this blind test was limited to only measuring boron. The results of the test, in which each sample was tested twice, are shown in Table 9 below. The measured difference was no greater than 0.3%

Table 9 - Results Summary from Blind Tests

Sample	Boron Concentration Difference
A	0.00%
A	0.03%
B	0.24%
B	0.30%

In addition to the low percentage differences, within each sample the repeatability was high.

7.5. Conclusion

PPG found these results to be highly satisfactory. Across all the elements, from the major constituents down to the trace elements, the LIBS analyzer results tracked the mining company results sufficiently closely for using the LIBS instrument in plant production.

Minerals have a natural variability, therefore perfect correlation between the mining company results and the LIBS results should not be expected. The mining company pulled one sample from a multi-ton shipment while we used a different sample pulled from the shipment for the LIBS tests. The accuracy and precision of the LIBS batch analyzer results should be viewed in light of this fact.

The LIBS system is permanently installed at PPG and is routinely used by PPG personnel.

8. Key Advances

8.1. Overall System Development

As shown in Chapters 4, 5, 6, and 7 the overall system and its individual components have been successfully designed and integrated such that two commercial systems are operating. This is the first time, to the authors' knowledge, that LIBS measurements of elemental concentrations in industrial settings have been achieved. The success of this project will lead to further installations and further development of the technology.

8.2. Batch to Continuous Furnace

The LIBS System makes feasible the conversion of a batch furnace, now used in the secondary aluminum industry, to a continuous furnace operation. This could result in large gains in productivity and reductions in energy and emissions.

8.3. Calibration Free Technique

Any LIBS method critically depends on converting the spectral data to concentration values. All current methods rely on the use of calibration curves. In this method, samples with known elemental concentrations are processed and a linear relationship is produced between the concentration and the spectral signal. However, the results from the calibration samples and the actual materials to be measured can differ significantly because of variability in the laser-material interaction due to, for example, changes in surface texture from sample to sample or the laser power diminishing slightly as the laser ages[6]. The end result is a change in the signal-to-concentration correlation because the amount of material vaporized by the laser pulses has likely changed, as well as the temperature and other properties of the vaporized material. The effect is most pronounced when different types of materials are compared, and it becomes impossible to use solid samples as calibration standards for molten materials.

Hence, for molten glass or aluminum measurements, calibration curves would need to be developed using molten calibration standards. This would be difficult to do routinely in an industrial plant environment, in which a limited number of trained personnel are available. In addition, it would be quite expensive to obtain certified samples each time a calibration was needed. Once melted, the standards could not be reused since some elements would volatilize, thus invalidating the concentration specification.

At ERCo, we have overcome these problems by modeling the plasma. Our work follows that of CNR's laboratory in Pisa, Italy[7]. Termed C-LESS (calibrationless) the plasma is modeled as follows. A LIBS plasma contains neutral and ionized atoms from each element present. Measuring the concentration of an element therefore requires measuring the concentration of each state of that element. At plasma temperatures typical of LIBS experiments, for these states, or species, only two are present of each element: the neutral

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[6] Chaleard, C. et al, "Correction of Matrix Effects in Quantitative Elemental Analysis with Laser Ablation Optical Emission Spectrometry", Journal of App. Atomic Spectrometry, Feb. 1997, vol. 12 (183-188)

[7] Ciucci, A. et al, "New Procedure for Quantitative Elemental Analysis by Laser-Induced Plasma Spectroscopy", Applied Spectroscopy, **53**, 8, 1999, pp.960-964

state and the singly ionized state For example, the total concentration of calcium in a sample would be the sum of the concentrations of the Ca I and Ca II atoms (where I designates neutral and II the singly ionized lines).

When the LIBS plasma is in a state of local thermodynamic equilibrium (LTE), the integrated intensity *I* of any emission line from a species *S* present at a concentration C_S can be written as (reference 7):

$$\overline{I_\lambda^{ki}} = F C_S A_{ki} \frac{g_k e^{-(E_k / k_B T)}}{U_S(T)},$$

where the line at wavelength λ is a result of an electronic transition from energy state *k* to energy state *i*. A_{ki} is the transition probability, g_k is the degeneracy of the state, E_k is the value of the upper energy state, k_B is the Boltzmann constant, *T* is the plasma temperature, and $U_S(T)$ is the partition function for the species at the plasma temperature.

F is an experimental factor which includes fluctuations in the plasma due to varying laser power, degree of focus, and surface character. The intensity *I* must be normalized by the spectral response of the light detection system for *F* to be independent of wavelength.

As shown in the test results in previous sections, the C-LESS method works well and allows the LIBS system to be operated with no training.

8.4. Eye Safe

The LIBS System has been designed to be eye safe and complies with 21 CFR 1040.10 and 1040.11 except for deviations pursuant to Laser Notice No. 50, dated July 26, 2001. Hence, no safety training is required and no special safety precautions need to be taken.

8.5. Software Development

As shown in Chapters 5 and 7, ERCo has developed software that incorporates the C-LESS technology and the eye safe system. Figure 23 on page 23, for example, shows the operator screen. A single push button is all that is required to extend the probe and begin taking data. No other actions are required.

8.6. LIBS Probe

The LIBS Probe consists of SiC sheath with a metal insert carrying the internal optics. The probe end immersed in the melt is open. Nitrogen is passed into the probe and exits this open end. The nitrogen creates a bubble at the open end, which acts as an aerodynamic window that prevents molten material from entering the probe. In addition, the laser light, coming from one of the fiber optic cables, is focused at the bubble-melt interface creating the plasma. The radiation from the plasma passes through the nitrogen and is picked up by the second fiber.

Figure 40 shows a six foot long probe built by ERCo for use in molten aluminum furnaces.

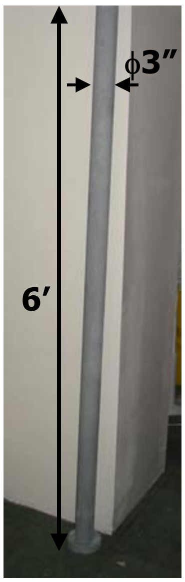

Figure 40 - SiC Probe Used in Molten Aluminum

The probe is inserted into molten materials and provides the path (fiber optic cables are used) for the laser light and the returning signal. The probe determines the exact location of the measurement within the melt. Further, the probe can be moved anywhere in the melt to provide spatial, as well as temporal, data. The function of the probe and fiber optic cable is to allow the electronics (laser, spectrometer, etc.) to be located some distance away from the melt to avoid costly packaging and maintenance. The fiber optic cables and optics are sheathed in a protective tube to avoid chemical attack and to provide strength for the otherwise fragile fiber cables.

ERCo has built a number of probes up to six-foot long for aluminum melts. We tested the probe material in an aluminum melt for 1450 hours and found no material degradation. In addition, ERCo has also tested fiber optic cables up to 64 feet long.

8.7. No Operator Training Required

From the above, no operator training is required. The operator simply presses a button and immediately data on the process is provided.

8.8. Worldwide Patent

A world wide patent has been issued – Patent number US 6,784,429 B2. In addition, a considerable amount of know-how and trade secrets have been developed. This includes ERCo's C-LESS techniques.

9. Energy Savings

9.1. Introduction

The energy and emission reductions, using Energy Research Company's Laser Induced Breakdown Spectroscopy (LIBS) probe, are reported. The following general assumptions were made:

- Projections are made to 2010.
- The detailed projections are given for just the aluminum industry, and only with the LIBS System being used to reduce the idle time of the furnace. Other energy savings opportunities are possible, some of which are also outlined below.
- The secondary aluminum industry uses mostly reverbatory, fossil-fired furnaces.
- There are, on average, three furnaces per plant.
- Commercialization of the LIBS probe started in 2002
- An average 6% per year market penetration is assumed, yielding a market share of 39% by 2010.

9.2. Secondary Aluminum Industry

9.2.1. Industry Characterization

The US industry operates 76 plants[8]. Table 10[9] shows the total secondary aluminum production for the industry of 8,126 million pounds, yielding an average plant production of 107 million pounds in 1997. It was expected that aluminum production will steadily increase due to the increased aluminum content of automobiles. In 1992, 200 pounds of aluminum were used in automobiles, and by 2000 it is expected to increase to 500 pounds[10]. Hence an annual growth rate of 2 to 4 % is likely, as shown in Figure 41. Using a growth rate of 3% yields an annual secondary aluminum production of 11,933 million pounds by 2010.

Table 10 - Supply (Millions of Pounds)

Primary Production	7,944	36%
Imports	6,183	28%
Secondary Production	8,126	37%
Total	22,253	100%

Presuming the average plant production is unchanged, then the total number of plants will increase to 112.

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[8] US Aluminum Industry Plant Directory, The Aluminum Association, November 1997
[9] Aluminum Statistical Review for 1997, The Aluminum Association.
[10] Phipps, H., "Scrap Aluminum Lower Sheet Raw Material Costs," Resource Recycling, March 1992.

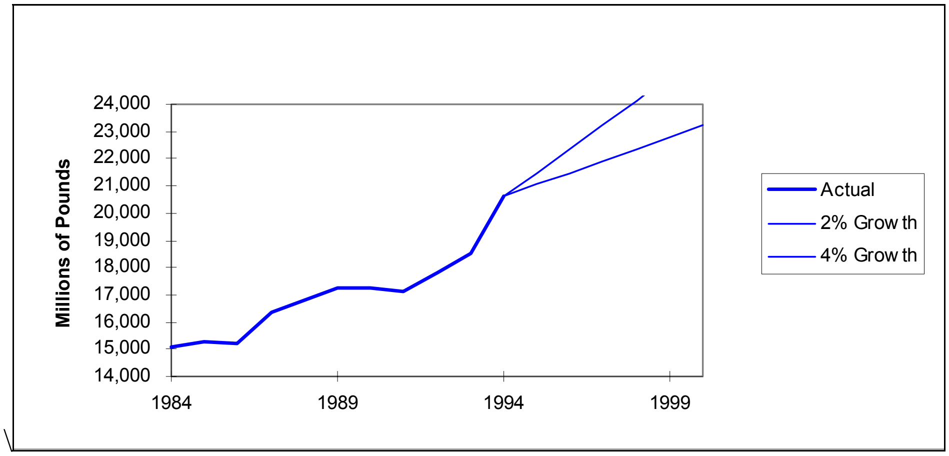

Figure 41 - Aluminum Industry Growth

The energy use of a secondary aluminum furnace will vary, depending on the plant's operation. Measurements[11] taken at Wabash (Formally Roth Bros.) in East Syracuse, NY yielded an energy use of 3000 Btu/lbm. However, recent plant improvements have probably reduced that to 2500 Btu/lbm. Hence, the total annual energy use for the secondary aluminum industry, in 2010, will be 29.8 trillion Btu, or 0.266 trillion Btu per plant.

9.3. LIBS Energy Reduction

9.3.1. Eliminate Furnace Idle Time During Conventional Melt Concentration Measurements

The near term application for the LIBS probe is to measure the melt constituent concentrations continuously, thus eliminating the time required to sample the melt, bring it to the lab, and adjust the melt. Reynolds Aluminum[12] (now part of Alcoa) stated that they could save ½ to 1 hour by use of the LIBS probe. Since a typical furnace will pour 4 times per day, an energy savings of 12½% results (0.75 hours divided by 6 hours). This yields an annual plant energy savings of 0.033 trillion Btu, and an industry wide savings of 3.7 trillion Btu. Using an average market penetration of 6% per year for 8 years yields a total market share of 39% by 2010. Hence, the market annual energy savings is 1.44 trillion Btu.

A summary of the information is given in the following tables provided by DOE. The following was used:

- One unit equals one plant, with an annual production of 105.5 million pounds.
- One LIBS probe is used in each plant, multiplexed to measure three furnaces simultaneously.

[11] Cole, W., et al., "Demonstration of a Long-Life Radiant Recuperator for the Secondary Aluminum Industry," Final Report, New York State Energy Research and Development Authority, December 1987
[12] Mark Walker, Personal Communication

- The heating value of natural gas is 911 Btu/ft^3.
- The capital cost ($/unit) is the installed cost of the LIBS probe only. It does not include the cost of the plant (i.e. unit).

Table 11 - Unit Impacts

	New Technology	Current Technology	Impact
Energy Use			
Natural-Gas (Trillion Btu)	0.233	0.266	0.033
Natural-Gas (billions of cubic feet)	0.256	0.292	0.036
Cost			
Capital Cost ($/unit)	$200,000	$100,000	$100,000
Non-energy Variable cost ($/unit/year)	$2,500	0	$2,500

Table 12 - Market Inputs

Total Market		Ultimate Potential Market		Market Penetration	
# Installed in US Market	112	Accessible Market	100%	Year of Commercial Introduction	2002
Year	2010	Likely Market Share	39%	Technology Class	
Annual Market Growth Rate	3%			Total Market	44

9.3.2. Continuous Furnace

A far-term application will be to use the LIBS probe to change a conventional reverbatory furnace into a continuous operation. From this, a production increase is possible. A typical conventional furnace produces about 120,000 pounds per day. If this furnace could be used in a continuous fashion, then the total daily furnace capacity would be about 206,000 pounds based on the amount of idle and non-melting times it undergoes. This is a 72% increase. In this case, the burners would be on high fire continuously.

Since the furnace idle time would be nearly eliminated, the energy use would be greatly reduced as well. Using an energy use of 2,500 Btu/lbm, the current furnace firing rate is about 12.5 MMBtu/hour. For a continuous furnace, the burners would be at this firing rate continuously. Using the production of 206,000 pounds per day, results in a specific energy use of 1,456 Btu/lbm. This represents a 42% reduction.

Assuming the same aluminum production and market penetration as above, results in a total industry annual energy savings of 4.9 trillion Btu by 2010, and an individual plant savings of 0.044 trillion Btu.

9.4. Other Industries

9.4.1. Glass Industry

For the glass industry, 350 trillion Btu were expended in 1995 with pack to melt rates of 85 to 93 % (i.e. 7% to 15% of the glass melt is scrapped). Hence, 24.6 to 52.5 trillion Btu are wasted each year. Rejected products result from variations in glass melt composition and non-repeatability in the mechanics of forming. Further, product rejections occur after all the energy intensive operations have been completed. With the proposed technology, it is estimated that packs can go up to 98%, saving 17 to 45 trillion Btu per year.

9.4.2. Steel Industry

Similar to aluminum and glass melting, process control in the steel industry is done through off-line sampling, which only determines whether chemistry and metallurgy are acceptable. Nearly 3% of all steel produced ends up being downgraded or scrapped. Steel industry consumes 1.7 Quads annually. It is estimated that ½ of all the downgraded/scrapped material needs complete rework - 26 trillion Btu wasted. In line measurements and closed loop control is the key to eliminating this waste.

10. Technology Transfer

Two LIBS Systems are operating commercially.

The following papers have been published:

1. De Saro, R., Weisberg, A., Craparo J., "In Situ, Real Time Measurement Of Aluminum Chemistry", Light Metals, 2003.
2. Weisberg A., De Saro R. and Craparo J. "Real Time, In-Situ Sensor for Feedstock Monitoring in Gasifiers", Proceedings 20th Annual Pittsburgh Coal Conference 2003, September 15-19, 2003
3. De Saro, R, Weisberg, A., Craparo J., "In Situ, Real Time Measurement Of Aluminum Melt Chemistry Using Laser Induced Breakdown Spectroscopy", 18th International Forum on Process Analytical Chemistry, Jan. 1-15, 2004.
4. Walsh, P., Shane Sickafoose, Douglas Scott, and Howard Johnsen, Michael Bartone and Robert De Saro, Carl Landham and Robert Dahlin, William Farthing, "Laboratory Investigation of Laser-Induced Breakdown Spectrometry as a Detector of Contaminants and Wear Particles for Integrated Gasification/Combined Cycle Power Systems" American Flame Research Committee 2004 Spring Meeting, The University of Utah, Salt Lake City, Utah, March 18-19, 2004
5. Weisberg, A., Poulos, A., Craparo, J., and De Saro, R., "Real Time, In-Situ Laser Composition Sensor for Feedstock and Ash in Coal-Fired Boilers and Gasifiers", Proceedings 29th Clearwater Coal Conference: International Technical Conference on Coal Utilization & Fuel Systems, April 18-22, 2004
6. De Saro, R. "In-Situ, Real Time Measurement Of Aluminum Melt Chemistry At an Aluminum Plant", Aluminum 2004 5th World Trade Fair and Conference, Essen, Germany, 22 September to 24 September 2004
7. De Saro, "LIBS Applications in the Aluminum, Glass, and Steel Industries", 3rd International Conference LIBS 2004, Laser Induced Plasma Spectroscopy Applications, Malaga, Spain, 28 Septemberto 1 October 2004
8. P. Walsh, S. Sickafoose, D. Scott, H. Johnsen, M. Bartone, R. De Saro, C. Landham, R. Dahlin, W. Farthing, "Laboratory Investigation of Laser-Induced Breakdown Spectrometry as a Detector of Contaminants and Wear Particles for Integrated Gasification/Combined Cycle Power Systems," LIBS_2004, 3rd International Conference on Laser Induced Plasma Spectroscopy and Applications, Torremolinos (Málaga), Spain, September 28 - October 1, 2004.

A world wide patent has been issued – Patent number US 6,784,429 B2. In addition, a considerable amount of know-how and trade secrets have been developed. This includes ERCo's C-LESS techniques.

A software package has been developed that uses ERCo's C-LESS techniques and is provided with the LIBS System.

ERCo has been selected to present at the World's Best Technology, 2005 in March, 2005.

ERCo's website provides information on its varied LIBS applications.

11. Conclusions

7. The LIBS System has been developed for industrial applications. This is the first time this has been accomplished.
8. Two commercial installations have been completed; one at Commonwealth and another at PPG.
9. Other installations are being negotiated.
10. Calibration free techniques have been developed such that instrument calibration is not required.
11. The systems have been certified to be eye safe.
12. Software has been developed to operate each system.
13. Coupled with the above three items, the system is easy to operate and requires no operator training.
14. The system is crosscutting and ERCo is evaluating seven applications, as reported in this report, and other applications to be reported later.
15. Funding from several sources has been obtained to augment the Sensors and Automation funding.
16. A business plan is being completed for each of the near term markets. ERCo is committed to achieving continued commercial success with the LIBS System.
17. The energy savings is substantial. The annual energy savings, by 2010, for each industry is estimated as follows:
    - Secondary Aluminum – 1.44 trillion Btu's
    - Glass – 17 to 45 trillion Btu's
    - Steel – Up to 26 trillion Btu's
18. The technology transfer has been significant. As mentioned above, two commercial systems are now operating. In addition, eight technical papers have been written, ERCo's website provides information on the system, ERCo will be presenting at the "World's Best Technology 2005" in March, and a world wide patent has been issued.