In Situ, Real Time Measurement of Aluminum, Steel, and Glass Melt Chemistries Using Laser Induced Breakdown Spectroscopy

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ABSTRACT

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

A probe, containing two fiber optic cables, is placed in the melt at any location and depth. A laser is repetitively fired through one of the cables vaporizing a small amount of the melt, creating a plasma. The resulting radiated light passes through the other fiber optic cable to a spectrometer. The wavelength of the light uniquely identifies the element and its amplitude its concentration. Hence, elemental compositions are obtained. ERCo has developed a Calibrationless technique, where the LIBS system is operated without the need to calibrate and without the need for a skilled operator.

Two commercial installations have been completed – one at Commonwealth Aluminum in Uhrichsville, OH and the other at PPG's fiberglass plant in Chester, SC. This paper will present the results at these plants, including the energy savings, measurement accuracy, and precision.

LIBS Description

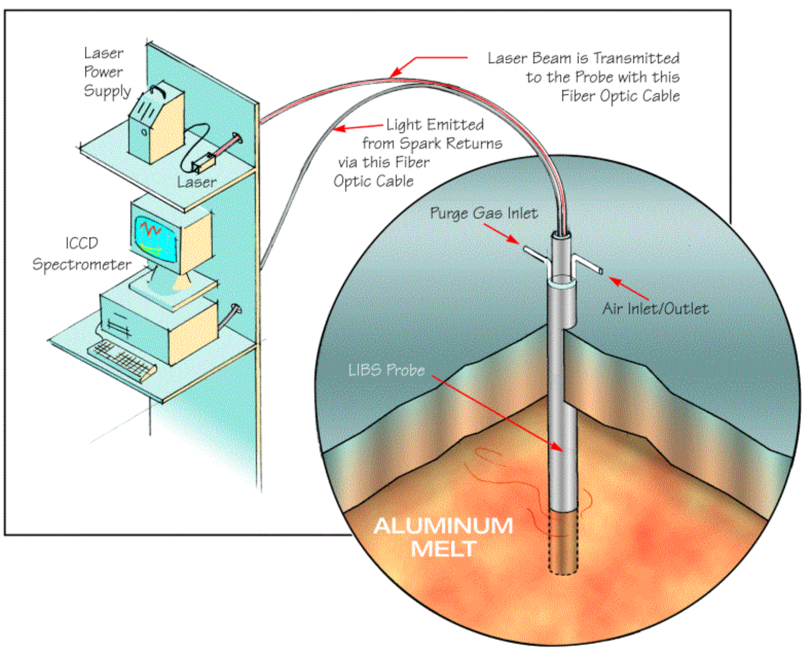
ERCo has developed a laser instrument to measure the elemental concentrations of industrial melts, in-situ and in real time. Termed LIBS for Laser Induced Breakdown Spectroscopy, the concept is shown in Figure 1. It is an optical atomic emission technique in which a high energy plasma is formed using 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, Cr for instance) and the emissions' strength are used to determine the concentration of each element. Figure 2 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 2, the 2024 alloy has about 4 to 5% copper, while the 1100 alloy has 0.05 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.

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.

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. 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 LIBS Sensor (the balance of the alloying would have been previously accomplished in the furnace in the conventional manner).

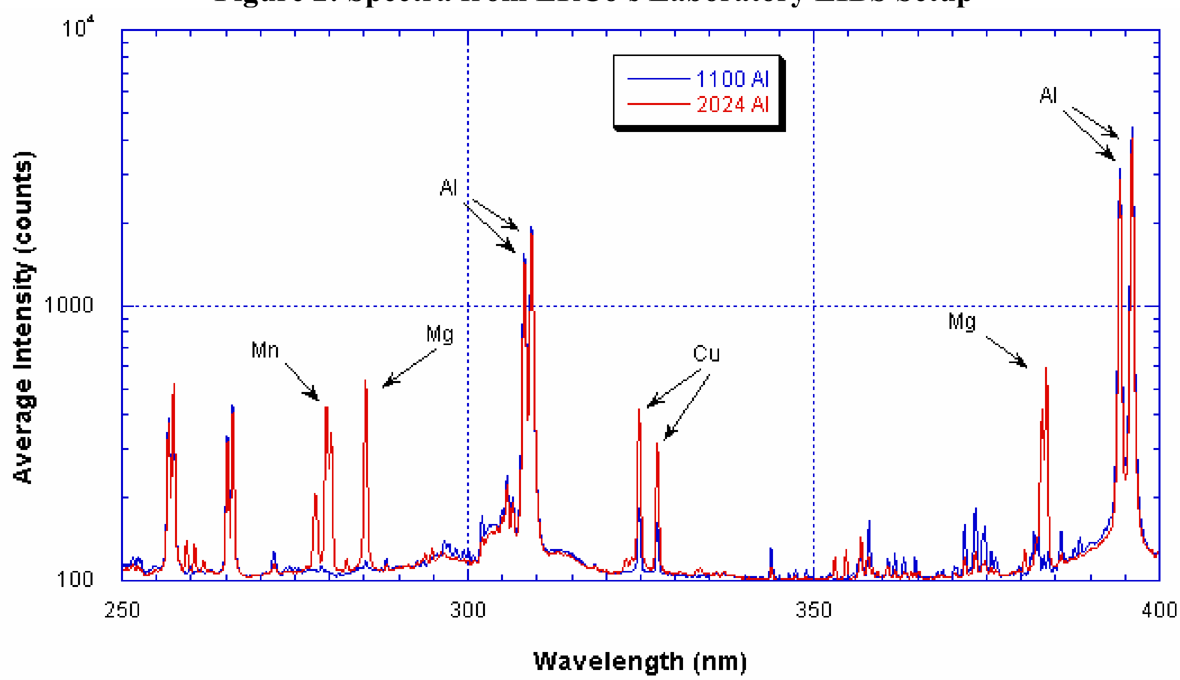
Figure 1: Schematic of a Probe in a Furnace



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.

Figure 2: 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. 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 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 (De Saro, 2004).
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 correlated to any independent variables under consideration. Also, existing computer models could be calibrated using the sensor.

Technical Breakthroughs

ERCo has made several technical breakthroughs that now allow the technology to be commercially saleable.

- 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.

Aluminum Industry Installation

The following two subsections discuss a commercial installation of the LIBS System at Commonwealth Aluminum and preliminary mixing tests at ERCo's laboratory, respectively. The Commonwealth installation demonstrates the near term potential and advantages of the LIBS system to the aluminum industry. The mixing tests demonstrate the possibility of using the LIBS System to better design future furnaces.

Commercial Installation at Commonwealth Aluminum

ERCo has installed a full-scale LIBS system at Commonwealth's aluminum melt in their Uhrichsville, OH plant, as shown in Figure 1. 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.

The photo in Figure 3 shows the LIBS probe installed in Commonwealth's filter bowl and 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 4 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 3: LIBS Probe Installed at Commonwealth (Left) and Instrument Cabinet (Right)

Table 1 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), a measure of the data variability, ranges from 4.5 to 11.6%.

The results from the Commonwealth installation show that the LIBS system is as accurate as the conventional spark spectrometer. Also, after some period of testing the probe suffered no adverse affects. Finally, the LIBS system continues to be used by Commonwealth as a process tool.

Figure 4: Operator Control Screen

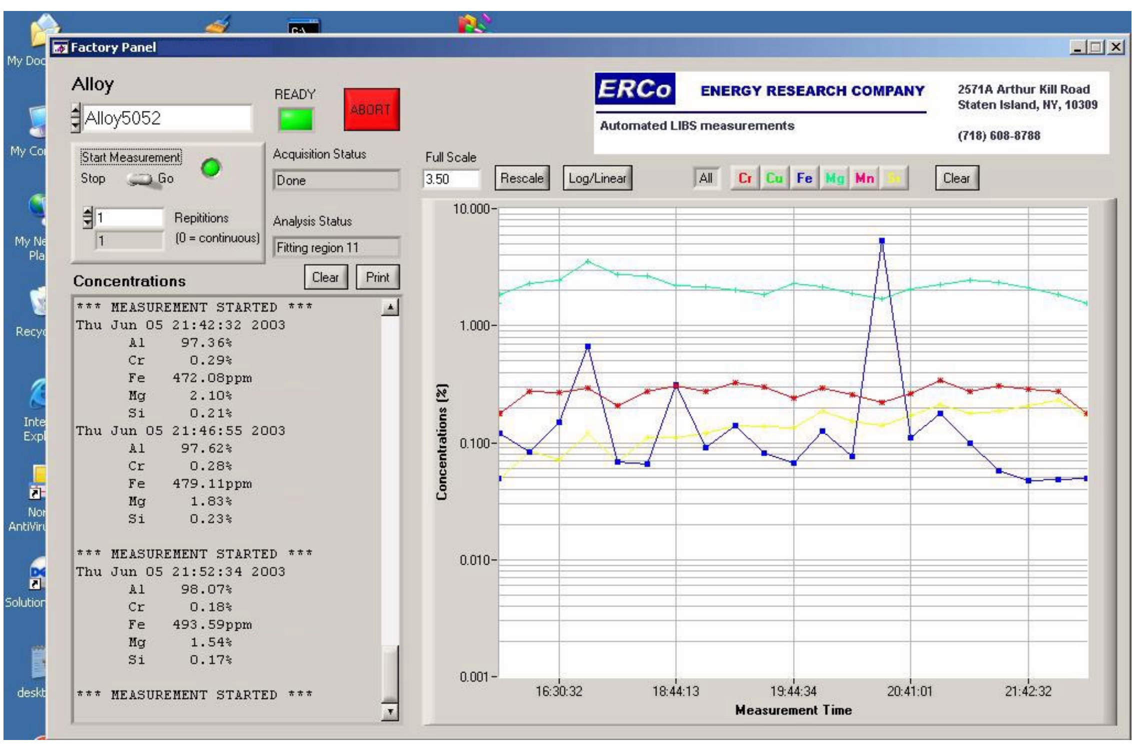


Table 1: 11/6/03 Data for 3105 Alloy

	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%

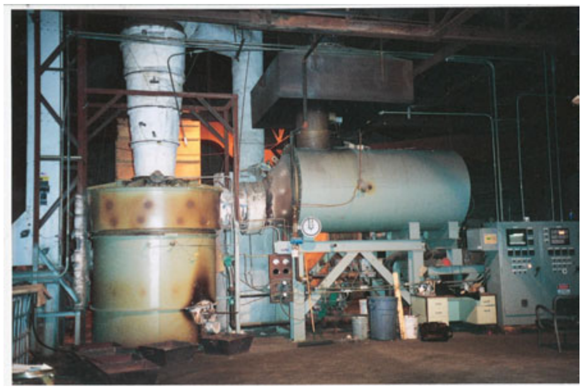
Aluminum Furnace Mixing Measurements

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 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 5. 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. Magnesium, chromium, copper, and manganese were added to the melt using aluminum hardners, in the proportions shown in Table 2.

In Figure 6, 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 5: Furnace Used for Mixing Tests



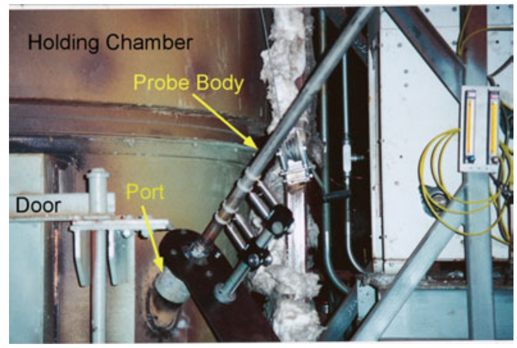
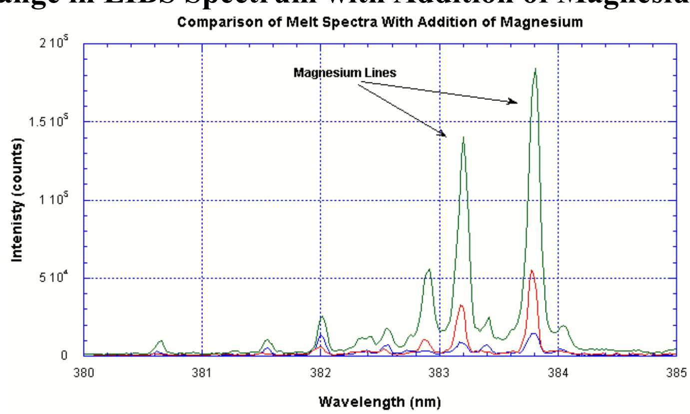


Table 2: Change in Aluminum Composition from Alloying Operations
(all quantities in % by weight)

	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%

Figure 6: Change in LIBS Spectrum with Addition of Magnesium to the Melt



Glass Industry Installation

The following two subsections discuss a commercial installation of the LIBS System at PPG, a fiberglass manufacturer, and molten glass tests at ERCo's laboratory, respectively. The PPG installation demonstrates the near term potential and advantages of the LIBS system to the glass industry. The molten glass tests demonstrate a future application being developed.

Installation at PPG Industries

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, 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's LIBS System was installed at PPG's Chester, SC plant. PPG is the largest fiberglass manufacturer in the US. The results of ERCo's LIBS batch analyzer show that high degrees of accuracy and repeatability are achievable. PPG personnel continue to operate the equipment and find it easy to use and the results well presented and easily understood.

ERCo's batch analyzer system components are shown in Figure 7. 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 8 (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 8 (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. The analyzer is controlled from by ERCo's LIBS software package, a "point and click" Windows program similar to that shown in Figure 4.

Powdered ulexite samples were measured in Chester, with the results shown in Table 3. The actual values are proprietary to PPG and are not shown. However, the difference between the LIBS measurement and the value reported by the mining company is shown. In all cases, the LIBS measurement was highly accurate.

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

Molten Glass Results in ERCo's Laboratory

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 ^oC (2282 ^oF). PPG supplied the chemical composition, and after melting the solidified glass was sent to Monarch, Inc., an independent laboratory, for chemical analysis.

Measurements were taken at the surface of the molten glass. Concentrations were determined using ERCo's 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 the 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 given the variation in the before and after reported values. 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 within the accuracy of lab equipment (XRF, etc.) currently in use in the glass industry.

Figure 7: Photograph of ERCo Batch Analyzer Equipment in PPG Chester Plant

Figure 8: LIBS Analyzer Sample Chamber

Table 3: Results

Element	Ulexite Component	Average Difference Between Reported and Measured Values
B	Major	0.54%
Ca	Major	1.51%
Na	Major	2.57%
Si	Minor	4.98%
Mg	Minor	4.06%
Sr	Trace	0.026%
Al	Trace	0.007%
Fe	Trace	0.003%

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	

Energy Savings

Secondary Aluminum Industry

The energy use of a secondary aluminum furnace will vary, depending on the plant's operation. Measurements (Cole, 1987) taken at Wabash Alloy (Formally Roth Bros.) in East Syracuse, NY yielded an energy use of 3000 Btu/lbm. However, recent plant improvements have likely reduced that to 2500 Btu/lbm. The industry operates 76 plants (Aluminum Plant Directory, 1997). The total secondary aluminum production for the industry was 8,126 million pounds, yielding an average plant production of 107 million pounds in 1997 (Aluminum Statistical Review, 1997). It was expected that aluminum production would steadily increase due to the increased aluminum content of automobiles. Using a growth rate of 3% yields an annual secondary aluminum production of 11,933 million pounds by 2010. 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.

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[1] (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.

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. The market penetration estimate is based on a LIBS System delivering greater savings than a conventional spark spectrometer with a significant life cycle cost advantage.

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[1] Mark Walker, Personal Communication

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%. For a single furnace operating at 250 tons per day and expending 4.5 MMBtu/ton, an energy savings up to 51,000 MMBtu, which at a natural gas cost of $7/MMBtu results in an annual cost savings of $358,000. Industry wide, a savings of 17 to 45 trillion Btu per year is possible.

Conclusions

1. The LIBS System has been developed for industrial applications. This is the first time this has been accomplished.
2. Two commercial installations have been completed; one at Commonwealth Aluminum and another at PPG.
3. Calibration free techniques have been developed such that instrument calibration is not required.
4. The systems have been certified to be eye safe.
5. Software has been developed to operate each system.
6. Coupled with the above three items, the system is easy to operate and requires no operator training.
7. The energy savings is substantial. The annual energy savings, by 2010, for the secondary aluminum industry is 1.44 trillion Btu's and for the glass industry is 17 to 45 trillion Btu's.

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