In-Situ Real Time Measurement of Molten Glass Properties

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Final Report

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Notice

Forward

The U.S. Department of Energy (DOE), Industrial Technologies Program, funded the work covered in this report through their Inventions and Innovation Program. This report covers the results of a project aimed at the development of a instrument to measure the chemistry and properties of molten glass melts. This is intended to improve the energy efficiency, production, and environmental performance of glass melting furnaces.

Acknowledgments

The authors wish to acknowledge and thank the Entrepreneurs for an Energy Efficiency (E-3) for their assistance in keeping the I&I program viable and for their continued marketing advice.

Executive Summary

Energy Research Company (ERCo) of Staten Island, NY has developed a sensor capable of measuring *in situ* and in real time, both the elemental composition and the temperature of molten glass. A prototype sensor has been designed, constructed and tested in ERCo's laboratory. The sensor was used to collect atomic emission spectra from molten fiberglass via Laser Induced Breakdown Spectroscopy (LIBS). From these spectra, we were able to readily identify all elements of interest (B, Si, Ca, Fe, Mg, Na, Sr, Al). The high signal-to-background signals achieved suggest that data from the sensor can be used to determine elemental concentrations, either through calibration curves or using ERCo's calibrationless method.

ERCo's technology fits in well with DOE's Glass Industry Technology Roadmap which emphasizes the need for accurate process and feedstock sensors. Listed first under technological barriers to increased production efficiency is the "Inability to accurately measure and control the production process".

A large-scale glass melting furnace, developed by SenCer Inc. of Penn Yan, NY was installed in ERCo's laboratory to ensure that a large enough quantity of glass could be melted and held at temperature in the presence of the water-cooled laser sensor without solidifying the glass.

Key Words

LIBS, Spectroscopy, Glass Melting, Elemental Analysis.

Table of Contents

Table of Figures

Table of Tables

1 BACKGROUND

1.1 GLASS INDUSTRY DESCRIPTION

The glass industry consists of the following segments and products:

- Container (SIC 3221, NAICS 327213) – Food, beverage, and pharmaceutical applications.
- Flat (SIC 3211, NAICS 327213) – Sheet, plate, and various forms of rolled glass, mostly for vehicle and building applications.
- Fiberglass (SIC 3296) – Fiberglass insulation, textiles, and optics.
- Pressed and Blown (SIC 3229, NAICS 327212) – Lamp enclosures, bulbs, tubing, flat displays, etc.
- Mineral Wool (SIC 3296, NAICS 327993) – Insulation

In 1999, the industry shipped 20 million tons of products worth $28.4 billion and expended 395.3 trillion Btu of energy[1], mostly in melting and refining.

Table 1 shows the number of glass companies in the US and NY[2] (Fiberglass is not catalogued by the Census Bureau though there are probably none in NY). There are a total of 61 glass companies in NY. These NY companies (not including container and flat) shipped $397 million worth of product, paid $84 million in payroll and employed over 2500 people. The container and flat sector data is not available and would greatly increase these numbers.

Table 1-Glass Companies in NY and the US

Industry Segment	New York Companies	NY Shipment Value ($ Million)	NY Payroll ($ Million)	No. NY Employees	US Companies
Container	2	D	D	500-999	65
Flat	1	D	D	250-499	36
Pressed and Blown	42	183	52	1273	525
Mineral Wool	16	214	32	568	304
Total	61	397	84	2591-3339	930

D - Withheld

1.2 THE INDUSTRY OPPORTUNITY

The US Department of Energy has performed assessments of various technology and industrial sectors that impact the US and has issued recommendations for the improvement of energy and production efficiencies in a series of "roadmaps". The Glass Industry Technology Roadmap[3] emphasizes the need for accurate process and feedstock sensors. Listed first under technological barriers to increased production efficiency is the "Inability to accurately measure and control the production process".

[1] Energy and Environmental Profile of the US Glass Industry, Table 1-3, Prepared by Energetics for the Office of Industry Technologies of DOE, April, 2002

[2] http://www.census.gov/econ/census02/

[3] Available at: http://www.oit.doe.gov/glass/pdfs/glass2002roadmap.pdf

Products from all segments of the glass industry are formed through melting of raw materials in a large furnace. The quality of the end product depends on an ability to maintain a uniform chemical composition over the course of a production run. Current methods for monitoring melt chemistry involve sampling the melt at discrete locations and sending the resulting solidified glass "buttons" to a laboratory for analysis. The time between sample collection and analysis can be hours, or even days. This approach has several problems:

- While waiting for the analytical results, the production engineer has no information on which to base a decision to adjust the chemistry, hence if a problem is eventually detected, a significant amount of wasted product is made before a correction can be implemented.
- During the time it takes to obtain an analysis, the chemistry of the melt could change. As a result, any process adjustments might not correspond to the current melt conditions.
- The samples are collected from a single location in a large furnace. The analytical results will therefore not necessarily represent the chemistry of the bulk melt.

Often, problems with glass composition are not detected until they appear as defects in the end product. This results in large product losses, while the problems are diagnosed and corrected. The container industry alone typically loses 7 to 15% of its product resulting in a loss of 25 to 52 trillion Btu per year. New York container companies make up 3% of the total US container industry, so the NY container loss is 0.8 to 1.6 trillion Btu per year.

ERCo has developed a laser-based sensor that can be inserted into a glass melt and used to measure the elemental composition and temperature of the molten glass in real time. The combined chemistry and temperature measurements will allow real-time determination of glass properties. This, in turn, will allow the forming of the glass product to be held to much tighter tolerances and quality problems could be observed and corrected before the glass was discarded. Large reductions in lost product and a commensurate reduction in energy use will result.

2 TECHNOLOGY DESCRIPTION

2.1 ELEMENTAL CONCENTRATION MEASUREMENTS

Energy Research Company has developed a laser-based technique to measure, in real time, the chemistry of molten materials as they are being formed into a product. This technique, known as Laser Induced Breakdown Spectroscopy (LIBS), will allow real time determination of molten glass properties. A probe containing several lenses and a fiber-optic cable is inserted beneath the surface of the molten glass at any depth and location. Laser pulses are directed into the probe, either through an optical fiber or via a system of laser mirrors, and focused through a lens onto the material to be analyzed. A minute amount of material (< 1 μg) is vaporized and ionized, forming a small, micro-plasma, which appears to the eye as a bright spark. Light from the plasma is collected through an optical fiber and directed to the entrance slit of a spectrometer, which resolves the light into its component wavelengths. The wavelengths of the resultant spectral peaks define the elements present (Si, Na, Ca, Mg, B, Al, Fe, Sr, Ti, Cr, for example) and the peak areas are proportional to the concentrations. This same probe/spectrometer combination can be used to collect thermal emission spectra, which can be used to estimate the bulk glass temperature.

Figure 1 is a representation of the design. The use of fiber-optic cables (depicted in the figure) and/or optical light guides allows the expensive equipment to be located in a controlled environment away from the furnace. An outer sheath is employed to protect the fibers and lenses from chemical and thermal attack and to provide a rigid support structure for the fragile optical components. Water is used to cool the sensor so that the optics do not exceed the design temperature of 400 ^{o}F. Either nitrogen or argon flows through the center of the probe creating a bubble at the probe tip. This serves to both keep molten material away from the optics and to form a stable interface on which the laser is focused to collect LIBS measurements.

Figure 2 shows a typical LIBS spectrum collected in ERCo's laboratory from solid glass, with spectral lines labeled from the elements of interest. To convert LIBS spectra to concentration measurements, the areas under the spectral peaks for different elements are measured and correlated to their concentrations. Increasing the concentration of an element leads to a relative increase in the areas under the corresponding peaks.

ERCo has made a significant advance in the process of translating spectral information into elemental concentrations. We have developed a mathematical model of the LIBS plasma allowing us to determine the elemental concentrations directly from the atomic emission lines, without the need for calibration curves. This technique has been well-developed for molten aluminum and will be further developed for molten glass using the information collected through the LIBS molten glass sensor.

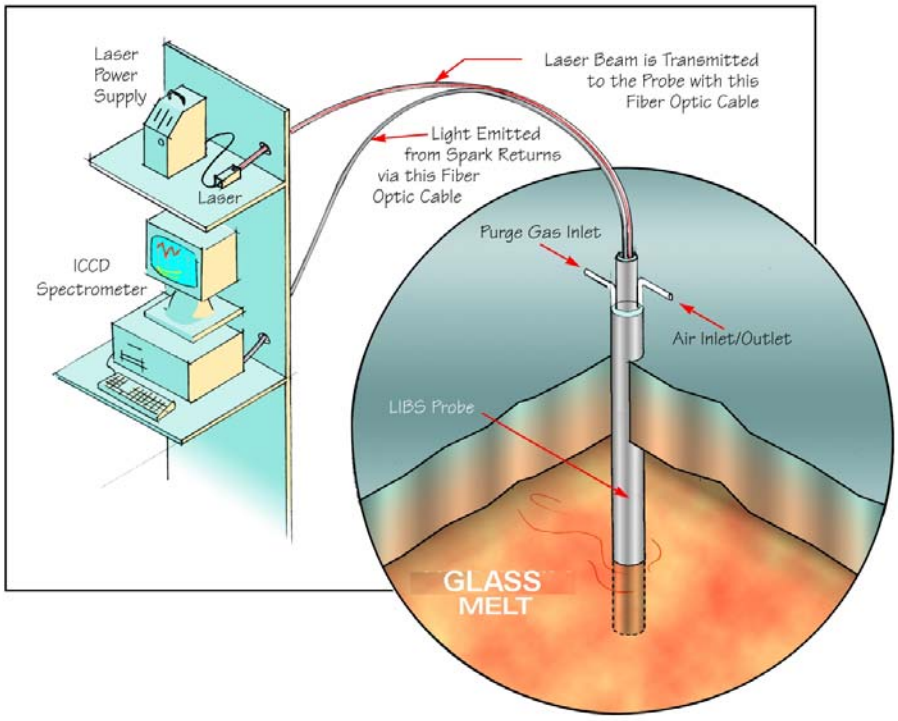

Figure 1 - Schematic of LIBS Probe for Molten Glass

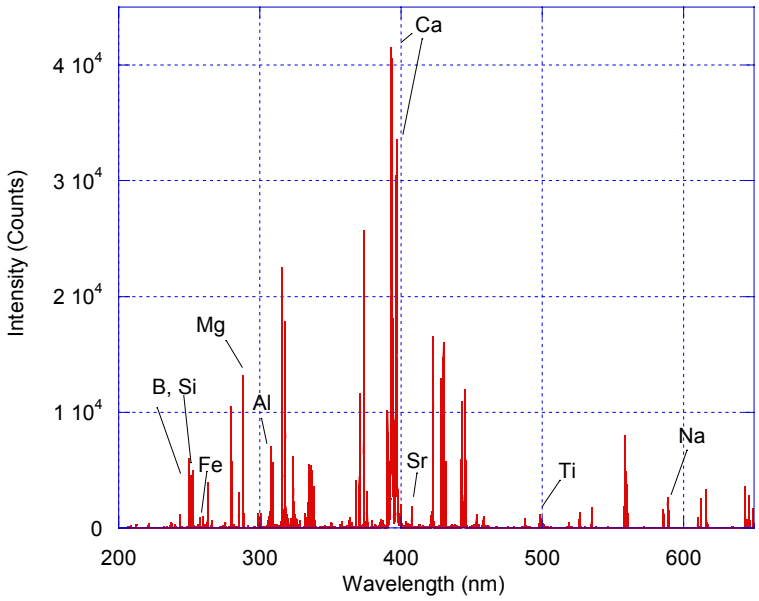

Figure 2 - Typical LIBS Spectrum from Solid Fiberglass

3 SENSOR DESIGN

3.1 HIGH TEMPERATURE OPTICS TESTING

Tests were conducted at Oak Ridge National Laboratory to determine suitable optical materials for an adiabatic (uncooled) probe for use in a molten glass environment. Two lenses, one made of fused silica and the other of sapphire were preheated in a furnace from room temperature to 1000°C at a rate of 5°C/min and then held at temperature for 40 minutes. The temperature was then raised to 1500°C at a rate of 10°C/min and held for 20 minutes. The lenses were then allowed to air-cool back to room temperature[4]. Figure 3 shows a photograph of the lenses following the experiment. The fused-silica lens became white under temperature and cracked upon cooling. There was no apparent change in the sapphire lens.

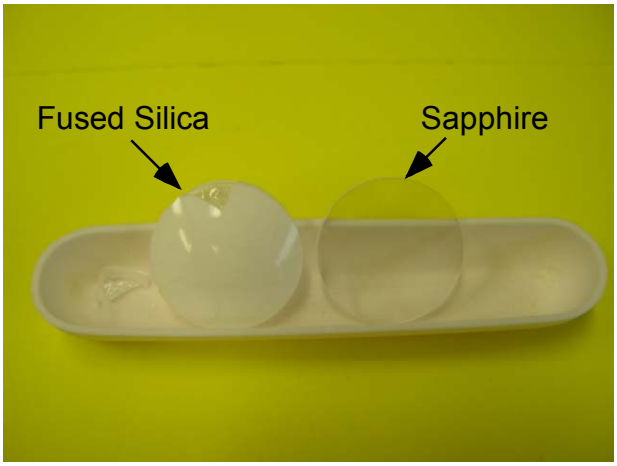

Figure 3 - Fused Silica and Sapphire Lenses after Exposure at 1500 C

The experimental results show that sapphire optics can be used at molten glass temperatures without active cooling. If fused-silica optics are used, they must be cooled to below a stable operating temperature of 1400°C.

Additional tests were conducted to measure the transmission through sapphire lenses and fibers as a function of wavelength. An ultraviolet source (MINERALLITE® model UVG-54) was directed into the entrance slit of a spectrometer, and the throughput was measured both with and without a 2mm thick sapphire window in front of the slit.
The results are shown Figure 4. A drop in intensity of approximately 20% was seen across all peaks. This is consistent with transmission curves for sapphire reported by manufacturers.

[4] These heating and cooling rates, while conservative, can be implemented in a commercial instrument if needed.

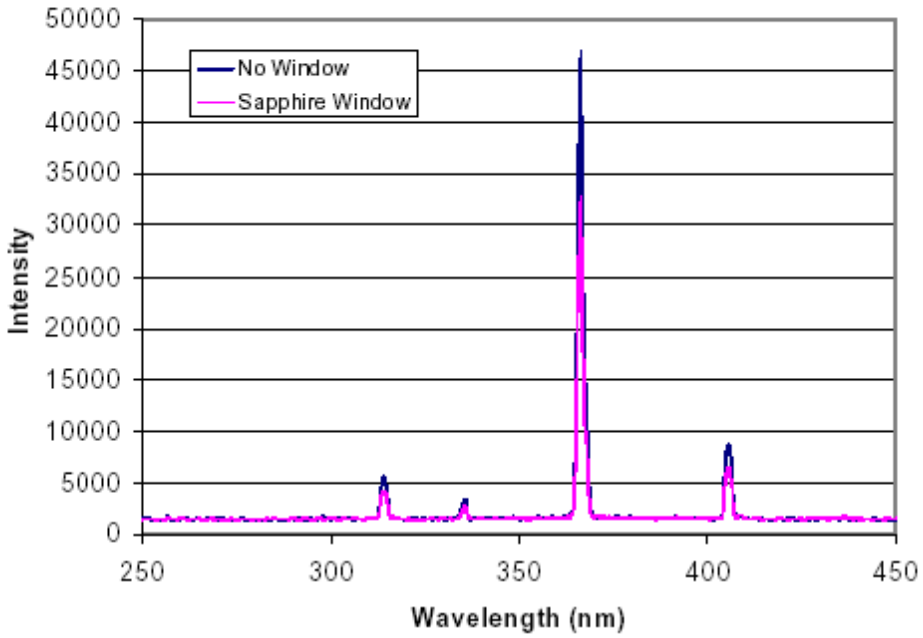

Figure 4- Transmission of UV Source With and Without Sapphire Window

A sapphire fiber (1.9m in length, 400µm diameter, unshielded) was tested in ERCo's laboratory as a possible replacement for the UV-Grade fused silica fiber located inside the probe. The throughput was evaluated by illuminating the fiber with two broadband sources, a Xenon arc lamp for evaluation in the deep UV, and a Quartz-Tungsten Halogen (QTH) lamp for evaluation in the visible and near infrared. Both sources and associated power supplies are made by Oriel Instruments. A 2m long, 600µm diameter solarization-resistant UV-grade fused silica fiber (manufactured by Ceram Optec Inc.) was used for comparison.

The results are shown in Figure 5. A multiplier of 0.32 was applied to the spectra collected using the fused-silica fiber to account for the difference in fiber diameters. The graph clearly shows that the fused silica fiber was far superior to the sapphire fiber at all wavelengths. From these results we conclude that the sapphire optics are inadequate for this application, while the fused silica optics is adequate.

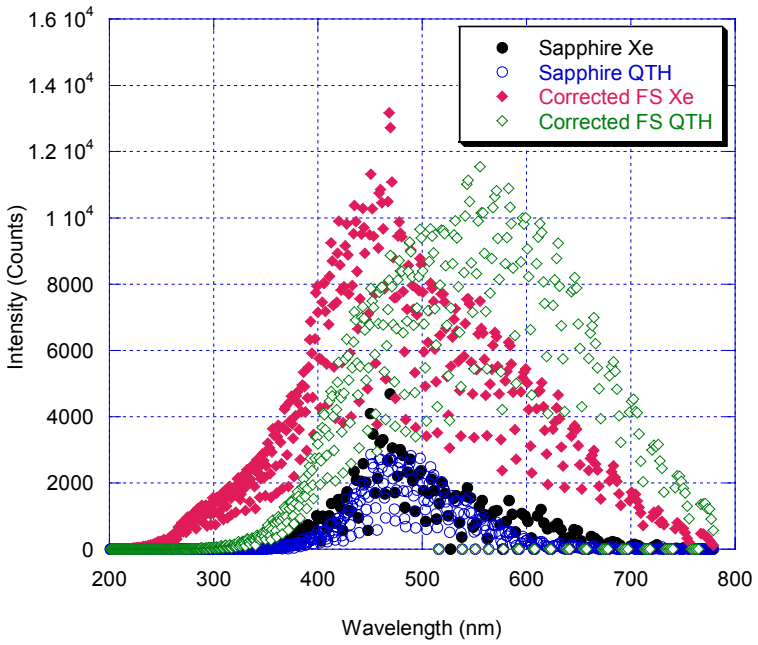

Figure 5 - Broadband Comparison of Sapphire and Fused Silica Fibers

3.2 FABRICATION

Photographs of the completed LIBS molten glass sensor are shown in Figures 6 and 7.

Figure 6 - LIBS Molten-Glass Sensor

(black hoses are water inlets, red are water outlets)

Figure 7 - Closeup of LIBS Sensor

(Laser enters through black central tube, Probe fiber seals against white ring seal)

3.3 LIBS PROBE COOLING TESTS

The LIBS probe was assembled and inserted into our small laboratory furnace for testing of the water-cooling system as shown in Figure 8. The probe was lowered into an empty crucible, placed inside the furnace to shield the heating elements in the event of a water leak. Water from the tap was continuously circulated through the probe as the furnace temperature was gradually increased from room temperature to 2400^{o}F. An in-line thermocouple was used to measure the outlet water temperature, and a type-K thermocouple was attached to the back face of the lens to monitor its temperature. A plot of these temperatures as a function of the furnace air temperature is shown in Figure 9. The results in this case were quite encouraging, since the water and lens temperatures did not exceed 70^{o}F and 90^{o}F, respectively even when the probe was exposed for an hour to the maximum furnace temperature.

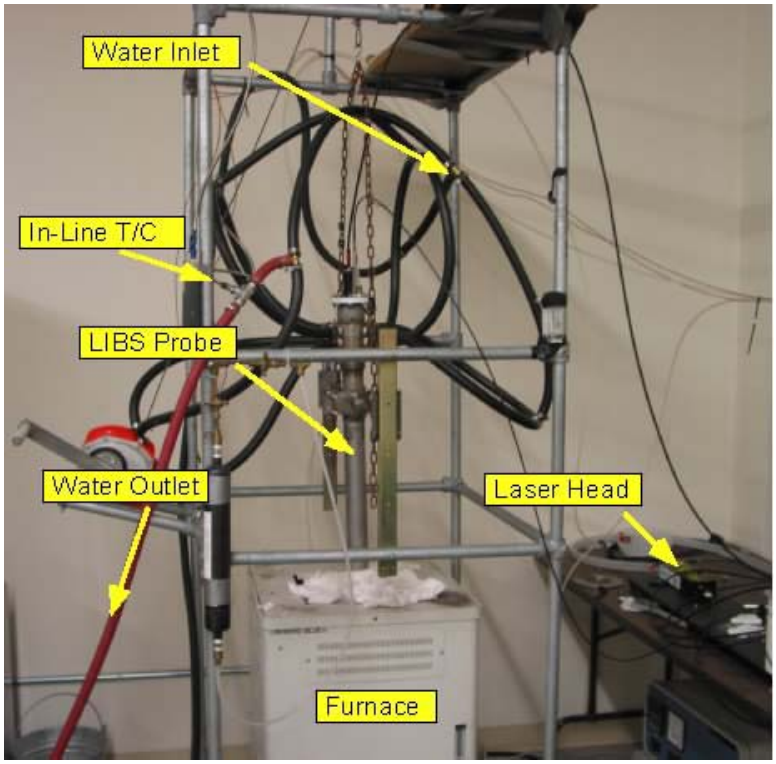

Figure 8 - Laboratory Setup for LIBS Probe Cooling Test

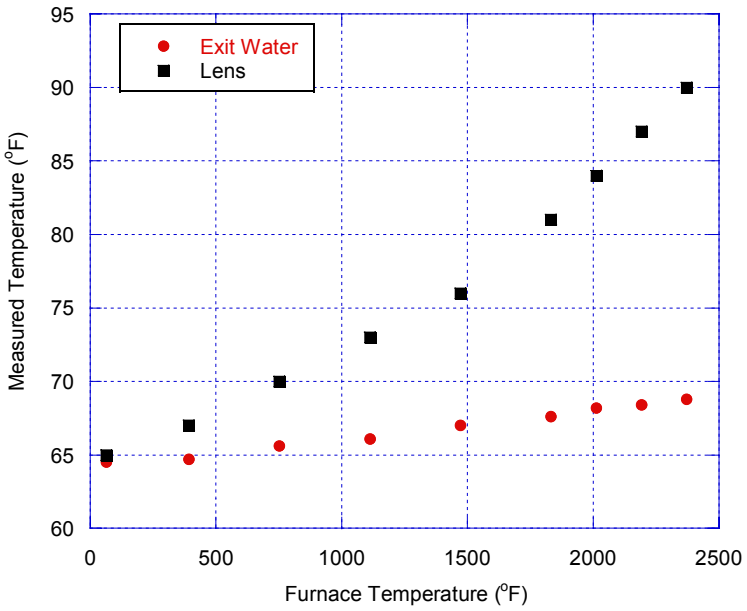

Figure 9 - Results of LIBS Molten Glass Probe Cooling Test

4 TESTING AND RESULTS

4.1 COLLECTION OF LIBS SPECTRA FROM MOLTEN GLASS

A quantity of fiberglass marbles, supplied by PPG Industries was melted in ERCo's laboratory furnace to a temperature of 2625 ^{o}F. The LIBS probe was then lowered into the furnace and LIBS spectra were collected.

Prior to melting, a spectrum was collected from solid glass for reference. A comparison of the solid and molten glass LIBS spectra for the boron and silicon atomic emission lines near 250 nm is shown in Figure 10. The absolute peak intensities from the molten glass were typically stronger than those collected from the solid samples. LIBS spectral peaks from the major elements of interest in fiberglass (B, Si, Al, Fe, Mg, Sr, Ca, Na) collected from the molten glass surface are shown in Figures 23-25. Table 2 shows the signal-to-background ratios (S/B) for characteristic atomic emission peaks. Typically, a signal-to-background ratio of 3 is the acceptable cutoff for "good" LIBS data. In this case, the S/B ranged from 6 to 35 for a range of elemental concentrations. The actual elemental concentrations are proprietary to PPG, so general ranges are listed in the table.

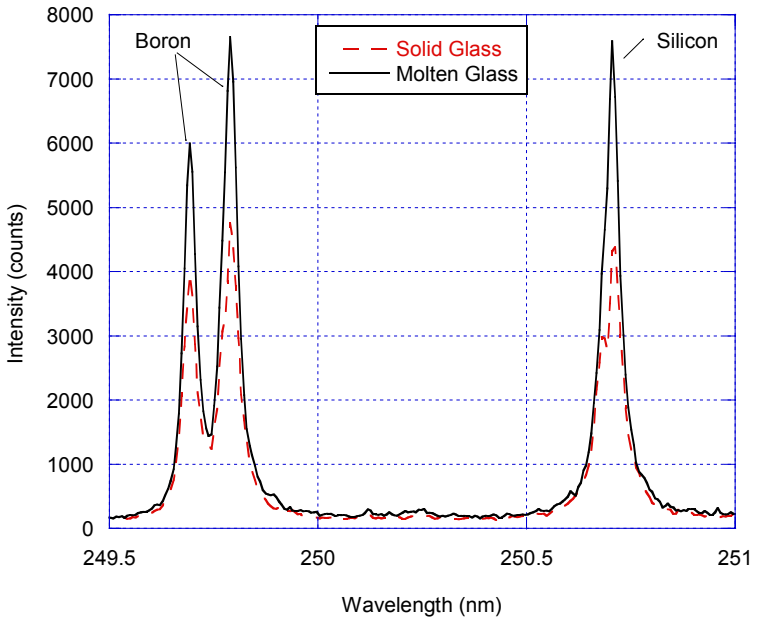

Figure 10 - Comparison of LIBS Spectra from Solid and Molten Glass

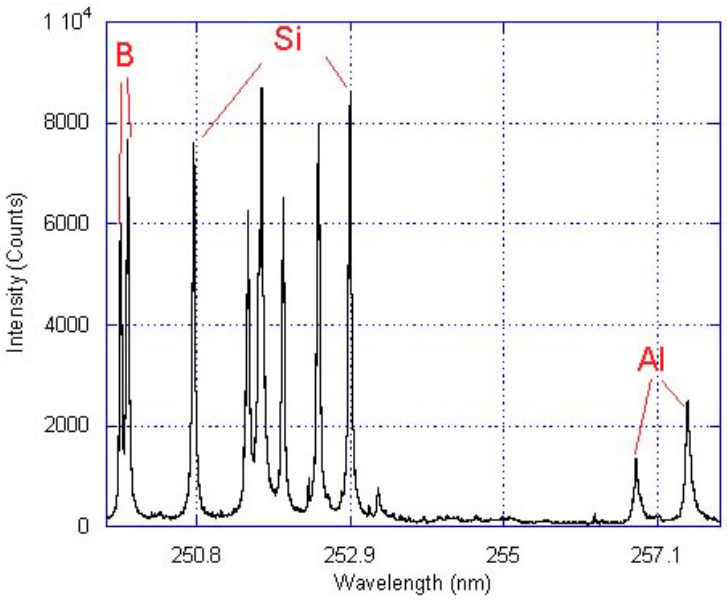

Figure 11 - LIBS Emission Lines from B, Si and Al in Molten Fiberglass

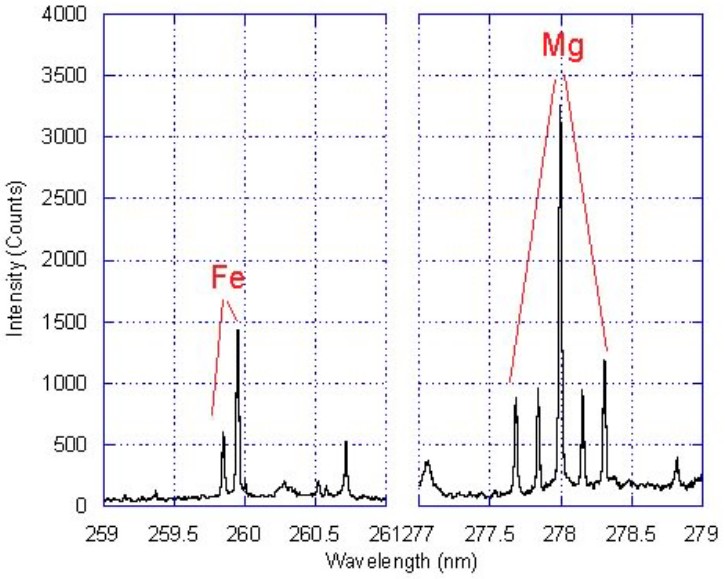

Figure 12 - LIBS Atomic Emission Lines from Fe and Mg from Molten Fiberglass

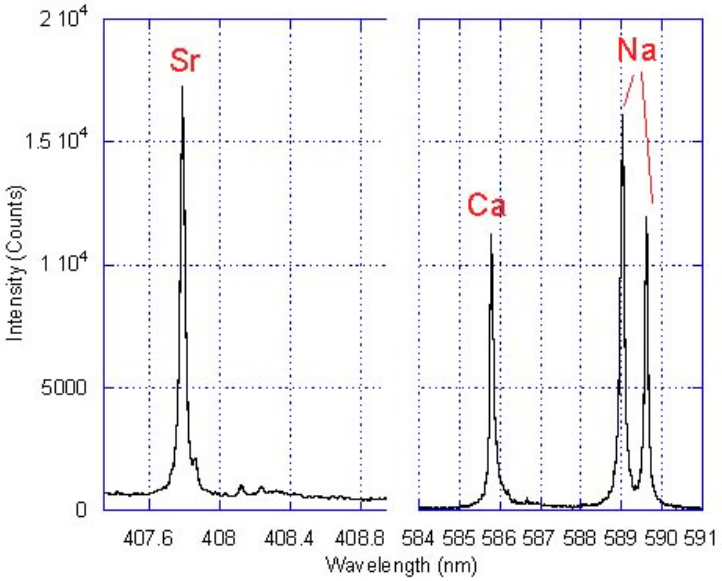

Figure 13 - LIBS Atomic Emission Lines from Sr, Ca and Na from Molten Fiberglass

Table 2 - Signal to Background for Characteristic LIBS Peaks

Element	S/B	Amount
B	31.6	Minor
Si	34	Major
Al	10	Major
Fe	6	Small
Mg	13	Minor
Sr	35	Small
Ca	22	Major
Na	30	Minor

Major - >5 wt%, Minor 0.5 wt%-5 wt%, Small - <0.5 wt%

The excellent signal-to-background observed through the LIBS sensor suggests that the peaks studied could potentially be used in our calibrationless algorithm to determine the elemental concentrations. An earlier test was conducted in ERCo's laboratory in which glass was melted in a small crucible in our laboratory furnace. The crucible of molten glass was then removed from the furnace and placed on an optical bench under a laser-focusing lens for LIBS analysis of the molten surface. Samples of the glass before and after melting were sent to an independent laboratory for chemical analysis. The results are compared to ERCo's C-LESS^{TM} analysis of the LIBS spectra in Table 3.

The C-LESS^{TM} results fell within the range of the certified measurements for all but a few elements. The difference between the LIBS and certified measurements for Mg and Ba can potentially be attributed to the fact that the LIBS measurements were restricted to the surface of the molten glass in air, rather than in an inert gas environment. It should also be noted that this analysis was conducted with a preliminary version of the C-

LESS™ algorithm, which had not been fully optimized for use with glass. Nonetheless, the results are very encouraging and we are confident that, with additional development, the C-LESS™ technique can be adapted for use with the LIBS molten glass sensor.

Table 3 - Elemental Analysis of Molten Glass

Element	Lab Analysis Before Melting	Lab Analysis After Melting	LIBS Analysis	Result	% Outside Range
Si	62.96	61.51	61.01	Good	0.81
Na	29.67	20.72	24.9	Good	
Ca	5.36	3.46	4.8	Good	
Mg	2.71	2.42	2.85	Out	5.2
Ba	4.66	0	4.79	Out	2.8
Fe	0.04	0.02	0.02	Good	
Sr	0.04	0	0.03	Good	
Mn	0.1	0	0.08	Good	

5 LARGE-SCALE FURNACE DEVELOPMENT AND TESTING

ERCo contracted SenCer Inc. of Penn Yan, NY to develop and construct a large-scale, electric furnace for use in this project. A photograph of the completed furnace is shown in Figure 14. The furnace is designed to melt over 2000 in^3 of glass and hold it at a maximum continuous operating temperature of 3000°F (1649 °C) with the water-cooled molten glass LIBS sensor in place. The hot zone is 24"x 24"x 20"and is lined with and supported by Ultra-Temp™ ceramic plates and structural members. Ultra-Temp™ is a state-of-the-art material that has been demonstrated to maintain its mechanical properties at temperatures in excess of 3250°F (1788 °C). In order to minimize creep, the roof of the furnace is reinforced with hexoloy™ (pure, sintered silicon-carbide) crossbeams. The outer kiln is insulated with layers of high-temperature alumina fiberboard totaling four inches in thickness and is supported by a solid aluminum and steel frame. Material is loaded from the bottom via a motor-driven dual-screw 1000 lb lift, as shown in Figure 15.

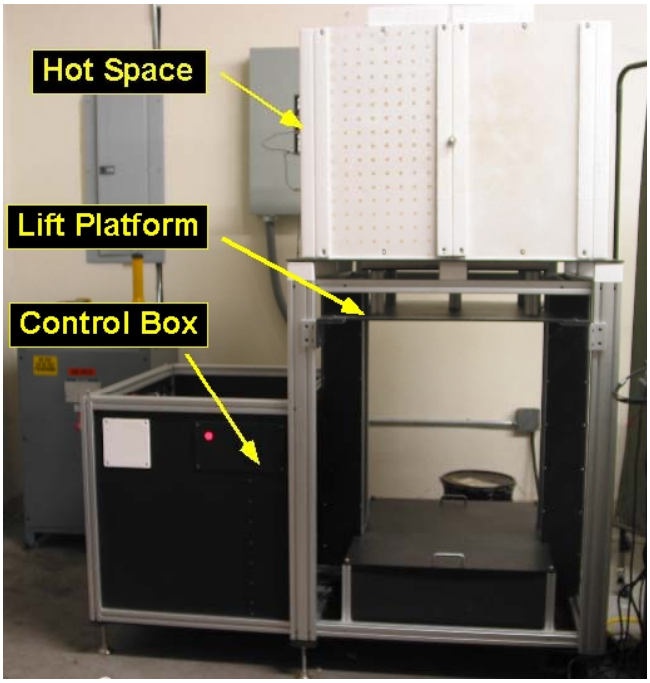

Figure 14 - Photograph of High Temperature Kiln

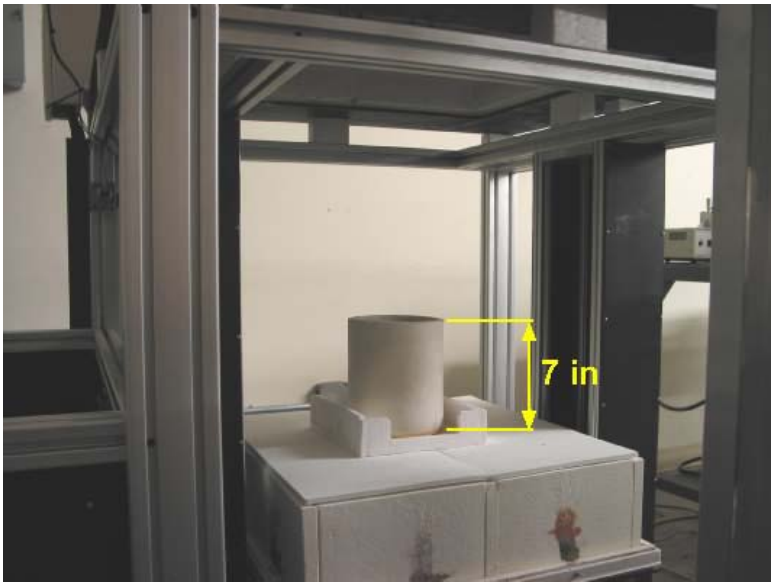

Figure 15 - Crucible Before Loading Into Furnace (from bottom)

The kiln is heated by twelve molybdenum disilicide elements connected in series as shown in Figure 16. Ultra-Temp™ cover plates (four of which are shown in the figure) shield the electrical connections to protect the operator and avoid interactions with the sensor, which will be lowered into the kiln through the central hole in the furnace lid (shown covered by a removable plug). All temperature and power parameters are controlled and monitored from a PC workstation. The user interface is shown in Figure 17.

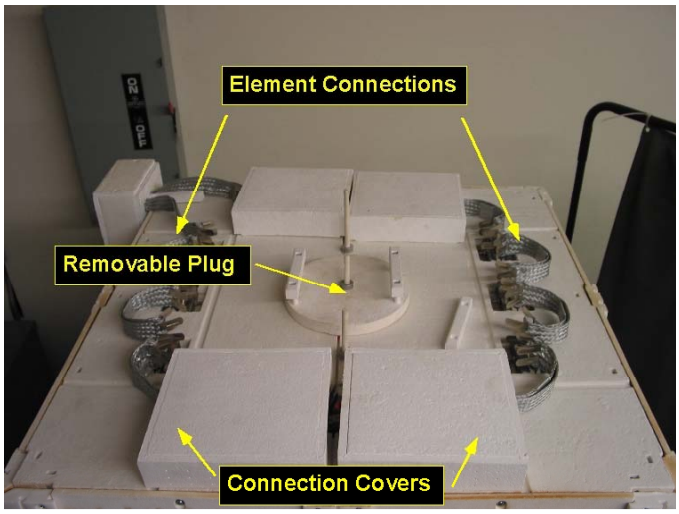

Figure 16 - Top View of Connections and Hot Space

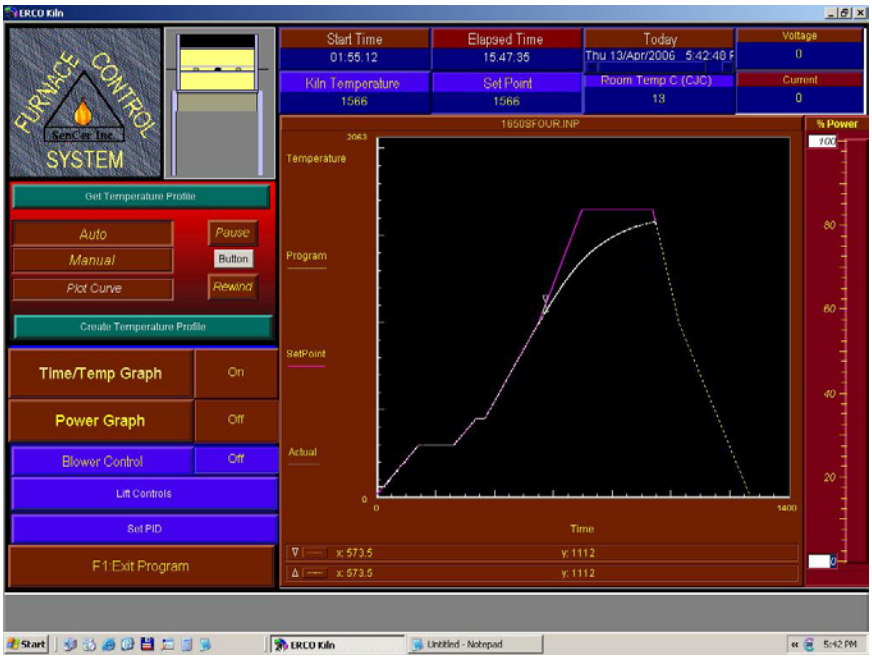

Figure 17 - Furnace Operator Control Screen

The furnace was tested and evaluated using different heating profiles and electrical configurations between the line power, the transformer, and the furnace SCR controller. The most-stable configuration was with a step-down transformer (208VAC/120VAC) between the line power and the furnace controls.

6 CONCLUSIONS

A LIBS sensor for making elemental concentration measurements in molten glass was designed, fabricated, and used to collect atomic emission spectra from the surface of molten fiberglass. This is the first time, to our knowledge, that such information has been collected directly from a glass melt. The following conclusions may be drawn from the test results:

- Atomic emission peaks with excellent signal-to-background ratios (>3) were detected through the LIBS sensor from the surface of molten fiberglass. The major elements of interest, including Al, B, Ca, Fe, Mg, Na, Si, and Sr were detected.
- The quality of the LIBS spectra collected from molten glass was comparable to spectra collected from solid glass. In a separate project, we have generated calibration curves for elements in solid fiberglass using LIBS, and have used these curves to measure elemental concentrations. This strongly suggests that the LIBS molten glass sensor can be used to measure elemental concentrations in molten glass by applying the same techniques.
- The strength of the LIBS spectra collected from the glass melt also opens the possibility that elemental concentrations might be obtained using a version of ERCo's calibrationless (C-LESS^{TM}) technique, currently applied to molten aluminum. Development of this technique for glass, while promising, was beyond the scope of this project.
- The water-cooling system is sufficient to maintain the outer probe surface and the optics at safe operating temperatures, even when immersed in molten glass.
- A large-scale glass-melting furnace was installed and evaluated in ERCo's laboratory.

7 TECHNOLOGY TRANSFER

Four papers were given that discussed the concept developed in this final report:

- De Saro, R., "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
- De Saro, R., Weisberg, A., Craparo, J., "In Situ, Real Time Measurement of Aluminum, Steel, and Glass Melt Chemistries Using Laser Induced Breakdown Spectroscopy", 2005 ACEEE Summer Study on Energy Efficiency in Industry, West Point, NY July 19-22, 2005
- Craparo, J.C, A. Weisberg, and R. De Saro, "Measurements of Batch and Cullet Using Laser Induced Breakdown Spectroscopy", *66th Conference on Glass Problems*, W.M. Kriven, Ed., pp. 105-118, John Wiley and Sons, NJ, 2006.
- Weisberg, A., J. Craparo, W.E. Engisch, and R. De Saro, "In-Situ LIBS Measurements of Molten Glass Below the Melt Line Using ERCo's Molten Glass LIBS Probe", Presented at the LIBS 2006 Conference, Montreal Ca, Sept. 5-8, 2006.

Website:

http://er-co.com/news.htm

8 APPENDIX A. FINAL TASK SCHEDULE

Final Task Schedule

Task Number	Task Description	Task Completion Date				Progress Notes
		Original Planned	Revised Planned	Actual	Percent Complete	
1	Design and Fabricate Prototype Probe	2/1/06		2/1/06	100%	Completed
2	Test Plan and Testing with Textile Fibers	8/1/06		8/1/06	100%	Completed
3	Analyze Data From Task 2	8/1/06		8/1/06	100%	Completed
4	Testing with Insulation Fiberglass and Container Glass	4/1/07		4/1/07	100%	Completed. Container glass was not tested as the results from the other glasses were sufficient to develop the instrument.
5	Analyze Data from Task 4	4/1/07		4/1/07	100%	Completed
6	Design Commercial System	5/1/07		5/1/07	100%	Completed
7	Update Business Plan	5/31/07		5/31/07	100%	Completed
8	Program Management and Reporting	7/31/07		7/31/07	100%	Completed

9 APPENDIX B. FINAL SPENDING SCHEDULE

Final Spending Schedule

Project Period: 8/1/05 to 7/31/07

Task	Approved Budget	Final Project Expenditures
Task 1 Design and Fabricate Prototype Probe	30,000	30,000
Task 2 Test Plan and Testing with Textile Fibers	90,000	90,000
Task 3 Analyze Data From Task 2	10,000	10,000
Task 4 Testing with Insulation Fiberglass and Container Glass	60,000	60,000
Task 5 Analyze Data from Task 4	10,000	10,000
Task 6 Design Commercial System	15,000	15,000
Task 7 Update Business Plan	10,000	10,000
Task 8 Project Management	25,000	25,000
Total	250,000	250,000
DOE Share	250,000	250,000
Cost Share	-	

10 APPENDIX C – FINAL COST SHARE CONTRIBUTIONS

Not applicable.

11 APPENDIX D. ENERGY SAVINGS METRICS

One Unit of Proposed Technology
A unit is a glass tank operating at 250 tons per day.

One Unit of Current Technology
A unit is a glass tank, identical to the above, but with a LIBS Sensor measuring the melt chemistry.

Energy Savings Metrics

Type of Energy Used	A	B	C=A-B	D	E=CxD
	Current Technology (MMBtu / yr / unit)	Proposed Technology (MMBtu / yr / unit)	Energy Savings (MMBtu / yr / unit)	Estimated Number of Units in U.S. by 2010 (units)	Energy Savings by 2010 (MMBtu / yr)
Oil / Gasoline					
Natural Gas	612,500	520,625	91,875	10	918,750
Coal					
Electricity (@ 10,500 Btu / kWh)					
Other Energy 1 (Explain)					
Other Energy 2 (Explain)					
Other Energy …n (Explain)					
Total Per Unit	612,500	520,625	91,875	10	918,750

Discussion of Energy Savings
There are often glass composition problems due to incorrect chemistry in the melt. The LIBS Sensor will identify these problems and allow furnace operators to correct their operation to avoid the product loss. This would allow the industry to avoid the 15% product loss which translates into the above energy savings.