ADMINISTRATIVE INFORMATION

1. **Project Name:** Measurement and Control of Glass Feedstocks

2. **Lead Organization:** Energy Research Company (ERCo)
   2571-A Arthur Kill Rd.
   Staten Island, NY 10309

3. **Principal Investigator:** Arel Weisberg, Ph.D.
   Ph: (718) 608-0935
   Fx: (718) 608-0933
   aweisberg@er-co.com

4. **Project Partners:** PPG Industries: Chi Tang, Ph.D. ctang@ppg.com
   Fenton Art Glass: Tom Fenton tkfenton@fentonartglass.com

5. **Date Project Initiated:** April 16, 2001

6. **Expected Completion Date:** April 15, 2005

PROJECT RATIONALE AND STRATEGY

7. **Project Objective:** ERCo will develop a laser induced breakdown spectroscopy (LIBS) based sensor for glass feedstock monitoring. The sensor will improve quality control on the material entering the glass melter, which will translate to improved energy and operating efficiencies.

   The dependence of production efficiency on feedstock composition has long been theorized, but is impossible to measure in a practical manner . ERCo's feedstock sensor is the enabling technology for quantitatively measuring the effects of fluctuating feedstock composition, and thereby opening the opportunity for controlling the glass production process in response to measured feedstock fluctuations.

8. **Technical Barrier(s) Being Addressed:** The two key technical barriers in this project are applying LIBS to measure wide range of elemental concentrations simultaneously in mineral powders, and "hardening" LIBS technology for industrial use. The issues involved include developing a simple user interface for the technology, reducing maintenance requirements, and ensuring safe operation.

9. **Project Pathway:** ERCo has addressed the issue of simultaneous monitoring of a wide range of elemental concentrations through innovative software and state-of-the-art instrumentation. By blending the best suited hardware on the market with ERCo's signal processing and LIBS expertise, successful monitoring of mineral composition has been achieved in the laboratory.

   Concurrent with this effort, ERCo has been addressing the issue of ruggedizing the sensor components. The sensor design incorporates only low maintenance equipment. Complementing this equipment is a custom software package enabling non-specialist plant employees to perform LIBS measurements using a point-and-click interface.

10. **Critical Technical Metrics:** The goal for the project, based upon discussions with our industrial partner PPG Industries, is to measure concentrations of elements in ulexite to within 5% on a relative basis, or 0.05% on an absolute basis, whichever is greater. For example, if an element is present at

1.0%, then the target is for the senor to read between 0.95% and 1.05%. If an element is present at 0.1%, then the target is for the sensor to read between 0.05% and 0.15%.

PPG will correlate the sensor's reported elemental concentrations with plant output and efficiency.

PROJECT PLANS AND PROGRESS

11. **Past Accomplishments:** Energy Research Company (ERCo) is developing an on-line sensor for controlling the quality of glass feedstocks, both batch and cullet. In the case of batch, the sensor can determine whether or not the batch was formulated accurately, and serve as part of a feedback loop in the plant to control glass quality. In the case of cullet feedstocks, the sensor can serve as part of a system to sort cullet by color and ensure that it is free of contaminants.

    The sensor is built around Laser Induced Breakdown Spectroscopy (LIBS) technology. LIBS utilizes a highly concentrated laser pulse to rapidly vaporize and ionize a small amount of the material being studied. As the resulting plasma cools it radiates light at specific wavelengths corresponding to the elemental constituents (e.g. silicon, aluminum, iron) of the material. The strengths of the emissions correlate to the concentrations of each of the elemental constituents. This technology has been successfully demonstrated in ERCo's LIBS laboratory for both batch analysis and cullet sorting. In the upcoming year, a batch sensor for installation at PPG's Chester, S.C. plant will occur in June.

    Among the most important project accomplishments has been the development of software for analysis of the LIBS signal that is unique to ERCo. In the case of batch the software provides elemental concentrations without utilizing conventional calibration curves. The software's proprietary calibrationless (C-LESS™) method frees the industrial user from having to calibrate and re-calibrate the instrument using expensive material standards. As a result, the system is made more robust, it requires less maintenance, and is simpler to operate. A plant employee with no training can therefore operate the system.

    In the case of cullet, ERCo's software allows the system to identify cullet by color and screen out cullet stream contaminants using only one LIBS spark per cullet stream particle. This capability is crucial to high speed sorting. In addition to requiring only one spark, the algorithm is amenable to high speed operation on commonly available computer hardware. The cullet sorting results were reported last year.

    Batch Measurements

    Samples for batch ingredients were provided by PPG Fiber Glass for evaluation of ERCo's LIBS batch sensor concept. We took quantitative measurements from clay, silica, and limestone, samples provided by PPG with ERCo's C-LESS™ method. These results were presented last year, and are available in prior reports. Representative results from limestone are shown below. Because the actual concentrations are proprietary PPG data, all the results are shown as a percent error.

    We report the error in major constituents on the traditional relative basis:

$$\%Error = \frac{|\text{Measurement} - \text{Reported}|}{\text{Reported}} \times 100\%,$$

    while for minor constituents we report the absolute percent error:

$$\%Error = \left|\text{Measurement\%} - \text{Reported\%}\right|,$$

reflecting the accuracy targets mentioned above in Section 10.

Table 1: Results of Limestone Analysis as Percent Error (relative) – Major Constituents

Element	Run A	Run B	Run C	Run D	Run E	Average
C	1.28%	0.62%	1.54%	1.59%	0.09%	**1.02%**
Ca	0.26%	0.09%	0.57%	0.41%	0.18%	**0.30%**

Table 2: Results of Limestone Analysis as Percent Error (absolute) – Minor Constituents

Element	Run A	Run B	Run C	Run D	Run E	Average
Mg	0.00%	0.00%	0.01%	0.01%	0.00%	**0.00%**
Al	0.01%	0.01%	0.00%	0.01%	0.01%	**0.01%**
Si	0.08%	0.07%	0.10%	0.10%	0.13%	**0.10%**
Fe	0.00%	0.00%	0.01%	0.04%	0.02%	**0.01%**

The results above were achieved using ERCo's C-LESS™ LIBS software. A second approach, conventional calibration curves, were also applied to the data. During the fall of 2003, PPG decided to focus the program on measurement of the mineral ulexite. Ulexite samples were sent from the PPG Fiber Glass plant in Chester, SC to ERCo for laboratory testing in December. Ulexite is a complex raw material, containing oxides of at least 8 elements: B, Ca, Mg, Si, Na, Al, Fe, and Sr. These elements are present in widely varying concentration ranges, from hundredths of a percent to upwards of 30%. Concentration measurements using the calibration curves are shown below in Table 3.

Table 3: Ulexite Measurements from 6 PPG Samples
Yellow: Relative Error in Major Constituents Gray: Absolute Error in Minor Constituents

Sample	B	Ca	Na	Mg	Si	Al	Sr	Fe
A	1.03	0.04	1.34	0.77	0.59	0.02	0.02	0.00
B	0.25	0.32	3.10	4.77	7.23	0.01	0.06	0.00
C	0.8	0.47	1.45	1.38	5.58	0.02	0.12	0.00
D	0.69	0.30	0.54	2.60	2.50	0.02	0.08	0.00
E	0.49	0.04	5.08	4.97	8.32	0.01	0.05	0.00
F	0.24	0.41	1.77	3.81	4.61	0.01	0.03	0.00
Average Error %	**0.58**	**0.26**	**2.21**	**3.05**	**4.81**	**0.01**	**0.06**	**0.00**
Max Error %	**1.03**	**0.47**	**5.08**	**4.97**	**8.32**	**0.02**	**0.12**	**0.00**
Min Error %	**0.24**	**0.04**	**0.54**	**0.77**	**0.59**	**0.01**	**0.02**	**0.00**

Relative errors for the major elements are under 5% for virtually all the measurements. In the cases of boron and calcium the percentage errors are mostly well under 1%. In the cases of the minor elements, the absolute errors are on the order of a few hundredths of a percent, with essentially perfect correlation for iron (results are rounded to the nearest 0.01%).

Automated LIBS Operation

ERCo has developed a hardware and software package to enable automated LIBS analysis in a glass plant. The hardware, which fits on a rolling cart, requires only minimal quarterly maintenance. ERCo's LIBS analysis software for Windows is completely automated. As described in prior reports, when the operator clicks on an on-screen button in ERCo's software the entire analysis is performed within a few minutes. This significant development renders LIBS suitable for industrial applications where a dedicated scientist is not available.

PPG Selects Host Site

PPG selected its Chester, SC fiberglass plant as the location for the LIBS batch analyzer installation. In addition to this decision, PPG determined that the LIBS batch analyzer would be of most use on individual raw materials rather than on mixed batch. By monitoring the individual raw materials, the source of any fluctuations could be immediately traced to the raw material at fault. As mentioned above, the mineral ulexite will be the first material tested.

12. **Future Plans:** During the second quarter of 2004, ERCo will test the LIBS sensor at PPG's Chester plant. Testing and sensor improvements will continue until the end of the program in April of 2005.

13. **Project Changes:** PPG requested that the sensor be able to analyze multiple materials that are widely distributed in the plant. In order to accommodate their request, the sensor design was changed to one in which a technician will place a small sample (a few grams) of material at a time into the sensor for off-line testing. By having the sensor off-line, rather than attached to one of the plant's pipelines of material, minerals from different areas of the plant can be tested in the sensor. For example, PPG requested that the second material tested in the sensor be limestone from the plant's exhaust scrubber. Analysis time is only a few minutes and automatic in the sensor, therefore PPG can test as many samples from around the plant as necessary with minimal effort.

14. **Commercialization Potential, Plans, and Activities:** ERCo is pursuing licensing agreements with companies that market equipment to glass and other industries with powdered feedstock, such as the coal power industry. ERCo serve as an OEM to the marketing companies.

15. **Patents, Publications, Presentations:** ERCo has one LIBS related patent pending. Results on applying LIBS to powdered coal feedstocks, using essentially the same technology as for powdered glass feedstocks, were presented at the 2003 Pittsburgh Coal Conference and the 2004 Clearwater Coal Conference.