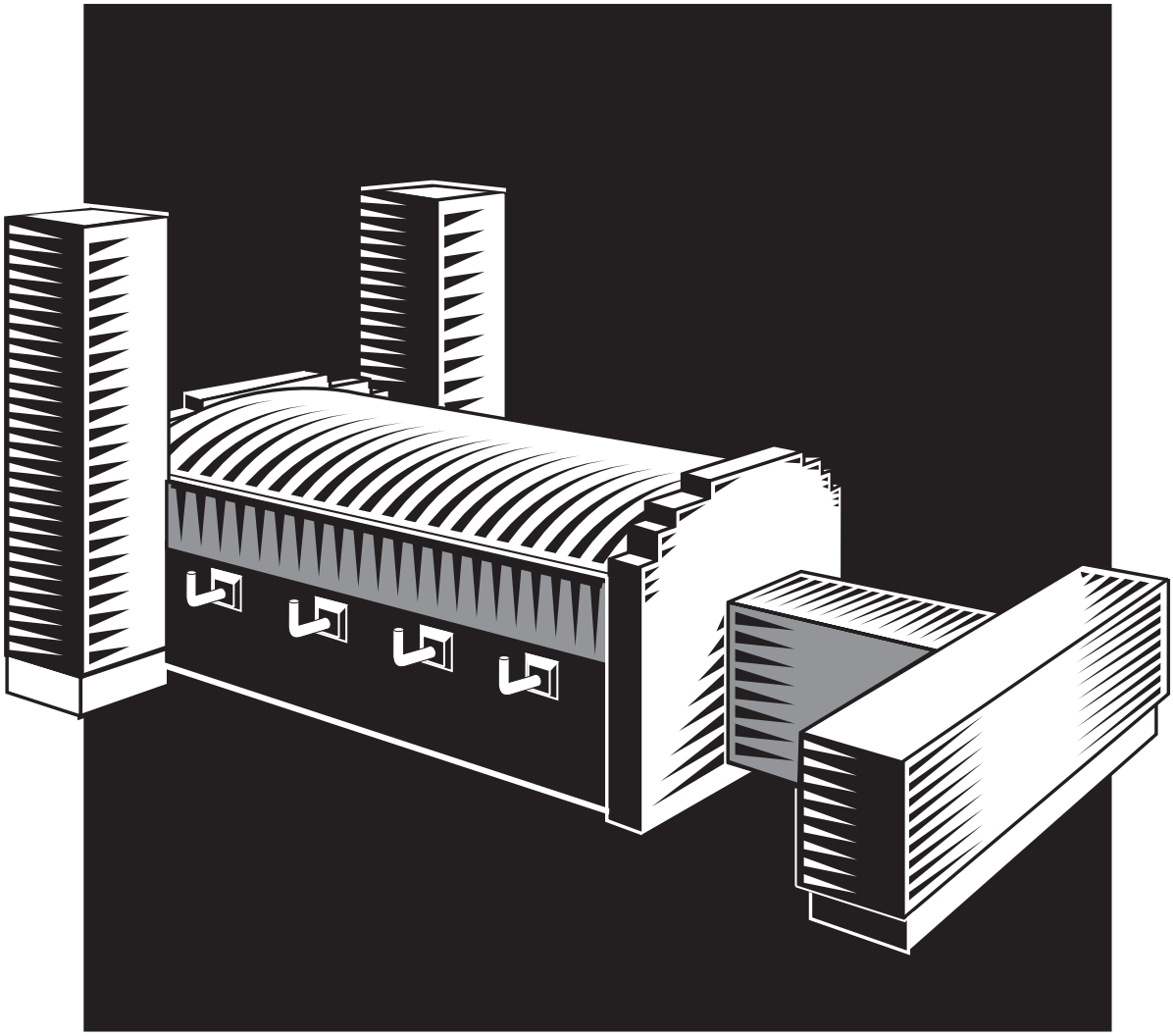
Glass Industry of the Future

Quarterly Status Reports

As of December 31, 2003



U.S. DEPARTMENT OF ENERGY

02-GA50113-03

Glass

Industry of the Future

Quarterly Status Reports

As of December 31, 2003

Contacts

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The Glass Manufacturing Industry Council (ID14318, CPS#01034) is instrumental in coordinating with contractors and providing the quarterly reports on their web site. The Glass Manufacturing Industry Council (GMIC) has accomplished a number of significant milestones towards the ultimate goal of reaching long-term “Vision” objectives.

Glass Projects

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ID14030, CPS#01609

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Measurement and Control of Glass Feedstocks

Weisberg: Energy Research Company

ID14030, CPS#01609

The quarterly report for the period ending December 2003 had to be late. The following is the most recent report as of February 10, 2004:

QUARTERLY PROGRESS REPORT

Project Title: Measurement and Control of Glass Feedstocks

Covering Period: July 1, 2003 through September 30, 2003

Date of Report: October 29, 2003

Recipient: Energy Research Company

Award Number: DE-FC36-01ID14030

Subcontractors: Oak Ridge National Laboratory

Other Partners: PPG Industries
Fenton Art Glass

Contact(s): Arel Weisberg, Ph.D.
(718) 608-0935
aweisberg@er-co.com

Project Team: DOE-HQ Contact: Elliot Levine
Contract Specialists: Brad Ring, Beth Dwyer

Project Objective: 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.

Background: The Glass Industry Technology Roadmap[1] 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." ERCo's LIBS sensor addresses this need by giving plant operators critical knowledge of their batch composition. In plants where cullet is used in glass production, the LIBS sensor can provide color sorted cullet free of contaminants, including those contaminants that are not detectable using current optical based color sorters.

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

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, designs of prototype sensors for installation at the program's industrial partners will be developed.

Status:

1. **Executive Summary**

Following last quarter's selection of PPG's Chester, SC plant for the installation of the LIBS sensor, Arel Weisberg of ERCo visited the plant in July. During this meeting a timeline was developed for the installation and testing of the LIBS batch sensor in the plant.

In September, ERCo gave an updated progress report at the OIT Glass Industry annual project review meeting in Boulder, CO.

Just after the close of the quarter, PPG selected ulexite as the mineral that will be monitored in the Chester plant by the LIBS sensor. Delivery of ulexite samples to ERCo for testing will take place in October and November.

2. **ERCo Visit to Chester, SC PPG Fiber Glass Plant**

Arel Weisberg visited the PPG Fiber Glass plant in Chester, SC at the end of July. The meeting was attended by the plant management and Cheryl Richards from PPG's Pittsburgh offices. After giving a presentation on the LIBS program and answering questions from the attendees, Cheryl Richards presented to the plant management her assessment of how the LIBS batch sensor can improve their operations.

Following this meeting, Dr. Weisberg was taken on a tour of the plant and potential installation locations for the LIBS batch sensor were discussed.

At the close of the visit, the plant's management emphasized their interest in the LIBS batch sensor, and in installing a full scale sensor for analyzing one component of their batch on-line. The selection of ulexite as the target material came at the end of the current reporting period.

Preliminary analyses of ulexite were undertaken in ERCo's LIBS facility during this quarter. This work will continue in the upcoming quarter with the new samples that will be provided by PPG.

3. **DOE OIT Glass Industry Annual Project Review**

In September, ERCo gave a summary of the progress made in this program during the past year at the annual project review in Golden, CO. A copy of the presentation is included with this report.

Plans for Next Quarter:

Ulexite samples from PPG are scheduled to arrive at ERCo's LIBS laboratory during the upcoming quarter. Results from analyses of these samples will be reported in the next quarterly progress report.

Patents: N/A

Publications/Presentations: The presentation given at the project review meeting in Golden, CO is included with this report.

Milestone Status Table:

ID Number	Task / Milestone Description	Planned Completion	Actual Completion	Comments
1	Laboratory Development			
1.1	Facility Modification	9/30/01	9/30/01	
1.2	Testing	3/31/02	2/28/02	
1.3	Initial Software Development	3/31/02	3/31/02	
1.4	Performance Evaluation	3/31/02	3/31/02	
2	Sensor Fabrication			
2.1	Facility Construction	9/30/02	8/31/02	
2.2	LIBS Testing	8/31/03		Pending PPG material
2.3	Modifications to PPG Facility	12/31/03		
2.4	Procure System	6/30/04		
3	Sensor Testing			
3.1	Testing at PPG	2/28/05		
3.2	System Integration	12/31/04		

Budget Data (as of 3/31/02):

			Approved Spending Plan			Actual Spent to Date		
Phase / Budget Period			DOE Amount	Cost Share	Total	DOE Amount	Cost Share	Total
	From	To						
Year 1	4/01	12/01	423,178	181,501	604,679	47,184.00		47,184.00
Year 2	1/02	12/02	509,525	710,613	1,220,138	361,692.58	200,316.42	562,009.00
Year 3	1/03	12/03	506,110	717,688	1,223,798	201,630.47	303,821.00	505,451.47
Year 4								
Year 5								
		Totals	1,438,813	1,609,802	3,048,615	610,507.05	504,137.42	1,114,644.47

Improvement of Performance and Yield of Glass Fiber Drawing Technology

Sanger: State of Ohio

ID14347, CPS#none

QUARTERLY PROGRESS REPORT

Project Title: Improvement of Performance and Yield of Glass Fiber Drawing Technology

Covering Period: October 1, 2003 through December 31, 2003

Date of Report: January 22, 2004

Recipient: State of Ohio, Office of Energy Efficiency
77 S. High Street
Columbus, OH 43215-6108

Award Number: DE-FC07-02ID14347

Subcontractors: Cleveland State University

Other Partners: PPG Industries Inc
Schott Glas
Johns Manville
U.S. Borax

Contact(s): Dr. Phillip A. Sanger -Principal Investigator
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Project Team:

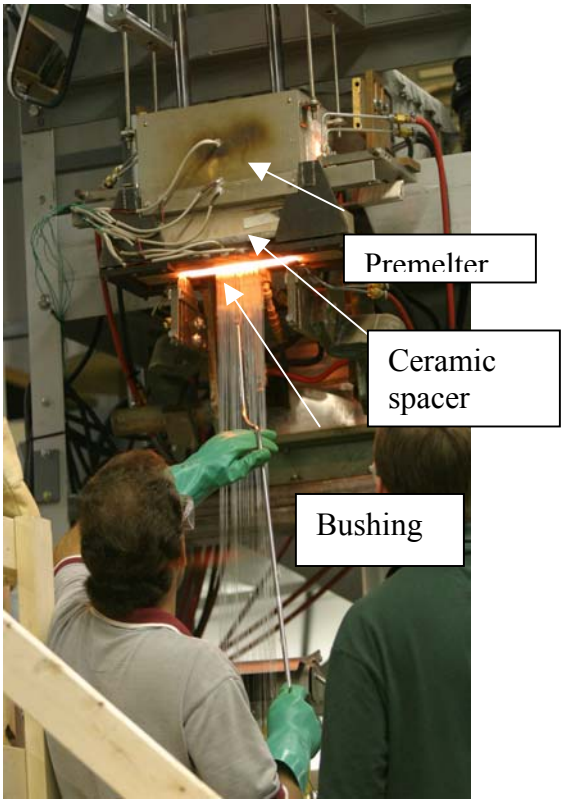
DOE-HQ Team Leader:	Elliott Levine
DOE Regional Team Leader:	Brian Olsen
DOE Project Manager:	Glenn Doyle
DOE Contract Specialist:	Tom Reynolds

Project Objective: Investigate the basic science of continuous glass fiber drawing and use that information to improve the drawing process: 1) demonstrate reduced break frequency on a state of the art fiber-drawing machine from 1 break per hour to 1 break per 4 hours, 2) reduce fiber diameter variation, 3) drive toward six-sigma* quality through process control and computer simulation.

Background: Fiber breakage is the single most important process variable in the drawing of continuous glass fibers limiting fiber quality and production throughput and resulting in over 500 10^9 BTU of energy wasted annually. Continuous glass fiber drawing in "state of the

art" glass industrial facilities is accomplished in the simultaneous drawing of up to 5000 filaments from a single bushing. The perturbation caused by the breaking of one filament which typically occurs once per hour quickly propagates toward disruption of all 5000 filaments. During the recovery time of 5-10 minutes, the glass is continuing to ooze through the bushing holes. Over 67,000 tons of unrecyclable glass annually and all the energy invested in the melting and forming of this wasted glass is lost. To address this problem, this project will apply six sigma quality methodology combined with fundamental glass science to reduce breakage, increase throughput and improve the quality of glass fiber.

Status: The second generation of bushing and melter, that had been installed and made operational last quarter, had to be modified this quarter due to a disintegrating ceramic block which contaminated the molten glass. A modified block was installed and the experimental program is now back in full swing. All the conventional diagnostics are up and running. Calibration of the in line fiber diameter scanner has been completed. Data collected at our partner's sites has enabled breakthroughs in model validation. Validation on our drawing tower will be completed in the coming quarter.



The ceramic spacer which was disintegrating was replaced with a Pt covered spacer.

Task 1 Build and Install Glass Fiber Drawing Tower

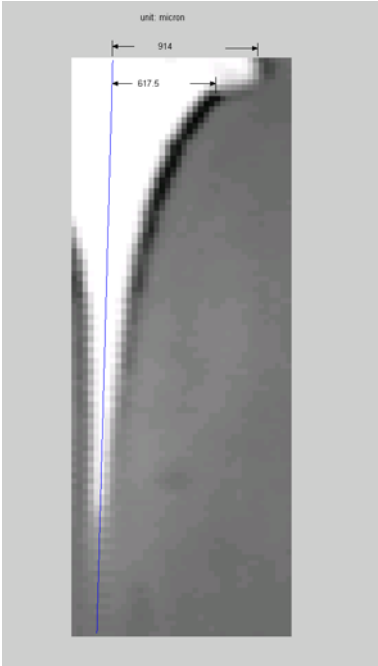
This quarter has seen several setbacks to our research plan from which we have recovered. During the early stages of operating the second generation drawing tower, excessive contamination in the glass appeared which resulted in plugged tips and fiber breakage. Samples of these white particles were taken and sent to our industrial partners for analysis. This analysis identified the source to be disintegration of the ceramic spacer block that separates the premelter from the bushing. While bare ceramic blocks of this type are common in glass production, this ceramic does not tolerate our operational mode of frequent thermal cycling. The solution was to replace the bare ceramic with a platinum covering preventing the glass stream from coming in direct contact with the ceramic. PPG produced a platinum covered block which was installed just before Xmas.

While this problem was being diagnosed, our system experienced a major failure of the power system. After evaluation of the event and reviewing the power drive system, an alternative configuration was developed that maintained full functionality without incurring significant cost. As of December 23, the drawing tower was fully functional.

Task 2 Develop diagnostic Instrumentation

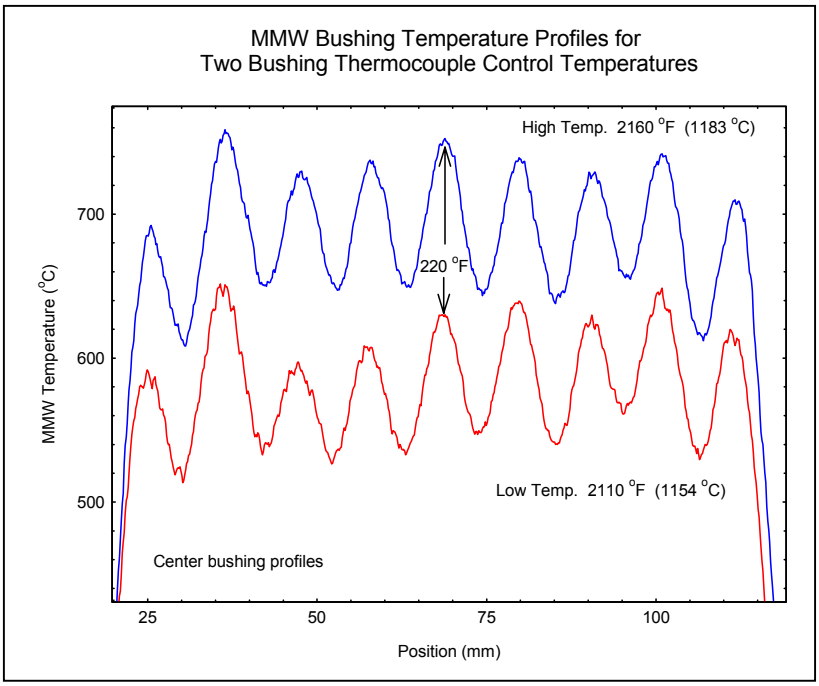
With the exception of the in line continuous diameter measure, our suite of diagnostic instrumentation is fully operational. The nuclear level meter has been installed and was incorporated into our premelter control system to maintain a constant glass head. Continuous laser speed measurement is operational. The two dimensional positioning platform for continuous pyrometry is operational. And continuous cone measurement with a one dimensional scanning ability across the front row of tips is operational.

Progress continues to be made in the development of the continuous fiber diameter measurement technique. The next step in the development was to produce glass samples that could be used for setup. Samples approximately 100 microns in diameters were made and measure optically. Agreement with the optical microscopic measurements was verified within 2% using illumination coming from the back side of the filaments. In the next phase we will establish the accuracy that is possible with front reflective lighting.



Cone shape has been digitized and is being characterized continuously during running.

In collaboration with PNNL under a G+ project, we also completed a series of trials using mm-Wave radiation to measure bushing temperatures. It was proposed that, since the wavelength of this radiation is long, fibers would not be obstacles to the temperature measurement. In the figure below, a temperature profile using mm wave radiation is shown. The nine peaks correspond to the nine double rows of tips. The trials not only verified that the fibers did not interfere with the measurement but also provided evidence that neither did the fins since the temperatures remained unchanged with and without the fins. The relative sensitivity of the



measurement to a deliberately applied temperature change of 50°F was excellent. Note: due to the short duration of the testing, no effort was made to obtain absolute calibration of the temperature. Several improvements were identified that would improve the efficacy of the technique and could be subject of subsequent proposals.

Task 3 Develop simulation models

Breakthrough in the validation of the simulation models has opened up an intense period of investigation. Correlation between observed and predicted breakage rates has been observed. As predicted the key factor driving breakage is fiber stress. In simplistic terms, the fiber stress during drawing is determined by the shape of the glass cooling cone once the glass leaves the tip. The two principal process variables that determine the fiber stress are 1) the temperature of the glass entering the cone and 2) the cone cooling rate (due to the fins or tubes and to the air stream velocity). Short cones result in high stresses and thus high breakage. Short cones can come from cold glass which "starves" the cone or from a high cooling rate due to close fins or high air velocities. Controlling these variables are the key to controlling breakage. This logic has been validated using the data collected at our partners' sites. We will complete that validation on our drawing tower in the next quarter.

Task 4 Optimize Glass Drawing Process

The focus of process improvement and reduction of breakage is clearly on the cone: its measurement and its control. Two approaches are being presently used at our partners: fins and cooling tubes. Each has its advantages and disadvantages. During the next quarter we will be evaluating options for cooling improvement as well as exploring the use of our cone photographic diagnostics on the production floor.

Plans for Next Quarter:

Extensive running of the drawing tower over a broad range of operating conditions will be carried out to finalize the model validation. Some of the diagnostic instrumentation will be used at PPG to confirm their utility in actual production conditions. We expect to complete the development of the inline diameter measuring system and initiate trials on the CSU drawing tower. Different approaches to fiber cooling will be evaluated and an improved approach selected.

Patents: One provisional patent disclosure on the technique for measuring the dimensional characteristics of a fiber bundle.

Publications/Presentations:

- Presentation to DOE Glass Project Review in Oct 2002
- Presentation to DOE Glass Project Review in September 2003
- Presentation to the 2003 Glass Problems Conference, October 28, 2003

Milestone Status Table:

ID Number	Task / Milestone Description	Planned Completion	Actual Completion	Comments
1	**Build and Install Drawing Tower**			
1.1	Install tower	1/10/03	3/20/03	
1.2	Complete debug process	05/15/03	4/20/03	
1.3	Install new design of bushing	11/15/03	8/30/2003	
2	**Develop diagnostic instrumentation**			
2.1	Install IR and high speed photo system	03/01/03	9/10/2003	
2.2	Implement dimensional characterization process	09/15/03		Calibration verified, lighting techniques being evaluated
3	**Develop simulation models**			
3.1	Initiate testing of models	12/20/02	11/30/02	
3.2	Complete transfer function	04/16/03	4/30/03	
4	**Optimize process**			
4.1	Validation	07/30/03		Solid agreement between model and data observed. Final confirmation on CSU drawing tower in progress
4.2	Demonstrate improved process	03/15/04		
5	**Disseminate technology**			
5.1	Hold first tech transfer training session	10/30/02	10/30/02	
5.2	Start final partner implementation	05/30/04		
6	**Final Report**	08/30/04		

Budget Data (December 31, 2003):

			Approved Spending Plan			Actual Spent to Date		
Phase / Budget Period			DOE Amount	Cost Share	Total	DOE Amount	Cost Share	Total
	From	To						
Year 1	July 11, 2002	July 30, 2003	$554,014	$166,070	$720,084	$531,676	$255,952	$787,628
Year 2	August 1, 2003	July 30, 2003	$419,935	$122,525	$536,410	$134,055	$62,552	$196,603
Totals			$967,899	$288,595	$1,256,494	$665,731	$318,504	$984,231

Advanced Oxy-Fuel Front-End System

Owens Corning

GO13091, CPS#14233

Owens Corning has not accepted the FY03 negotiated award yet. Discussions are ongoing.

Energy Efficient Glass Melting: The Next Generation Melter

Gas Technology Institute

GO13092, CPS#14231

As of February 10, 2004, no status report is available on the Golden web site for this project.

High Intensity Plasma Glass Melter

Gonterman: Plasmelt

GO13093, CPS#14232

QUARTERLY PROGRESS REPORT

Project Title: High-Intensity Plasma Glass Melter

Covering Period: 11/01/03 to 12/31/03

Date of Report: January 23, 2004

Recipient: Plasmelt Glass Technologies, LLC
2845 29th Street, Boulder, CO 80301

Award Number: DE-FC36-03GO13093

Subcontractors: James K. Hayward
InnovaTech Services, Inc.
N.Sight Partners, LLC
Laboratory of Glass Properties, LLC
Tooley Design Services

Other Partners: Advanced Glassfiber Yarns
Johns Manville

Contact(s): J. Ronald Gonterman, 270-524-5110, Ron@plasmelt.com
Michael A. Weinstein, 303-530-2727, Mike@plasmelt.com

Project Team: Elliott Levine (DOE Glass Industry Liaison), Brad Ring (DOE Project Officer), Beth Dwyer (DOE Contract Officer), Matea McCray (DOE Technical Analyst)

Project Objective: Develop an efficient 500 lb / hr transferred arc plasma melting process that can produce high quality glass suitable for processing into a commercial article.

Background: The purpose of this project is to demonstrate the energy efficiency and reduced emissions that can be obtained through the use of a dual torch dc plasma transferred arc melting system. Plasmelt Glass Technologies, LLC was formed to solicit and execute the project, which will utilize a full-scale test melter system. The system is similar to the one that was originally constructed by Johns Manville, but Plasmelt has added significant improvements to the torch design and melter system. The original JM design has been shown to achieve melt rates 5 to 10 times faster than conventional gas or electric melting, with improved energy efficiency and reduced emissions. The Project began on 7/29/03.

Status: During this quarter, significant progress has been made. Several equipment systems have been engineered and installation is either complete or is underway in the Plasmelt Boulder Lab:

- Plasma Torches and Supporting Systems
- Water Chilling and Cooling Systems
- Melter Shell and Accessory Systems
- Vent Hood and Electrode Positioning Systems
- Mezzanine Structure

The glass batch delivery equipment and a dust collection system are currently being specified and the parts acquired. This equipment is on order with delivery expected in Boulder by the end of February.

Some equipment was contributed by Cost Share Partner—Johns Manville. This JM-pledged equipment, which was relocated from the JM facility in Littleton, Colorado to the new Boulder Lab, is currently undergoing refurbishment. Several missing or defective parts were identified and had to be replaced in order to render this equipment operational. From our inspections, it has become obvious that it is more cost effective to purchase a complete replacement batch feeder system than to purchase replacement parts for the JM contributed batch feeder unit. This replacement equipment is now on order. Since it is known that the accuracy, precision, and stability of the batch feed rate is critical to the overall success of the program, this alternative batching equipment MUST meet the required tolerances for delivering a consistent amount of batch per unit of time. As a result of this change in plans, we have incurred slight time delays and have expended unplanned capital. With the exception of the batch feeding and handling system, which may require an additional 2 to 3 weeks, all construction should be complete by 2/15/04.

The building electrical system to support the plasma arc melter requires a 1.2 MW capacity. The system was engineered by Xcel Energy in conjunction with Mike Weinstein. During subsequent meetings with the Electrical Inspector for the City of Boulder, significant changes were imposed that caused significant reengineering work by Xcel and Weinstein. Some of these requirements were over and above the electrical code requirements and added significant cost to the electrical upgrade for the building. Combined with our overly optimistic original estimate in both cost and timing, the electrical upgrade has become the single most high risk line item. The original estimated and budgeted amount of $50,000 and 12/31/03 have translated to more than $125,000 and an ECD of January 31, 2004. We will attempt to manage the cost overrun of the Electrical Upgrade Line Item within the total project funding level by making other tradeoff decisions.

In December, 2003 a goal alignment meeting was held in the Plasmelt Boulder Lab with the two Cost Share Partners. As a result of this meeting, we now have an understanding among all team members of the Year 1 plans as well as partner requests for additional priority work that is beyond the scope of the Year 1 Objectives and Plans. In the next Cost Share Partner/Plasmelt planning session, the Year 2 plans will be outlined. We expect to file for a Year 2 project extension in order to carry the Project beyond the first anniversary of July, 2004.

A Market Study, to be conducted by Gabe Tincher, is now underway. The scope of work for this Study includes the identification of glass industry segments and companies that will find economic advantage by using the attributes of the plasma melting system. In addition to the Market Study, a technical and economic analysis (TEA) is being performed to compare the projected operating and maintenance costs using the plasma melting system to the costs of the current systems used by the cost share partners. This TEA will be built upon several assumptions that will be validated by the next six months of work in the research program. This study will serve as the foundation for the development of a Plasmelt business plan in Year 2 in which our goal is broad implementation of plasma technology within the glass industry. The Study will also identify any likely early adopters of this technology, on which we plan to focus our initial efforts.

A letter was received on January 5, 2004 from the State of Colorado, Department of Public Health and Environment, stating that, based on our expected low emissions level from our research operation, a construction permit and an Air Pollutant Emission Notice are not required for the operation of our Boulder Lab DOE Project. Plasmelt may now begin the Boulder Lab operation with no further permitting.

Plans for Next Quarter (Jan-Mar, 2004):

- Complete the installation of all equipment
- Continue to conduct the market study
- Complete the construction of the electrical, melter, torch, cooling, exhaust/dust collection, dust collection, and batch systems
- Complete the design of the controls package for the operation of the melter and accompanying systems
- Start-up, integrate, and de-bug the entire system by beginning to melt glass at the 100 – 200 pounds per hour level

- Initiate the design/engineering of the glass delivery system that will transfer glass from the melter drain orifice to the marble forming position

Patents: None

Publications/Presentations:
No publications/presentations were made during this reporting period.

Milestone Status Table: This should be a complete list of project milestones, anticipated completion dates and actual completion dates. The milestone identification number should correspond to the task numbers in your agreement to aid in tracking (example below).

ID Number	Task / Milestone Description	Planned Completion	Actual Completion	Comments
M 1	Project Startup: Establish WBS and Schedule, operating agreements, IP terms, subcontract agreements	10/31/03	10/31/03	
M 2.1	Melter Design: Develop Project Request Documents, specifications, materials lists, engineering packages	10/31/03	10/31/03	
M.2.2	Laboratory Preparation: Identify candidate facilities, sign lease agreements, establish environmental permits	12/31/03	10/31/03	Notification of Exemption Letter received from Colorado DPHE
M.2.3	Construct Melter: Subcontract fabrication and construction, install melter at site	12/31/03	2/29/04	Melter construction and fabrication underway. Slight overall construction delay due to additional extensive building electrical upgrade requirements.
M 3	Market Survey	5/31/04		Work scope has been defined and PO has been written to subcontractor. Work has begun.
M 4	Melter/Process Test Program: Startup and operation at 500 #/hr rate [GO/NO GO DECISION], preliminary energy balance, preliminary report	7/27/04		

ID Number	Task / Milestone Description	Planned Completion	Actual Completion	Comments
M 5	Assess Glass Quality: marble forming installation, marble production and fiberizing testing [GO/NO GO DECISION]	1/31/05		
M 6.1	Optimization: Process refinement, energy balance updates [GO/NO GO DECISION]	6/30/05		
M 6.2	Final Reporting to DOE	7/27/05		

Budget Data (as of 12/31/03): The approved spending should not change from quarter to quarter. The actual spending should reflect the money actually spent on the project in the corresponding periods.

			Approved Spending Plan			Actual Spent to Date		
Phase / Budget Period			DOE Amount	Cost Share	Total	DOE Amount	Cost Share	Total
	From	To						
Year 1	7/28/03	7/27/04	$956,198	$394,119	$1,350,317	$365,613	$218,477	$584,090
Year 2								
Year 3								
Year 4								
Year 5								
Totals			$956,198	$394,119	$1,350,317	$365,613	$218,477	$584,090

*NOTE: $365,613 is the total amount of advance and reimbursement invoices that have been submitted by Plasmelt to DOE-Albuquerque: $215,000 cash advance + reimbursements of $150,613 ($13,712.37 + $43,101.55 + $28,525.55 + $34,148.55 + $31,124.77)

Development and Validation of a Coupled Combustion Space/Glass Bath Furnace Simulation

Petrick: Argonne National Laboratory (Techneglas)

CPS#01025

QUARTERLY PROGRESS REPORT

Project Title: Development/Validation of an Advanced Multiphase Glass Furnace Model

Covering Period: October 1, 2003 through December 31, 2003

Date of Report: January 31, 2004

Recipient:

Argonne National Laboratory
9700 S. Cass Avenue
Argonne, IL 60439

Techneglas, Inc.
727 E. Jenkins Avenue
Columbus, OH 43207

Award Number: *DE-SC02-97CH10875 and DE-SC02-00CH11037*

Subcontractors: Mississippi State University, Purdue University

Other Partners: Libbey, Inc., Osram-Sylvania, Owens Corning, Visteon

Contact(s):

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John Chumley
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Project Team: *Elliot Levine, OIT DOE–HQ contact; Matea McCray,DOE-ID, Project Mentor*

Project Objective: This project is the second phase of a program to develop a "state of the art" glass furnace model which couples the combustion space to the glass melt through a rigorous spectral radiation model. The key technical objectives of this follow on program is to incorporate glass chemistry models into the glass melt, activate gaseous phase transport (bubbles/foam) in the glass melt, develop/incorporate chemistry/nucleation models to model the transport of gases/particulates emanating from the batch/molten glass into the combustion space, develop/incorporate glass quality indices, develop/validate several furnace simulations of different types of furnaces, disseminate a beta version of the code to the glass industry participants (GMIC members), and to conduct a workshop at the end of the project to transfer the technology (code) to the entire glass industry.

Background: A substantial effort has been expended during the past several decades to develop furnace models to predict furnace performance as evident by the accelerating number of publications in the literature. These efforts, in general, have had varying and limited objectives. The models developed generally have required or been based upon major underlying assumptions that substantially impact the predictions, (such as assumed surface temperature and heat flux distributions). Also, very little experimental data has been obtained from operating furnaces which has hampered assessment of the validity of the models. The models

developed thus far do not have many analytical capabilities required by the industry.

This program which was initiated in CY 1998, has been structured to develop a validated CFD furnace model that will have the desired analytical capabilities which can be used by the glass industry to define and evaluate opportunities to modify furnace operating and geometrical parameters to improve glass quality and productivity (glass throughput) while minimizing energy use and gaseous and particulate emissions. The successful development and incorporation of these models will provide the industry with a state of the art furnace model that will represent a step change in analytical capability. The ultimate utility of the state of the art model will be in the development of furnace control software to adjust operating conditions to achieve and/or maintain predetermined glass quality and furnace performance targets.

Status:

Program progress is presented in accordance with the work breakdown structures adopted for each phase of the program. Task I.# refers to a task number from the first phase while Task II.# refers to a task number from the second on-going phase. A brief summary of progress in tasks pursued during the last reporting period follows.

Task II.2: The foam distribution and thickness that was calculated in the melt model has been coupled to the combustion space. The effects on the radiative heat transfer due to this foam layer have been incorporated in the combustion space model. The task is completed.

Task II.5: After consultation with the industrial partners, a set of glass quality indices has been incorporated into the melt model. This set of indices includes the 'industry standards' such as the melting index and temperature homogeneity currently being used by the industry as well as newly developed indices based on the unique multiphase capabilities inherent in the GFM. Testing and debugging pf the indicies was completed.

Task II.13: The industrial partners continued to interact with ANL to refine and complete their sensitivity studies. Several minor code improvements were incorporated as a result of this interaction. The studies are essentially complete.

Task II.15: The industrial participants have begun to assemble a collective beta test site report that reflects their individual experiences in using the code during the conduct of the parametric and sensitivity studies. The report is expected to be completed during the 2nd. quarter of 2004.

Task II.16 The effort to transfer the technology developed (the GFM code) to the Glass Industry has been expanded into a formal follow on program that has been structured to promote the utilization of the code by the industry and to provide the requisite technical support. The program is to be initiated 1/15/04. The users manual and the final report will have been completed and be available in time for distribution to the new code users.

Plans for Next Quarter:

THE GFM CODE DEVELOPMENT PROGRAM HAS BEEN SUCCESSFULLY COMPLETED ON SCHEDULE AND WITHIN BUDGET. AS INDICATED THE FOLLOW ON PROGRAM TO PROMOTE THE UTILIZATION OF THE CODE BY THE INDUSTRY WILL BE INITIATED 1/15/04.

Patents: The Glass Furnace Model software (GFM 1.0) was copyrighted (May 14,2001).

The Glass Furnace Model software (GFM 2.0) was copyrighted (ANL-SF-01-030b) (May 17, 2002).

Publications/Presentations: (from this quarter only)

Milestone Status Table:

ID Number	Milestone Description	Planned Completion	Actual Completion	Comments
1	**Part I**			
1.1	Select Furnace	10/1/98	10/1/98	
1.2	Combustion space simulation completed	12/1/99	10/1/99	
1.3	Glass bath simulation of furnace completed	10/1/99	10/1/99	
1.4	Verification of selected diagnostic instrumentation capabilities completed	10/1/99	10/1/99	
1.5	Combustion and glass bath simulations integrated into overall furnace studies	7/1/00	5/15/00	
1.6	NOx kinetic model incorporated into furnace simulation	7/1/00	4/15/00	
1.7	Preliminary validation of furnace simulation completed	10/1/00	9/15/00	
1.8	Acquisition of furnace performance data for code validation completed	5/1/01	2/20/01	
1.9	Furnace simulation validation completed	7/1/01	7/1/01	
1.10	Workshop to introduce industry to the furnace simulation software	10/1/01	10/21/02	
	Part II			
2.1	Reduced batch/melt chemistry/kinetic models developed	10/1/01	10/1/01	
2.2	Development of advance furnace model completed	4/1/02	01/04	.
2.3	Simulation of selected furnace types completed	10/1/02	12/1/02	
2.4	Performance data acquired from selected furnaces	2/1/03	10/08/02	
2.5	Validation of furnace model completed	4/1/03	6/17/03	

ID Number	Milestone Description	Planned Completion	Actual Completion	Comments
2.6	Beta sites established to test furnace model	10/1/03	01/1/04	
2.7	Advanced furnace model made available to industry via a workshop	12/1/03	N/A	Superceded by the Follow On Technology Transfer Program
2.8	Support center to assist industry in the use of furnace code	12/1/03	1/1/04	

Budget Data (as of 4/30/03): The approved spending should not change from quarter to quarter. The actual spending should reflect the money actually spent on the project in the corresponding periods.

				Approved Spending Plan			Provided to Date	Actual Spent to Date
Phase/Year/ Budget Period				DOE Amount	Cost Share	Total	DOE Amount	DOE Amount
		From	To					
1	1	12/01/97	11/30/98	490.5	331.9	822.4	696.0	46.7
1	2	12/01/98	11/30/99	484.0	314.4	798.4	81.6	409.6
1	3	12/01/99	11/30/00	479.1	407.4	886.4	565.5	674.0
2	1	09/01/00	08/31/01	512.7	665.6	1178.4	300.0	486.9
2	2	09/30/01	09/30/02	588.7	415.9	1004.7	627.0	610.4
2	3	09/30/02	12/31/03	262.1	681.9	944.0	547.0	589.5
			Totals	2817.1	2817.1	5634.3	2817.1	2817.1

*Program started officially 07/31/98

Monitoring and Control of Alkali Volatilization and Batch Carryover for Minimization of Particulates and Crown Corrosion

Blevins: Sandia National Laboratories (Gallo Glass Co.)

CPS#01608

Quarterly Progress Report

Project Title: Monitoring and Control of Alkali Volatilization and Batch Carryover for Minimization of Particulate Emissions and Crown Refractory Corrosion in Glass Melting Furnaces

Covering Period: October 1, 2003 to December 31, 2003

Date of Report: January 30, 2004

Laboratory: Sandia National Laboratories
7011 East Avenue
Livermore, CA 94550

FWP/OTIS Number: M1ID156-HA, EEW34126, ED1805000

Subcontractors: none

Other Partners: Gallo Glass Company, 605 South Santa Cruz Avenue, Modesto, CA 95354

Contacts: Linda G. Blevins
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Project Team: DOE-HQ Contacts: Elliott Levine

Industry Contact: John Neufeld
Gallo Glass Company, Modesto, CA 95354

Project Objectives: The objectives of the project are: (1) reduction of particulate matter emissions, (2) increase in length of furnace campaigns, and (3) improvement of melting efficiency, through simultaneous minimization of batch dust carryover, minimization of alkali volatilization, and optimization of oxygen-to-fuel ratio during glass melting and fining using wide flame oxy-fuel burners. The anticipated improvements in performance are to be achieved by reduction of alkali and particulate at its sources, reduction of unburned combustibles and waste heat losses, maximization of flame radiation through intelligent control of melting furnace conditions, and optimization of batch composition.

Background: Entrainment of batch particles in flue gas and vaporization of the alkali metals, sodium and potassium, from melting batch and molten glass are associated with a number of negative impacts on the glass melting process and melting tank performance. Among the negative effects are: (1) corrosion of superstructure and crown refractories, (2) plugging of regenerator checkers, (3) fouling and corrosion of flue ducts, (4) particulate matter emissions, and (5) loss of raw materials. The relative importance of these effects depends upon the type of glass being melted, the design and materials of construction of the furnace, and local emissions regulations. The causes of batch particle entrainment and alkali volatilization are, for the most part, well understood. However, alteration of batch composition and furnace conditions to minimize entrainment and volatilization may have negative impact on other aspects of furnace operation and glass quality. For example, volatilization could be reduced by distributing heat input so as to make the peak glass surface temperature lower and the distribution of surface temperatures more uniform, but this would suppress glass circulation in the melt and result in

poorer glass quality at a given pull rate. As another example, batch dusting could be reduced by minimizing heat input and gas velocity over the batch blanket, but the shift of fuel heat input away from the batch blanket toward the fining zone might increase batch coverage, result in poorer overall transfer of heat to the load, and would likely increase the glass surface temperature in the fining zone, leading to increased alkali volatilization and seeds in the product. Intelligent optimization of these conflicting requirements is the subject of the project. The great variability of the rates of refractory corrosion, particulate emissions, and heat requirements from furnace to furnace and the excellent performance of some furnaces suggest that an optimum set of furnace conditions exists and that significant reductions in emission and corrosion rates and improvements in the efficiencies of poorly performing furnaces are possible.

The method being used to measure carryover and volatilization is laser-induced breakdown spectroscopy (LIBS), a continuous monitoring technique for metals demonstrated in previous trials at Gallo Glass. By observing the correlation of metals concentrations with operating conditions over long periods, the batch properties and furnace conditions associated with batch carryover and alkali volatilization will be identified. Because the oxygen-to-fuel ratio is expected to be among the critical process variables, the work also includes simultaneous measurements of furnace efficiency, so that this measure of performance can be incorporated in the furnace optimization scheme.

The work has been greatly facilitated by the sooner-than-expected arrival on the market of echelle grating spectrometers, capable of recording signals from all of the elements in the LIBS spark simultaneously, permitting the identification of individual particle types and their sources or mechanisms of formation. The echelle grating instrument, originally planned for application to the problem in March 2003, was incorporated in the LIBS system during the first 5 months of the project and has been used in two sets of field trials at Gallo Glass. Though the echelle spectrometer has provided very useful data, it has not performed as well as expected. In the first round of measurements, in December 2001, the spectrometer was found not to have sufficient sensitivity for determination of element concentrations in individual laser sparks. This would preclude the determination of joint particle size-composition distributions. However, the apparent size distributions of individual elements can still be determined using the original Czerny-Turner spectrometer, so relatively infrequent large particles carried over from batch can be distinguished from the more uniform concentration of submicrometer particles formed from volatile species. During the most recent field test, in June 2002, both the echelle and conventional grating spectrometers were run side-by-side, for direct comparison of their performance.

Status: Extended measurement campaigns were conducted in May 2003, June 2002, and December 2001. Analysis of the data from the first and second campaigns is complete. Analysis of the data from the third campaign is mostly complete, but a few tasks remain. This quarter, we have continued data analysis from May 2003 and begun planning our final field test at Gallo.

<u>May 2003</u>: Measurements were performed in the vertical flue just downstream from the furnace exit on Tank #1. Flue gas temperature and concentrations of O_2, CO, NO, and SO_2 were recorded simultaneously with LIBS signals for multiple elements. Gallo Glass systematically varied oxygen-to-gas ratio while tests were being performed.

As the average oxygen-to-gas ratio increased from 1.98 to 2.18, average O_2 concentration increased, average NO concentration increased, and average SO_2 concentration decreased or remained constant. For the lowest oxygen-to-gas ratios (1.98 to 2.04), CO occasionally

appeared in the exhaust.

Hourly ambient temperature data were obtained from the National Weather Service. The actual O/G in the furnace appeared to change as a function of ambient temperature—reaching a minimum when ambient temperature was maximum in the late afternoon. The most likely cause was a temperature-dependent change in the amount of air leaking into the furnace. This may happen because of air entrainment into the cooling wind or through the burner blocks. Offline discussions at the glass review meeting revealed that this trend has been observed by other manufacturers operating in the California Central Valley, where the difference between the maximum and minimum daily temperatures is large. Interestingly, bridge wall temperature appears to vary directly with ambient temperature, while melter bottom throat temperature varies inversely with ambient temperature.

LIBS signals were collected as two-minute averages with the echelle detection system and as single-shot measurements every 200 ms with the Czerny-Turner detection system. The echelle system detected elemental emission between 250 nm and 900 nm simultaneously. The elements targeted during echelle data reduction were sodium at 589.0 nm and 589.6 nm, potassium at 766.5 nm and 769.9 nm, and calcium at 393.4 nm and 396.8 nm. The Czerny-Turner detection system was tuned to four different spectral windows, with measurements being made in each window for two hours apiece. The windows corresponded to the spectral detection regions for silicon and magnesium (258 nm – 293 nm), potassium (731 nm to 766 nm), sodium (571 nm t0 606 nm), and calcium and aluminum (386 nm – 421 nm).

When products of fuel-rich combustion appeared in the furnace, SO_2 concentration increased dramatically. Interestingly, sodium and potassium LIBS signals from both detection systems decreased dramatically as well. Calcium LIBS signals remained constant in the presence of rich products. This is surprising, since the presence of CO is expected to increase alkali volatilization. A plausible explanation was found for the decrease of sodium and potassium signals for fuel-rich conditions. The LIBS signal is probably absorbed by alkali atoms in the combustion products. Equilibrium calculations demonstrate that alkali metal atoms become more prevalent in the furnace for rich conditions than for lean conditions.

During the first quarter of FY2004, we investigated the unusual sodium and potassium signals further. We searched databases for another set of atomic emission lines to be analyzed for each element. Our criterion for the search was that the lines terminate in an energy level higher than the ground state energy level for each atom; in theory, emission from these spectral lines would not be absorbed by the abundant ground-state sodium and potassium atoms in the furnace. Sodium lines matching this criterion were found at 818.3 nm and 819.5 nm. Potassium line pairs at 578.2/580.2 nm and 691.1/693.9 nm also satisfied the requirement. We analyzed these lines in our spectra—one advantage of using a broadband analyzer like the echelle spectrometer was realized because the entire spectrum between 300 nm and 900 nm was available from the tests. The signals from the new sodium lines were strong enough for analysis, but the signals from the new potassium lines did not have adequate signal-to-noise ratios for analysis. However, by chemical analogy, it is reasonable to assume that the potassium signals will track the sodium signals. The new sodium signals proved to be unsusceptible to the sodium atom absorption. The new lines decreased in intensity as the concentrations of incomplete combustion products increased, but the trend was less dramatic than that for the previous lines. A certain fraction of the sodium atoms in the furnace may be in an excited state; further analysis is underway of these interesting sodium and potassium signals.

Single-shot measurements of calcium show a baseline amount of calcium present due to volatilization as well as the occasional large signal that indicates the presence of batch particles in the LIBS probe volume. Silicon, aluminum, and magnesium did not show significant baseline amounts, but batch particles containing these elements were seen passing through the measurement location from time to time. The frequency of calcium batch particles was 5713 hits out of 581,580 shots; magnesium batch particles were found in 466 of 662,580 shots; silicon batch particles were found in 399 of 662,580 shots; aluminum batch particles were found in 213 of 581,580 shots. Calcium-containing batch particles originating from limestone in the batch were the most abundant of the four types of batch particles detected. Silicon particles originated from sand in the batch. Magnesium and aluminum particles originated from additives or contaminants in the batch. Additional batch particles may have originated from the recycled glass added to the batch. To our knowledge, this is the first time that batch particles have been detected in real time in the flue of a glass furnace.

Based on the single-shot results, batch particle size distributions were computed. Calculations were performed assuming spherical particles with predefined compositions containing only one type of targeted element per particle. The particles were assumed to be calcium oxide, magnesium oxide, silicon dioxide, and aluminum oxide. In the calculated number distributions, particles with sizes of abut 0.5 μm are most abundant for magnesium oxide and calcium oxide. For silicon dioxide and aluminum oxide, 1 μm to 2 μm particles are most abundant. Sharp decreases in furnace pressure were found to correlate with rapid increases in batch particle carryover.

During the first quarter of FY2004, we have continued our analysis of the batch particle results. In addition to the calcium, aluminum, magnesium, and silicon batch particles previously analyzed, we have analyzed sodium and potassium batch particles. The occurrence of batch particles of any kind—expressed in particles per ten minute period—increases when a change in furnace operating condition occurs. Further analysis is underway.

Also underway during the first quarter of FY2004 were attempts to quantify the LIBS signals from the May 2003 field test. New methods of achieving the high concentrations of metals needed in the calibration rig have been developed and tested. Quantitative concentration data should be available next quarter.

An energy balance on the furnace for the May 2003 tests was completed this quarter. For the analysis, all of the energy inputs and outputs were expressed in units of energy per unit mass of glass pulled from the furnace. Energy inputs (fuel and electric boost) were obtained for the entire May 2003 test from plant control room records. The solid feed to the melter was assumed to contain raw materials, cullet, and moisture. The gases exiting the furnace were considered to contain batch gases, combustion products (carbon dioxide, water, and the small amount of nitrogen present in natural gas), excess oxygen, combustibles (primarily carbon monoxide, with little unburned hydrocarbons and soot), and air in-leakage. Appropriate temperatures from the control room records and from our own thermocouple measurements were used in the analysis. An optimum value of furnace excess oxygen concentration that minimizes energy loss in the flue gas while avoiding CO production was identified.

The largest fraction of the energy required for batch reactions and melting goes into heating the glass. Because the temperature at the throat is a set point, there is only slight variation in the sensible energy content of the glass, even with change in pull. The energy required for the batch reactions, per unit mass of glass, is completely unaffected by any of the conditions in the furnace. In contrast, the enthalpy of the batch gases depends upon the furnace exit gas

temperature, but the temperature is only subject to relatively small fluctuations. The total energy required for melting is close to 50% of the total energy input at the pull rate of 322 ton/day.

June 2002: Flue gas temperature and concentrations of O_2, CO, NO, and SO_2 were recorded synchronously with sodium, potassium, calcium, and aluminum LIBS signals. Measurements were performed in the vertical flue. Both Czerny-Turner and echelle spectrometers were used with the LIBS system. Natural gas and oxygen input flows for the furnace were captured in strip charts from Gallo Glass. Other operating data such as furnace pressure, glass level, electric boost amount, and radiometric wall temperatures were also obtained from Gallo Glass. Plots of these variables as a function of time were digitized from the Gallo strip charts. Their values were interpolated so that the data points corresponded to the times associated with the LIBS measurements. Mathematical cross-correlations were performed.

For the June 2002 data, sodium and potassium concentrations in the flue were found to mathematically correlate with the north and south breast wall temperatures. Additionally, there were correlations of alkali concentrations with exhaust oxygen concentration and with exhaust sulfur dioxide concentration for some days but not for all days. Two different glass pull rates were examined (336 and 435 tons/day), so trends were established for different furnace loads. The oxygen to gas ratio was consistently 2.12. Alkali concentrations showed a stronger dependence on temperature than on stoichiometry. There is some evidence that the relationship between alkali release and furnace stoichiometry is temperature dependent.

A significant level of potassium was observed in the flue gas in June 2002. The combination of potassium with sodium is expected to be a more aggressive agent for corrosion of silica refractory than sodium alone. The high measured amount of potassium is inconsistent with the chemical analysis of dust collected at the exit of the electrostatic precipitator (ESP) and with the parent glass chemistry. Since the ESP processes the exhaust of four separate furnaces, the dust chemistry may not be consistent with that of any individual furnace. Enrichment of potassium relative to sodium in the exhaust of glass furnaces and other combustion devices such as biomass boilers has been observed previously. To examine this trend further, we collected alkali particles near the LIBS sampling point using an extractive probe and aqueous bath during May 2003 testing.

The June 2002 data hint that an optimum furnace stoichiometry will minimize alkali concentration and avoid carbon monoxide emission. Sulfur dioxide and nitric oxide emissions are relatively insensitive to stoichiometry except under reducing conditions. Calcium and aluminum were also observed in the flue, but at much lower concentrations than sodium and potassium.

The apparent particle size distribution for sodium determined from the June 2002 LIBS data is narrow and centered about a large particle size (several microns). This suggests a high number density of fine particles or a fume and a few large particles originating from volatilization rather than carryover.

December 2001: LIBS measurements of sodium, potassium, calcium, magnesium, aluminum, boron, and silicon were performed using the echelle spectrometer in the furnace exhaust duct upstream of the electrostatic precipitator. At this location, the exhaust is diluted by a factor of about 3.5:1. Simultaneously, O_2, CO, NO, and SO_2 concentrations were recorded. Natural gas rate of flow, oxygen rate of flow, furnace pressure, glass level, electric boost amount, and

radiometric process temperatures were captured in strip charts from Gallo Glass. The pull rate was about 430 tons/day, and the oxygen to gas ratio was about 2.16.

The potassium and sodium concentrations correlated with each other. Additionally, the calcium, magnesium, and aluminum concentrations correlated with each other. However, the potassium and sodium concentrations did not correlate with the calcium, magnesium, or aluminum concentrations. This suggests two different release processes. One is related to the alkali metals and the other is related to the more refractory calcium, magnesium, and aluminum. The alkali metal concentrations showed a mild correlations with furnace breast wall temperatures.

In the December 2001 measurements, flue gas composition showed cyclic variations on two time scales, one of about 12 minutes, and the other of about 1½ hours. The longer scale corresponds to the control room record of gas and oxygen flow rates; the 12-minute cycle is correlated with furnace pressure. The cycles in the sodium and potassium concentrations correspond very roughly to the cycles in gas and oxygen flows (high heat input corresponds to high sodium and potassium), but the correspondence is by no means perfect. During ceramic welding in December 2001, the aluminum concentration in the flue increased and silicon was also observed.

The indicated sodium concentration in the flue was higher during December 2001 than during the 1998 tests conducted in collaboration with Corning, Gallo Glass, OIT, and Visteon. The Czerny-Turner spectrometer used in 1998 was brought back for comparison with the new echelle spectrometer during the June 2002 tests. The sodium concentration was lower during June 2002 than during December 2001. The reasons for the discrepancy in alkali concentrations are being examined.

A model for crown corrosion by sodium was developed and the values of its parameters determined from measurements during the first oxygen/gas furnace campaign on Tank No. 1 at Gallo Glass. The model provides a rational basis for assessment of the costs and benefits, with respect to refractory corrosion, from changes in operating conditions that influence sodium volatilization. An interesting prediction of the model is that when sodium reaches two or three hundred parts-per-million in the combustion space, increasing the crown temperature increases, rather than decreases, the silica corrosion rate.

Changes that will improve signal-to-noise ratio have been made to the LIBS instrument and will be deployed in the next test. These improvements will hopefully allow us to measure the concentration of a larger number of elements simultaneously. Additionally, we should be able to measure the important elements more accurately. An optimum set of LIBS instrument settings has been systematically found for the next test. Some of the parameters examined were saturation behavior, on-camera and off-camera averaging, binning selections, calibration curve linearity, time constant determination, purge flow settings, optimum delay and gate times, laser power consistency, and differences between the Czerny-Turner and echelle spectrometers. Computational fluid dynamic modeling of the interaction of the LIBS purge flow with the furnace cross flow has been undertaken.

Linda G. Blevins of Sandia is leading the project. Peter Walsh of the University of Alabama Birmingham is a consultant. Shane Sickafoose, Doug Scott, and Alejandro Molina of Sandia are the current project participants. Gary Hubbard is a programming consultant.

Plans for Next Quarter: Data reduction for the May 2003 field test should be complete in the next quarter. Tasks remaining include experiments examining the effect of combustion gases,

high temperatures and high particle loading on the LIBS spark. Data quantification from May 2003 will be completed this quarter, and the next field trial will be planned and scheduled.

Patents: none

Publications/Presentations:

Blevins, L.G., Molina, A., Scott, D.D., Sickafoose, S.M., Neufeld, J.W., Walsh, P.M., "Effect of Variations in Oxygen to Gas Ratio on Flue Gas Composition, Process Temperature and Alkali Metal Concentration in an Oxygen/Natural Gas Glass Melting Furnace," Fall Technical Meeting, Western States Section of The Combustion Institute, Los Angeles, California, October 2003.

Blevins, L.G., Shaddix, C.R., Sickafoose, S.M., and Walsh, P.M., "Laser-Induced Breakdown Spectroscopy in High-Temperature Industrial Boilers and Furnaces," *Applied Optics*, V. 42, pp. 6107-6118, 2003. (Results featured on the cover of the journal.)

Walsh, P.M., Blevins, L.G., Sickafoose, S.M., Johnsen, H.A., Molina, A., Ottesen, D.K., Scott, D.D., Steinhaus, R.J., Christy, R.H., and Neufeld, J.W., "Laser-Induced Breakdown Spectrometry: Application to Measurement of Inorganic Particulate Emissions from Combustion in Engines and Furnaces," Third Mediterranean Combustion Symposium, Marrakech, Morocco, June 8-13, 2003.

Walsh, P., Allendorf, M. Nilson, R., Griffiths, S., Blevins, L., Sickafoose, S., Johnsen, H., Molina, A., Scott, D., Moore, D., Neufeld, J., Lemings, L., Brown, J., Wu, K.T., "Sodium Volatilization and Silica Refractory Corrosion in an Oxygen/Natural-Gas-Fired Container Glass Furnace," Hotbels Seminar, Lexington, KY, April 2003.

Blevins, L.G., Molina, A., Sickafoose, S.M., Walsh, P.M., and Neufeld, J.W., "Alkali Metal Concentrations in an Oxy-Fuel Glass Furnace Exhaust," presented at the 3rd Joint US Meeting of the Combustion Institute, Chicago, Illinois, March 2003.

Walsh, P.M., Sickafoose, S.M., Scott, D.D., Steinhaus, R., Johnsen, H.A., and Neufeld, J., "Monitoring and Control of Alkali Volatilization and Batch Carryover for Minimization of Particulate Emissions and Crown Refractory Corrosion in Glass Melting Furnaces" DOE Glass Industry Project Review, Livermore, CA, September 10, 2002.

Milestone Status Table:

ID Number	Task / Milestone Description	Planned Completion	Actual Completion	Comments
1	Data acquisition system	7/31/01	6/20/02	*
2	CO and O_2 monitors	9/30/01	12/14/01	
3	Furnace exit gas temperature	10/31/01	6/20/02	
4	Flame and refractory radiation	11/30/01	6/20/02	
5	Synchronized records	12/31/01	6/20/02	*
6	Measurements of sodium	2/28/02	12/14/01	
7	Sources of sodium	3/31/02	9/30/02	
8	Conditions influencing sodium	4/30/02	9/30/02	
9	Maximum furnace efficiency	5/31/02	1/30/04	

ID Number	Task / Milestone Description	Planned Completion	Actual Completion	Comments
10	Measurements of silicon	7/31/02	12/14/01	
11	Measurements of calcium	9/30/02	12/14/01	
12	Correlations for metals	11/30/02	01/15/03	
13	Broad-band LIBS instrument	3/31/03	10/31/01	
14	Software for LIBS instrument	5/31/03	10/31/01	
15	Simultaneous measurements of Na, K, Ca, and Si	7/31/03	12/14/01	
16	Relationship between Na and K	8/31/03	02/01/03	
17	Optimum stoichiometry	9/30/03	09/30/03	
18	Sodium and calcium monitor	1/31/04		
19	Control strategy	3/31/04		
20	Demo in melting research facility	4/30/04		
21	Method for monitoring and control of volatilization and carryover	5/31/04		

*It has not been possible to collect data from the control room in real time; printouts of the data acquisition system records of furnace conditions are used instead. The furnace radiation, exit gas temperature, and flue gas composition data are, however, synchronized with LIBS.

Budget Data (as of September 30, 2003)**:**

			Approved Spending Plan ($000)			Actual Spent to Date ($000)		
Phase / Budget Period			DOE Amount	Cost Share	Total	DOE Amount	Cost Share	Total
	From	To						
Year 1	6/01	5/02	350	350	700	350	350*	700
Year 2	6/02	5/03	350	350	700	350	350*	700
Year 3	6/03	5/04	350	350	700	250	250*	500
Totals			1,050	1,050	2,100	950	950*	1,900

*Sandia National Laboratories' estimate.

Development of Process Optimization Strategies, Models, and Chemical Databases for On-Line Coating of Flat Glass

Allendorf: Sandia National Laboratories

CPS#01640

Quarterly Report

Title:	Development of Process Optimization Strategies, Models, and Chemical Databases for On-Line Coating of Float Glass
Covering Period:	October 1, 2003 – December 31, 2003
Date:	January 15, 2004
Laboratory:	Sandia National Laboratories 7011 East Avenue Livermore, CA 94551-0969
B&R No. **FWP/OTIS:**	820101000
Subcontractors:	None
Industrial partner:	PPG Industries
Contact:	Mark D. Allendorf (925)294-2895 mdallen@sandia.gov
Project Team:	Jill Troup Glass Technology Research Center P.O. Box 11472 Pittsburgh, PA 15238-0472 (412)820-8520 jtroup@ppg.com

Project Objectives

This project addresses the need to improve the efficiency of on-line atmospheric pressure chemical vapor deposition (APCVD) processes used primarily to deposit coatings on float glass, but also on glass containers. APCVD processes in the flat-glass industry at present can be as little as 10% efficient (i.e., only 10% of the incoming precursor chemicals are converted to coating), resulting in annual production and waste-treatment disposal costs to the industry of nearly $23 million. In addition, remelting of glass due to defects in the coatings results in over 1.1×10^{11} Btu/year of unproductive energy usage.

The objectives of this proposal are as follows:

1. Identify modifications to existing APCVD coater designs and/or new coater designs that will double the efficiency of reactant utilization, thereby substantially reducing waste emissions and purchases of raw materials.

2. Develop validated computational models to predict defects due to thickness nonuniformity and haze; use these to reduce defect frequency and improve the overall energy efficiency of the process by reducing the amount of rejected glass that must be remelted.
3. Generate a database of fundamental thermodynamic and kinetic information for APCVD.
4. Provide enhanced understanding of the underlying chemical reactions that control APCVD, which will enable the development of improved process models and control strategies for float-glass coating and other types of glass, such as containers, that use APCVD coatings.

Background

The use of on-line atmospheric pressure chemical vapor deposition (APCVD) techniques to manufacture coatings on glass is a critical technology in the flat-glass industry, responsible for the production of approximately 110 million ft^2/year of highly value-added products. These consist primarily of low-emissivity ("low-E") and solar-control glasses for architectural applications, but also include coatings for solar cells, computer screens, automotive applications, and xerography. The markets for these products are strong and growing. Coated glass for energy-conserving windows constitutes a roughly $600 million market for the raw glass alone; the total value of the final manufactured product (primarily dual-pane glass units) is in the billions of dollars. APCVD is a virtual necessity for maximizing coating production rates, since it can be performed at atmospheric pressure and can deposit material at rates fast enough to be compatible with glass ribbons speeds on typical float lines (about 1 ft/s). APCVD is thus an economically attractive, but technologically very challenging, manufacturing process.

Status

Project management activities

- A project review meeting was held at PPG's Glass Technology Center in Pittsburgh December 1 – 2, 2003. Communication between Sandia and PPG continues on a regular basis through phone conversations and email exchange of data.

Task 1 Deposition mechanisms

- Efforts this quarter focused on determining which of two deposition mechanisms reported last quarter provide the best description of pilot-scale data obtained by PPG. The first mechanism is

$C_4H_9SnCl_3 + H_2O \rightarrow C_4H_9SnCl_3(H_2O)$ (a gas-phase complex) (1)
$O_2 + 2OS(s) \leftrightarrow 2O(s)$ (OS(s) is an open site on the surface) (2)
$C_4H_9SnCl_3(H_2O) + O(s) \leftrightarrow SnO_2(solid) + 3HCl + 2C_2H_4 + OS(s)$ (3)

A second, fully heterogeneous, mechanism is generated by replacing reaction (1) with a reaction in which MBTC ($C_4H_9SnCl_3$) reacts with an open surface site. Rate constants for both mechanisms were determined by fitting to deposition-rate data obtained in Sandia's stagnation-flow reactor (SFR) under Task 5 (see below). Both mechanisms predict similar deposition rates when using the one-dimensional modeling code SPIN and are in qualitative agreement with all trends observed (e.g., temperature, MBTC concentration, flow rate), with the first mechanism in somewhat better agreement with the oxygen dependence of the growth rate. However, CFD

calculations (Task 4, see below) indicate that the two mechanisms predict quite different spatial profiles for the growth rate in the PPG pilot-scale experiments. Those experiments and modeling suggest that the second mechanism may provide a better overall description of the data. An additional problem is that the absolute value of the growth rate predicted by the 1-D SPIN code does not agree well with the CFD calculations, as was expected to be the case. This issue is not fully resolved as of the date of this report and we are conducting some additional SPIN and CFD calculations in an attempt to resolve it.

Task 2 Gas-phase and surface chemistry measurements

- Quantum-chemistry calculations to predict the thermodynamic properties of MBTC-H_2O complexes were completed last quarter. The size of the molecules caused the calculations to run for several weeks before fully converging. Data from these calculations will be analyzed next quarter and used to assist our efforts to identify the correct deposition mechanism.

Task 3 On-line monitoring

- Task complete.

Task 4 Computational fluid dynamic modeling

- Extensive CFD calculations were performed this quarter using Sandia's CURRENT code to predict the spatial profile of the tin oxide growth rate in PPG's pilot-scale reactor. We find that the two mechanisms described in Task 1 above give remarkably different profiles. The gas+surface mechanism yields a relatively flat profile, while the all-surface mechanism produces a profile that agrees extremely well with the measured one. Unfortunately, the predicted growth rate is too high by a large factor (as much as a factor of 20). Much of this quarter was devoted to a search for the source of this disagreement. Our latest calculations include the measured substrate temperature profile (which is quite nonuniform) provided by PPG for their experiments. PPG has also competed an assessment of potential errors in the various experimental parameters, none of which appear to be sufficiently large to account for the observed disagreement. Since shape of the predicted growth is in such good agreement with experiment, we feel that it is likely that the mechanism accurately reflects the relevant chemistry and could thus be used to provide qualitative guidance for process optimization. Nevertheless, we will redouble our efforts next quarter to trace the source of this problem so that quantitative as well as qualitative predictions can be made.

Task 5 Deposition experiments

- Tin oxide growth rates were measured in the SFR as a function of MBTC concentration in the 300 – 400 C range of substrate temperatures. Growth data were also obtained for reactor pressures up to 400 Torr. The MBTC concentration data, when compared with the predictions of five potential deposition mechanisms, allowed us to eliminate three of those mechanisms and narrow the field to the two described in Task 1 above. The pressure-dependence of the growth rate, when combined with data obtained earlier in the SFR, now extends from 25 Torr to 400 Torr. Growth rates predicted by the surface-only mechanism are within a factor of two of the SFR data at

all pressures, giving us confidence that we should be able to extend the mechanism to 1 atm total pressure at which the pilot-scale experiments were conducted.

Task 6 Process optimization

- A set of experiments varying MBTC concentration, water concentration, glass temperature, coater height, inlet gas temperature, and oxygen concentration were conducted in the PPG pilot-scale coater and the data partially analyzed this quarter. The results were sent to Sandia for comparison with CURRENT predictions and the two deposition models.

- A set of experiments exploring the effect of coater geometry changes and water concentration were conducted at PPG's full-scale manufacturing facility in Mt. Zion, Illinois during October. Preliminary results indicate that the two process-optimization strategies suggested by SNL, based on their extensive modeling of the tin oxide deposition process, are in agreement with observation. MBTC conversion efficiencies (i.e., the percent of tin precursor converted to tin oxide film) increased dramatically as a result of the suggested changes. *Indications at this time are that it should be feasible to double the efficiency of MBTC use, which meets the primary objective of the project*. Additional full-scale plant trials are planned for next quarter to further validate these strategies.

Plans for next quarter

- Analyze results of quantum-chemistry calculations to obtain thermodynamic data for potential MBTC-water complexes.

- Conduct second set of full-scale manufacturing tests to evaluate the effect of changing reactor geometry and water concentration.

- Perform CFD simulations of the Sandia SFR to validate the CURRENT predictions of growth rate. If these are in good agreement with both the growth rates measured in the SFR and the SPIN predictions, we will revisit the issue of potential error in experimental parameters for the pilot-scale coater experiments.

Patents We are exploring which parts of the intellectual property developed during the project are potentially patentable at this time and plan to file, at minimum, a patent disclosure next quarter. Discussions are underway with PPG concerning the potential licensing opportunities that may exist.

Publications/Presentations

None this quarter. We note that we still have extensive data obtained at Sandia concerning the gas-phase kinetics of MBTC pyrolysis that have not been fully analyzed. We have every intention of publishing these, but it is likely that the work will not be completed prior to the end of this project. A second publication describing tin oxide growth kinetics and modeling is in preparation at this time and we hope to submit it for publication by spring 2004.

Milestone Status Table (dates in project months):

Task	Task/Milestone Description	Completion Date		Comments
		Planned	Actual	
1.1	Develop thermodynamic data base	9	12	
1.2	Gas-phase model development	24		Anticipated completion month 30 (see Note 3)
1.3	Surface model development	24		Anticipated completion month 33
1.4	Mechanism testing/validation	24		Anticipated completion month 35
1.5	Chlorine defect model	24		See note 5 below
2.1	Gas-phase rates	18		Preliminary analysis complete
2.2	Gas-phase intermediates	24		See note 2 below
3.1	Equipment modification/calibration	18	18	
3.2	On-line monitoring in PPG facility	36	30	See Task 3 discussion
4.1	Non-reacting model: pilot-scale	6	6	
4.2	Reacting model: pilot scale	18	24	
4.3	Non-reacting model: full-scale	24	--	See note 1 below
4.4	Reacting model: full-scale	36	--	See note 1 below
5.1	Pilot-scale deposition experiments: Phase 1	9	15	
5.2	Pilot-scale deposition experiments: Phase 2	21	24	See note 6 below
5.4	SFR MBTC/O_2/H_2O deposition rates	18	24	See note 4 below
6.1	SFR tests	24		See note 4 below
6.2	Pilot-scale tests	27	35	
6.3	Full-scale tests	35		
	Final report	38		

Notes:

1. Computational fluid dynamic simulations of the full-scale coater could be more effectively done by a subcontractor to PPG, such as Fluent. SNL would provide a validated deposition model and associated gas-phase chemistry for use in such an effort. Experiments and modeling of the pilot-scale coater are deemed sufficient to test and validate process optimization strategies under most circumstances.
2. Laser-induced fluorescence measurements initially planned may not be necessary if data on MBTC product formation prove adequate for model validation.
3. Experiments to provide model validation will continue to near the end of the project. We expect to make use of the data to refine our models as much as possible, although the gas-phase model is now essentially complete.
4. Additional SFR experiments will be conducted until the end of the project to provide data necessary for model validation, due to progress made in model development efforts.
5. The source of chlorine defects was identified and a solution found by PPG during the early stages of this project, so this task was dropped from project activities.

6. As described above in Task 5, PPG continues to provide pilot-scale data substantially beyond what was originally envisioned in the project plan.

Budget Data (in thousands of $)**

			Approved Spending Plan			Actual Spent to Date*		
Phase/Budget Period			DOE Amount	Cost Share	Total	DOE Amount	Cost Share	Total
	From	To						
PY 1	3/01	2/02	500	500	1,000	538	408	946
Year 2	3/02	2/03	500	500	1,000	635	436	1,071
Year 3	3/03	2/04	500	500	1,000	275	541	816
		Totals	1,500	1,500	3,000	1,448	1385	2833

*Note: PY = project year (March – Feb), which does not coincide with the DOE fiscal year (Oct – Sept).

Index of CPS and Award CID Numbers

Index of CPS and Award CID Numbers

HQ CPS:
CPS#01025 6
CPS#01608 7
CPS#01609 1
CPS#01640 8
CPS#14231 4
CPS#14232 5
CPS#14233 3
CPS#none..... 2

Award CID:
GO13091..... 3
GO13092..... 4
GO13093..... 5
ID14030 1
ID14347 2

				Subtotals						**13,450,179**	**7,659,616**	**16,389,626**	**47%**	**4,565,818**		
n	**qsr**	**.**	**CID**	**Recip**	**Title**	**CPS#**	**a**	**Prj Beg**	**Prj End**	**Approved DOE**	**Approved Share**	**Total Approved**	**% CS**	**Need After FY03**	**All Prev Obl**	**.**
1	qsr i	.	ID14030	ERCo	Measurement an	1609	a	4/16/01	4/15/04	1,283,813	1,609,802	2,893,615	56%	605,635	678,178	.
1	.	.	_lab	ORNL	Measurement an	1609	b	4/16/01	4/15/04	155,000	0	155,000	0%	105,000	50,000	.
2	qsr i	.	ID14347	St of OH	Improvement of I	state		7/11/02	7/31/04	967,899	288,595	1,256,494	23%	0	967,899	.
3	nee	.	GO13091	Owens Co	Advanced Oxy-F	14233		9/4/03	8/20/05	887,803			n/a	642,803	245,000	.
4	nee	.	GO13092	GTI	Energy Efficient	14231		9/4/03	8/30/06	3,832,366			n/a	2,956,182	876,184	.
5	qsr	.	GO13093	Plasmelt	High Intensity Pl	14232		8/5/03	7/27/05	956,198	394,119	1,350,317	29%	356,198	600,000	.
6	qsr	.	_lab	ANL	Development / V	1025		11/1/98	12/31/03	2,817,100	2,817,100	5,634,200	50%	(200,000)	3,017,100	.
7	qsr	.	_lab	SNL	Monitoring and C	1608		6/1/01	5/31/04	1,050,000	1,050,000	2,100,000	50%	100,000	950,000	.
8	qsr	.	_lab	SNL	Development of I	1640		2/1/01	9/30/04	1,500,000	1,500,000	3,000,000	50%	0	1,500,000	.

				Subtotals				3,513,558	2,454,525	1,573,178	565,500	81,600	696,000	.
n	**qsr**	**.**	**CID**	**Recip**	**Title**	**CPS#**	**a**	**FY03**	**FY02**	**FY01**	**FY00**	**FY99**	**FY98**	**.**
1	qsr i	.	ID14030	ERCo	Measurement an	1609	a	0	305,000	373,178				.
1	.	.	_lab	ORNL	Measurement an	1609	b	0		50,000				.
2	qsr i	.	ID14347	St of OH	Improvement of I	state		495,374	472,525					.
3	nee	.	GO13091	Owens Co	Advanced Oxy-F	14233		245,000						.
4	nee	.	GO13092	GTI	Energy Efficient	14231		876,184						.
5	qsr	.	GO13093	Plasmelt	High Intensity Pl	14232		600,000						.
6	qsr	.	_lab	ANL	Development / V	1025		547,000	827,000	300,000	565,500	81,600	696,000	.
7	qsr	.	_lab	SNL	Monitoring and C	1608		250,000	350,000	350,000				.
8	qsr	.	_lab	SNL	Development of I	1640		500,000	500,000	500,000				.